$\Delta G = 0$, at equilibrium stage.

6.2.0 LAW OF MASS ACTION

This law was given by **C.M. Guldberg and P. Waage in 1864**. They studied a lot of reversible reactions and gave a **generalization**. A more general statement of law of mass action is that the **rate of a chemical reaction is proportional to the product of molar concentrations raised to a power equal to the number of times, the particular substance appears in stochiometric equation.**

6.2.1 Equilibrium Constant or Equilibrium Law:

Keeping in mind the law of mass action, we can have relationship between concentrations of reactants and products with the rate constants of forward and backward steps.

Let us consider a general reaction,

$$A + B \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C + D$$

The rate at which a substance react is directly propotional to the ~~conc of~~ active masses and rate of chemical reaction is propotional to the [A] product of active masses of reacting substance

The co-efficients for the reactants and products are unity for the sake of convenience. The rates of reactions at equilibrium stage depend upon the concentrations of reactants.

Rate of forward reaction $\propto$ [A][B]

Rate of forward reaction = k_f[A][B]

Rate of backward reaction $\propto$ [C][D]

Rate of backward reaction = k_b[C][D]

[A] mol dm^{-3}

Active mass ⇒ concentration in mol dm^{-3}

'k_f' and 'k_b' are the rate constants for the forward and the reverse reactions. At equilibrium stage the two rates are equal.

$$k_f[A][B] = k_b[C][D]$$

$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]} \quad \ldots\ldots \quad (1)$$

According to this equation (1), the concentrations of reactants and products have a certain ratio (کوئی نسبت) and this ratio depends upon the forward and backward rate constants (رفتار کے متعلق مستقل مقدار).

If the ratio of two rate constants 'k_f' and 'k_b' is put equal to another constant 'K_c', then

$$K_c = \frac{k_f}{k_b} \quad \ldots\ldots \quad (2)$$

This 'K_c' in equation (2) is called equilibrium constant (توازن کا مستقلہ).

The square brackets denote the concentrations in moles dm^{-3}. So, symbol 'K_c' is used, when concentrations of 'A', 'B', 'C', and 'D' are taken in moles dm^{-3}.

If the reversible reaction has co-efficients in the balanced equations as,

$$aA + bB \rightleftharpoons cC + dD + \ldots\ldots$$

Then

$$K_c = \frac{[C]^c[D]^d\ldots}{[A]^a[B]^b\ldots} \quad \ldots\ldots \quad (3)$$

Hence equilibrium constant is the **product of equilibrium concentrations of products divided by the product of equilibrium concentrations of reactants and each concentration term is raised to the power equal to the co-efficients of the substance in the balanced equation.**

This above equation is called law of **chemical equilibrium**.

equilibrium constant expression.
reactions always cancell in such a way as to give the indicated expression for the equilibrium constants.

6.2.3 Law of Chemical Equilibrium for Non-ideal Solutions

(غیر معیاری سولیوشنز کے لئے کیمیائی توازن کا قانون)

It should be made clear at this stage, that the expression for 'K_c', which has been derived above is strictly true (بالکل ٹھیک ہے) for ideal dilute solutions. It in not applicable to non-ideal solutions. If the solutions are non-ideal, then the chemical reactions depend on the effective concentrations and not actual concentrations. We should not consider the molar concentration (جو مقداریں با اثر ہوں). We know that non-ideal behaviour is shown by a solution of substances in the case of ionic species. In that case, activities (چستی) must be used in the expression, if exact calculations are required. The equilibrium constant is denoted by 'K_a' in such cases.

$$K_a = \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

6.2.4 Equilibrium Constant in Terms of Partial Pressures:

(ہر جزو کے ذاتی دباؤ کی شکل میں توازن کا مستقلہ)

Those reversible reactions which involve the gases should be handled by measuring their partial pressures (جزوی دباؤ) and equilibrium constant is indicated by 'K_p'.

