

লাল-সবুজে
দাগানো

TEXT BOOK



Chemistry
1st Paper



UNMESH

Medical & Dental Admission Care

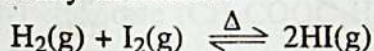
Characteristics of a Catalyst :

- (i) A catalyst does not participate directly in the reaction. Hence it remains unchanged in composition and mass at the end of the reaction.
- (ii) A small quantity of catalyst is sufficient to effect large quantity of the reactants.
- (iii) A catalyst does not initiate or stop a reaction, it only accelerates or retards a reaction and does not disturb other catalysts.
- (iv) A catalyst is generally specific for a particular reaction.
- (v) Catalyst generally lowers the activation energy of a reaction.

4.5 Chemical Equilibrium

Definition : When the rate of a forward reaction is equal to that of the backward reaction, then the state is known as chemical equilibrium.

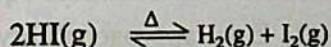
Example : When a mixture of H_2 gas and iodine is heated to a temperature, 450°C in a sealed container, then hydrogen and iodine react to form hydrogen iodide. Since with the increase of time the amounts of hydrogen and iodine decrease, then the rate of this reaction gradually decreases.



Initially there was no hydrogen iodide, so there was no backward reaction. But when the forward reaction starts to form HI and gradually its amount increases, then backward reaction *i. e.* dissociation of HI to H_2 and I_2 begins to occur. After sometime the rates of forward and backward reactions become equal. This state of both the reactions is called **chemical equilibrium**.

Again if we heat pure hydrogen iodide in a sealed container, similar situation arises.

Then the dissociation of hydrogen iodide to hydrogen and iodine is the forward reaction and formation of hydrogen iodide from hydrogen and iodine is the backward reaction.



At one stage the chemical equilibrium will be reached when the rates of these two reactions (forward and backward) will be same. In both the cases **at equilibrium the ratio of these substances will be the same. This is the condition of equilibrium.**

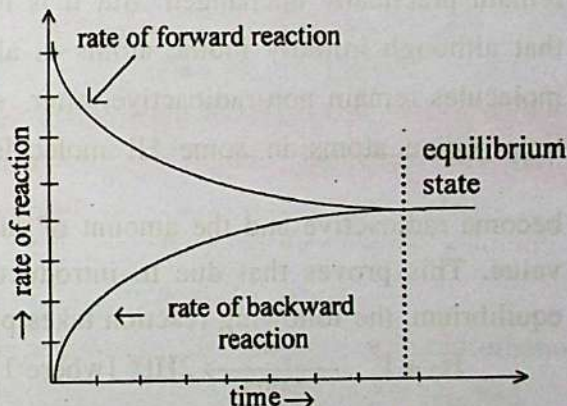
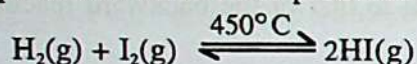


Fig. 4.10: Change of rates of forward and backward reactions with time and attainment of chemical equilibrium

4.5.1 Dynamic Nature of Equilibrium

Theoretical basis of chemical equilibrium : At the equilibrium of the reversible reaction, it is reality that reactant molecules constantly react to form the product molecules and at the same time the product molecules react to form the reactant molecules. So the chemical equilibrium is dynamic not static.

Proof of dynamic nature : The dynamic nature of chemical equilibrium can easily be proved by using radioisotopes in reaction chambers. For example, when a mixture of H_2 and I_2 is kept at a certain temperature in a sealed tube, at the beginning H_2 and I_2 react fast to produce HI, then the rate of reaction decreases and after some time the reaction apparently stops and no more HI is produced. In fact then the chemical equilibrium has been reached.