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

V. Imp

6.3.0 RELATIONSHIP BETWEEN DIFFERENT TYPES OF EQUILIBRIUM CONSTANTS

The values of equilibrium constants for a certain reaction depend upon the units (اکائیاں) of concentration chosen (انتخاب شدہ). Equilibrium constant 'K_p' is employed (لگایا جاتا) when the concentrations are in partial pressures (جزوی دباؤ), 'K_c' when concentrations are moles dm^{-3}, 'K_x' when we have mole fractions (مول کا حصہ) and K_n is used when we have simple number of moles of reactants and products. Suppose we have a general reaction.

$$aA + bB \rightleftharpoons cC + dD$$

The reaction under consideration (زیرِ غور) is consisted (مشتمل ہونا) of ideal gases. The activity of each substance is proportional to the partial pressure and to its molar concentration.

For an ideal (معیاری) system, we shall be able to write down the expressions (مساواتیں) of 'K_p', 'K_c', 'K_x', and 'K_n' as follows.

$$K_p = \frac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$$

$$K_c = \frac{C_C^c \cdot C_D^d}{C_A^a \cdot C_B^b}$$

$$K_x = \frac{X_C^c \cdot X_D^d}{X_A^a \cdot X_B^b}$$

$$K_n = \frac{n_C^c \cdot n_D^d}{n_A^a \cdot n_B^b}$$

In these expressions the symbol p, C, X and n stand for partial pressure, moles dm^{-3}, mole fraction and number of moles respectively

6.3.1 Relationship Between K_p and K_c: 15

Keeping in view the general gas equation, and the Dalton's law of partial pressures (ڈالٹن کا جزوی دباؤ کا قانون), we can write down

$$p_iV = n_iRT \qquad \text{......} \quad (1)$$

'i' is the name of any one of the component.

or $$p_i = \frac{n_iRT}{V}$$

Since $\frac{n_i}{V} = C_i$ = conc. of component '*i*' in moles dm^{-3}

$$p_i = C_iRT \qquad \text{......} \quad (2)$$

'p_i' is the partial pressure (جزوی دباؤ) of the gas 'i' in the mixture of gases, n_i is its number of moles, $\frac{n_i}{V}$ is in moles dm^{-3} and has a unit of concentration. The volume and temperature as 'V' and 'T' are same for all gases.

In our reaction there are gaseous substances as 'A', 'B', 'C', 'D'. According to the above equation (1) their partial pressures in equilibrium mixture are

$$\left.\begin{aligned} p_A &= \frac{n_A}{V}RT = C_ART \\ p_B &= \frac{n_B}{V}RT = C_BRT \\ p_C &= \frac{n_C}{V}RT = C_CRT \\ p_D &= \frac{n_D}{V}RT = C_DRT \end{aligned}\right] \qquad \text{......} \quad (3)$$

The expression of K_P is

$$K_p = \frac{p^c{}_C\, p^d{}_D}{p^a{}_A\, p^b{}_B} \qquad \text{......} \quad (4)$$

Putting values of partial pressures from equations (3) into (4)

$$K_p = \frac{(C_C RT)^c (C_D RT)^d}{(C_A RT)^a (C_B RT)^b} = \frac{C^c_C \, C^d_D \, (RT)^{c+d}}{C^a_A \, C^b_B \, (RT)^{a+b}}$$

$$K_p = K_c \, (RT)^{(c+d)-(a+b)}$$

$$(c+d) = n_P \qquad (a+b) = n_R$$

So, $$K_p = K_c (RT)^{n_P - n_R}$$

$$\boxed{K_p = K_c \, (RT)^{\Delta n}} \qquad \ldots\ldots \; (5)$$

Where Δn is the difference of number of moles of products (n_p) and number of moles of reactants n_R. So $\boxed{n_p - n_R = \Delta n}$ With the help of equation (5) we can interconvert K_p and K_c.

اگر $\Delta n = 0$ تو $K_P = K_C$، اگر n مثبت ہے یعنی پراڈکٹس کے مولز زیادہ ہیں تو $(RT)^{\Delta n}$ ایک سے بڑا ہے لہٰذا ایسے تعامل کا K_P بڑا ہے - K_C

لیکن اگر Δn منفی ہے۔ تو اس کے الٹ نتائج نکلیں گے۔

$$K_p = \frac{}{(C_ART)^a(C_BRT)^b}$$

$$K_p = K_c\,(RT)^{(c+d)-(a+b)}$$

$$(c+d) = n_P \qquad (a+b) = n_R$$

So, $K_p = K_c(RT)^{n_P - n_R}$ ...... (5)

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

Where Δn is the difference of number of moles of products (n_p) and number of mo reactants n_R. So $\boxed{n_p - n_R = \Delta n}$. With the help of equation (5) we can interconvert K_p and K_c.