After the equilibrium is reached, if small amount of radioactive iodine ($^{128}_{53}I_2$) is introduced as tracer into the reaction chamber, then there is no appreciable change in the equilibrium, since the amounts of H_2 , I_2 and HI remain practically unchanged. But it is found that although initially iodine atoms in all HI molecules remain non-radioactive, after some time iodine atoms in some HI molecules

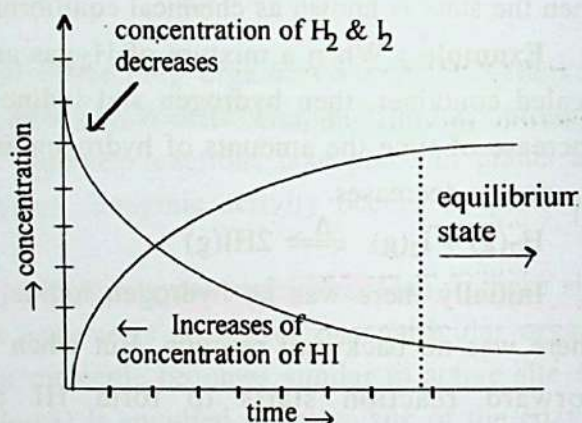
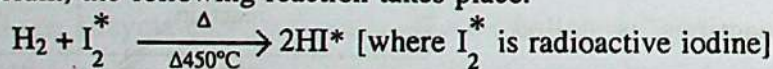
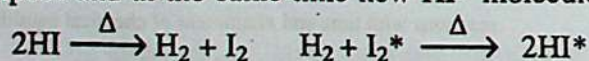


Fig. 4.11 : Change of concentration of H_2 , I_2 and HI with time and get equilibrium

become radioactive and the amount of such HI molecules increases gradually to a definite value. This proves that due to introduction of radioactive iodine after the attainment of equilibrium, the following reaction takes place.



Since the total amount of HI molecules remains unaltered, hence some HI molecules decompose and at the same time new HI^* molecules form.



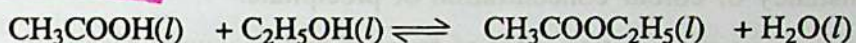
4.5.2. Characteristics of Chemical Equilibrium.

The followings are the characteristics of chemical equilibrium :

(1) Stability of equilibrium, (2) Easy approachability from both sides, (3) Incompleteness of reaction, (4) Ineffectiveness of catalyst.

(1) Stability of Equilibrium : Once a chemical system attains equilibrium it will stay in equilibrium for ever, if the external conditions like pressure, temperature and concentration are not changed. For example, When 1 mol ethanoic acid and 1 mol ethanol are allowed to

react at 100°C, then till the equilibrium is reached 0.667 mol of each reactant reacts to produce 0.667 mol of ethylethanoate and 0.667 mol water. So after the equilibrium is reached the reaction mixture contains 0.333 mol ethanoic acid, 0.333 mol ethanol, 0.667 mol ethyl ethanoate and 0.667 mol water.



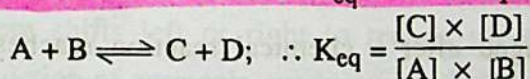
At first stage :	1 mol	1 mol	0 mol	0 mol
At equilibrium :	0.333 mol	0.333 mol	0.667 mol	0.667 mol

If the reaction mixture is kept at 100°C for a very long time no change occurs in the composition of the mixture. It will remain in equilibrium.

(2) **Easy approachability from both sides** : The equilibrium of a reaction can be attained from both directions. For example, when the reaction is started with 1 mol acetic acid (CH_3COOH) and 1 mol ethanol ($\text{C}_2\text{H}_5\text{OH}$) at 100°C, after the equilibrium is attained the reaction mixture contains 0.333 mol CH_3COOH , 0.333 mol ethanol, 0.667 mol ethyl ethanoate ($\text{CH}_3\text{COOC}_2\text{H}_5$) and 0.667 mol H_2O . Again if the reaction is started with 1 mol ethyl ethanoate ($\text{CH}_3\text{COOC}_2\text{H}_5$) and 1 mol H_2O at 100°C, then the same reaction mixture will be obtained at the equilibrium.