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6.3.2 Relationship Between K_p and K_x:

In order to derive the relationship between 'K_p' and 'K_x', we take the help from Dalton's partial pressures, that is

$$p_i = X_iP \qquad \text{...... (6)}$$

Where p_i is the partial pressure of a gas 'i' in a mixture and 'X_i' is its mole fraction.

According to this equation, the partial pressure of any gas depends upon the mole frac that gas (اس گیس کا مکسچر کے اندر اپنا مولر حصہ) and total pressure 'P' of the mixture. The values of p pressures of four substances i.e. 'A', 'B', 'C' and 'D' are as follows.

$$\left.\begin{aligned} p_A &= X_AP \\ p_B &= X_BP \\ p_C &= X_CP \\ p_D &= X_DP \end{aligned}\right] \qquad \text{...... (7)}$$

Putting these values of equation (7) in the expression of K_p of equation (4)

$$K_p = \frac{p^c_C\,p^d_D}{p^a_A\,p^b_B} \qquad \text{...... (4)}$$

$$K_p = \frac{(X_CP)^c(X_DP)^d}{(X_AP)^a(X_BP)^b}$$

$$K_p = \frac{X^c_C\,X^d_D}{X^a_A\,X^b_B}\,\frac{P^{(c+d)}}{P^{(a+b)}}$$

$$K_p = K_x\,(P)^{(c+d)-(a+b)}$$

Let $\Delta n = (c+d) - (a+b)$

So, $\boxed{K_p = K_x\,(P)^{\Delta n}}$ ...... (8)

This equation (8) shows that if we multiply 'K_x' with pressure of the system with a cert power, then we get 'K_p'. So in order to interconvert 'K_p' and 'K_x', we should know the total pressure reaction mixture at equilibrium stage and the difference of number of moles of reactants and produc i.e. 'Δn'

6.3.3 Relationship Between K_p and K_n.

We again take the help of Dalton's law of partial pressures:

Since, $p_i = X_i P$

Where, $X_i = \frac{n_i}{N}$

N = total number of moles of reactants and products at equilibrium sage

n_i = number of moles of component 'i'

So, $$p_i = \frac{n_i}{N} P \quad \text{...... (9)}$$

Let us apply this relationship to calculate the partial pressures of four components in the general reaction already mentioned

$$\left.\begin{aligned} p_A &= \frac{n_A}{N} P \\ p_B &= \frac{n_B}{N} P \\ p_C &= \frac{n_C}{N} P \\ p_D &= \frac{n_D}{N} P \end{aligned}\right] \quad \text{.... (10)}$$

Putting these values of partial pressures from the set of equations (10) in the expression of 'K_p' in equation (4).

$$K_p = \frac{p_C{}^c \, p_D{}^d}{p_A{}^a \, p_B{}^b} \quad \text{...... (4)}$$

$$K_p = \frac{\left(\frac{n_c}{N} P\right)^c \left(\frac{n_D}{N} P\right)^d}{\left(\frac{n_A}{N} P\right)^a \left(\frac{n_B}{N} P\right)^b}$$

$$K_p = \frac{n_C{}^c \, n_D{}^d}{n_A{}^a \, n_B{}^b} \left(\frac{P}{N}\right)^{(c+d)-(a+b)}$$

$$K_p = K_n \left(\frac{P}{N}\right)^{(c+d)-(a+b)}$$

$$\boxed{K_p = K_n \left(\frac{P}{N}\right)^{\Delta n}} \quad \text{...... (11)}$$

In order to know the relationship between 'K_p' and 'K_n', we should know the values of total pressure, total number of moles of reactants and products, and the difference of number of moles of reactants and products.

اس مساوات (11) کو اس طرح زیر بحث لائیں جیسے پہلی مساوات کو کیا ہے۔

When we join all these relationships, then we can say that

$$\boxed{K_p = K_c(RT)^{\Delta n} = K_x(P)^{\Delta n} = K_n\left(\frac{P}{N}\right)^{\Delta n}} \quad \cdots\cdots \quad (12)$$

If the number of moles of reactants and products are equal, then $\Delta n = 0$

Hence, $(RT)^{o} = 1 \, (P)^{o} = 1 \left(\frac{P}{N}\right)^{o} = 1$

So, $\boxed{K_p = K_c = K_x = K_n} \quad \cdots\cdots \quad (13)$

We reach the important conclusion that when the **number of moles of reactants products in a reaction are equal, then all equilibrium constants have the same values.**

Sample Problem (6.1)

The value of the K_C for NH_3 synthesis at 500°C is 6.01×10^{-2}. Calculate the numerical valu K_p.

$\rightleftharpoons 2NH_{3(g)}$

8.1.6 The Le-Chatelier's Principle

Imp line.

Le-Chatelier studied the effects of concentration, pressure and temperature on equilibria. v.v.Imp(S).

This principle states that if a stress is applied to a system at equilibrium, the system acts in such a way so as to nullify, as far as possible, the effect of that stress.

cancel

The system cannot completely cancel the effect of change, but will minimize it. The Le-Chatelier's principle has wide range of applications for ascertaining the position and composition of the physical and chemical equilibria.

determine

(a) Effect of Change in Concentration

In order to understand the effect of change in concentration on the reversible reaction, consider the reaction in which $BiCl_3$ reacts with water to give a white insoluble compound BiOCl.

Effect of change in 'T' :-

$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad \Delta H = -41.84\ J/mo$

$$K_C \propto \frac{1}{T}$$

T ↓ → Rex forward.

T ↑ → Rex reverse.

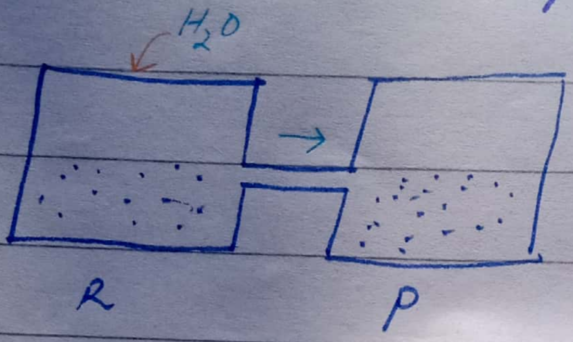
$KI_{(s)} \rightleftharpoons KI_{(aq)} \quad \Delta H = 21.4\ KJ/mol$

$K_C \propto T$

T ↑ → Rex forward

T ↓ → Rex reverse.

Le-Chatelier's Principle:



1) Effect of change in concentration

$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$

if HCl added → backward.

H_2O added → Reverse

In short.

Addition of substance in 'R' or
Removal of substance in R

↓

shifts rexn in forward.

→ Addition of substance in 'P' or
removal of substance in R

↓

shifts rexn in reverse.

Effect of change in P/V:-

Condition:

1) For gaseous rex
2) $\Delta n \neq 0$

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$$

Avogadro's law:

$$V \propto n$$

Also we know

$$P \propto \frac{1}{V}$$

* If decrease in V (stress) at eq. stage → Rex moves forward due to less 'n'

* If increase in V (stress) at eq. stage → Rex moves reverse due to more 'n'

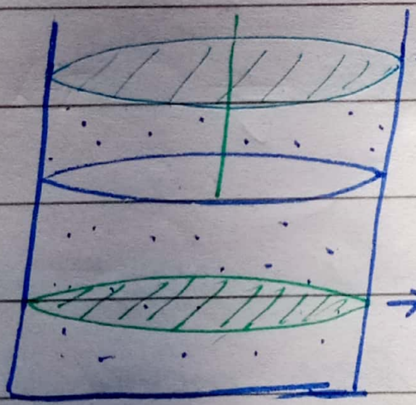
3) Quantitative effect of 'V' on Equilibrium position:

$$2SO_2 + O_2 \rightleftharpoons 2SO_3$$

$t=0$	a	b	0
$t\neq0$	$a-2x$	$b-x$	$2x$

↓ increase → Rex forward.

$$K_c = \frac{4x^2V}{(a-2x)^2(b-x)}$$



→ V increase ↓ Rex reverse.

→ V decrease ↓ Rex forward

If V ↑ x ↓ → Rex reverse

V↓ x ↑ → Rex forward.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

$t=0$	a	0	0
$t\neq 0$	$a-\boxed{x}$ → decrease → rex backward	x	x

$$K_c = \frac{x^2}{V(a-x)}$$

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$K_c = \frac{4x^2}{V(a-x)}$$

* If No. of moles of products are more than reactants then 'V' appears in "denominator"

i.e., $K_c \propto \frac{1}{V}$

* V ↓ then x ↓

↓

Rex moves backward.

* V ↑ then x ↑

↓

Rex moves forward.

4 Effect of change in 'T' :-

$CO + H_2O \rightleftharpoons CO_2 + H_2$ $\Delta H = -41.84\ J/mol$

$$K_c \propto \frac{1}{T}$$

T ↓ → Rex forward.

T ↑ → Rex reverse.

$KI_{(s)} \rightleftharpoons KI_{(aq)}$ $\Delta H = 21.4\ kJ/mol$

$K_c \propto T$

T ↑ → Rex forward

T ↓ → Rex reverse.

$$BiCl_3 + H_2O \rightleftharpoons BiOCl + 2HCl$$ artificial milk

The equilibrium constant expression for above reaction can be written as

$$K_c = \frac{[BiOCl][HCl]^2}{[BiCl_3][H_2O]}$$

Aqueous solution of $BiCl_3$ is cloudy, because of hydrolysis and formation of BiOC small amount of HCl is added to this solution, it will disturb the equilibrium and force system to move in such a wav so that effect of addition of HCl is minimized. The reaction move in the backward direction to restore the equilibrium again and a clear solution wi obtained. However, if water is added to the above solution the system will move in the forw direction and the solution will again become cloudy. The shifting of reaction to forward backward direction by disturbing the concentration is just according to Le-Chateli principle.

So, in general, we conclude that addition of a substance among the reactants, or removal of a substance among the products at equilibrium stage disturbs the equilibriu position and reaction is shifted to forward direction. Similarly, the addition of a substanc among the products or the removal of a substance among the reactants will derive th equilibrium towards the backward direction. Removing one of the products formed ca therefore increase the yield of a reversible reaction. The value of K_c however remain constant. This concept is extensively applied in common ion effect and follows the Le Chatelier's principle.

decrease in conc. eq. will move in same direction.

Imp

(b) Effect of Change in Pressure or Volume

The change in pressure or volume are important only for the reversible gaseous reactions where the number of moles of reactants and products are not equal. Le-Chatelier's principle plays an important role, to predict the position and direction of the reaction. Take the example of formation of SO_3 gas from SO_2 gas and O_2 gas.

$$2SO_2(g) + O_2(gas) \rightleftharpoons 2SO_3(g)$$

This gas phase reaction proceeds with the decrease in the number of moles and hence decreases in volume at equilibrium stage. When the reaction approaches the equilibrium stage, the volume of the equilibrium mixture is less than the volume of reactants taken initially. If one decreases the volume further at equilibrium stage, the reaction is disturbed. It will move to the forward direction to minimize the effect of disturbance. It establishes a new equilibrium position while K_c remains constant. The reverse happens when the volume is increased or pressure is decreased at equilibrium stage.

(c) Quantitative Effect of Volume on Equilibrium Position

The quantitative effect of change of volume or pressure can be inferred from the mathematical expression of K_c for SO_3 (g) synthesis.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$K_c = \frac{4x^2 V}{(a-2x)^2(b-x)}$$

Where 'V' is the volume of reaction mixture at equilibrium stage, 'a' and 'b' are the number of moles of SO_2 and O_2 present initially and 'x' are the number of moles of oxygen which has reacted at equilibrium. According to the above equation, when volume is increased, then 'x' has to be decreased to keep K_c constant. The decrease of x means that reaction is pushed to the backward direction. From the amount of the increase in volume, we can calculate the amount of x which has to be decreased to keep K_c constant.

Similarly, increasing the pressure on the above reaction at equilibrium, will decrease the volume and hence the value of K_C will increase. In order to keep the value of K_C constant the reaction will move in the forward direction.

In the same way, we can explain the effect of change of pressure on the equilibrium positions for the dissociation of PCl_5 and N_2O_4 reactions. These reactions are homogenous gaseous phase reactions.

PCl_5 dissolves to give PCl_3 and Cl_2.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

K_C for this reaction is as follows:

$$K_C = \frac{x^2}{V(a-x)}$$

The dissociation of N_2O_4 gives NO_2 gas

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

The K_C for this reaction is as follows

$$K_C = \frac{4x^2}{V(a-x)}$$

Both these reactions have the factor of volume present in the denominator. The reason is that numbers of moles of products are greater than those of reactants. So, increase in pressure will decrease x to keep the value of K_c constant and the reaction will be pushed to the backward direction. The equilibrium position is disturbed but not the K_c value.

$H_2 + I_2 \rightleftharpoons HI$ → Those both reactent and product are equal

Remember that, those gaseous reactions in which number of moles of reactants and products are same, are not affected by change in pressure or volume. Same is the case for reactions in which the participating substances are either liquids or solids.

bec
no.
mole are eq

(d) Effect of Change in Temperature

Most of the reversible chemical reactions are disturbed by change in temperature. If we consider heat as a component of equilibrium system, a rise in temperature adds heat to the system and a drop in temperature removes heat from the system. According to Le-Chatelier's principle, therefore, a temperature increase favours the endothermic reactions

Kc -- R↓

and a temperature decrease favours the exothermic reactions.

The equilibrium constant changes by the change of temperature, because the equilibrium position shifts without any substance being added or removed. Consider the following exothermic reaction in gas phase at equilibrium taking place at a known temperature. For exothermic → $\boxed{K_c \propto \frac{1}{T}}$

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H = -41.84\,kJ\,mole^{-1}$$

At equilibrium stage, if we take out heat and keep the system at this new lower temperature, the system will readjust itself, so as to compensate the loss of heat energy. Thus, more of CO and H_2O molecules will react to form CO_2 and H_2 molecules, thereby liberating heat because reaction is exothermic in the forward direction. It means by decreasing temperature, we shift the initial equilibrium position to the right until a new equilibrium position is established. On the برعکس contrary, heating the reaction at equilibrium will shift the reaction to the backward direction because the backward reaction is endothermic.

An interesting feature of Le-Chatelier's principle is the effect of temperature on the solubility. Consider a salt such as KI. It dissolves in water and absorbs heat.

$$KI(s) \rightleftharpoons KI(aq) \quad \text{For endothermic} = \boxed{K_c \propto T} \quad \Delta H = 21.4\,kJ\,mole^{-1}$$

Let us have a saturated solution of KI in water at a given temperature. It has attained equilibrium at this temperature. A rise in temperature at equilibrium favours more dissolution of the salt. Equilibrium is shifted to the forward direction. On the other hand cooling will favour crystallization of salt. Hence the solubility of KI in water must increase with increase in temperature.

For some salts the heat of solution is close to zero (heat is neither evolved or absorbed). The solubility of these salts in water is not affected by the change in temperature. Formation of aqueous solution of NaCl is an example of such a salt.

Those substances, whose heats of solutions are negative (exothermic), decrease their solubilities by increasing temperature, as LiCl and Li_2CO_3, etc. Na_2CO_3.

✓ Imp

(e) Effect of Catalyst on Equilibrium Constant

In most of the reversible reactions the equilibrium is not always reached within a suitable short time. So, an appropriate catalyst is added. A catalyst does not affect the equilibrium position of the reaction. It increases the rates of both forward and backward reactions and this reduces the time to attain the state of equilibrium.

Actually, a catalyst lowers the energy of activation of both forward and reverse steps by giving new path to the reaction. "Substance which alter (may increase or decrease) rate of a chemical reaction"

8.2 APPLICATIONS OF CHEMICAL EQUILIBRIUM IN