(3) **Incompleteness of reaction** : A reversible reaction is never completed, because due to backward reaction, the initial reactants are always reproduced together with products.

If the reaction completes in one direction, the value of equilibrium constant K_{eq} will be infinity as it is the ratio of molar concentration of products and molar concentration of reactants. But the value of K_{eq} is never equal to infinity.



For example in the reaction between equimolar amounts of ethanoic acid and ethanol only two thirds of the reactants are converted to the products when equilibrium is reached.

	$\text{CH}_3\text{COOH}(l)$	$+ \text{C}_2\text{H}_5\text{OH}(l)$	\rightleftharpoons	$\text{CH}_3\text{COOC}_2\text{H}_5(l)$	$+ \text{H}_2\text{O}(l)$
	ethanoic acid	ethanol		ethyl ethanoate	
At initial stage :	1 mol	1 mol		0 mol	0 mol
At equilibrium :	0.333 mol	0.333 mol		0.667 mol	0.667 mol

(4) **Ineffectiveness of catalysts** : The catalysts have no effect on chemical equilibrium. In a reversible reaction catalyst speeds up both the forward and backward reactions to the same degree.

This proves that even after attainment of equilibrium, both the forward reaction and backward reaction continue to take place to maintain chemical equilibrium.

Know more-'How to detect equilibrium state'.

The criteria to detect the equilibrium in reactions are :

- (1) Stability of colour-change of the reactants and products.
- (2) Constancy of colour concentration of precipitate.
- (3) Determining the reaction rates of forward and backward reactions.

For example, thermal decomposition of nitrogen tetraoxide (N_2O_4) is a reversible reaction. Here N_2O_4 is colourless; but the product nitrogen dioxide (NO_2) is a brown gas. At the primary stage of reaction, the colourless N_2O_4 remains in closed reaction-flask; but after a few moments, when decomposition of N_2O_4 begins, then light brown gas appears; on further decomposition, the brown colour begins to be dense. After a definite period, the brown colour remains constant. Here constancy of dense brown colour confirms the equilibrium of the reversible reaction. N_2O_4 (colourless) $\xrightleftharpoons{\Delta}$ 2NO_2 (brown)

Here at equilibrium, the ratio of the square of molar concentration of product NO_2 and molar concentration of the reactant N_2O_4 is called **equilibrium constant (K)**. But at any time after beginning of the reaction, the ratio of the concentration terms of the product and reactant that we write for a given reaction, is called **reaction quotient (Q, or mass-action expression)** :

$$Q = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}; \text{ At equilibrium, } Q = K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]}$$

4.6 Le-Chatelier's Principle

When the external conditions are not changed after a chemical reaction reaches its equilibrium state, then this will remain in equilibrium for ever. Factors like temperature, pressure, concentration etc. control the equilibrium. If any one of these factors is changed, then the equilibrium is changed and is shifted to a new equilibrium. The direction of the change is expressed in Le-Chatelier's Principle.

Le-Chatelier's Principle : If a change occurs in one of the controlling factors, such as temperature, pressure, concentration etc. under which a system is in equilibrium, then the system will tend to adjust itself in such a way so as to reduce the effect of that change.

or, If a system in equilibrium is disturbed by change of any factor like temperature, pressure or concentration, then equilibrium will shift so as to reduce the effect of that change.

So, the position of equilibrium depends on three factors : (i) Temperature, (ii) Pressure, (iii) Concentration of the components.

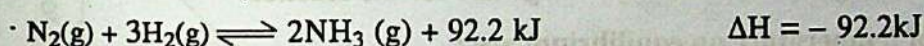
★ (i) It is to be mentioned that if the pressure or concentration is changed keeping the temperature constant, then the equilibrium is shifted, But the values of K_p and K_c do not change.

★ (ii) On the other hand if the temperature is changed, not only the equilibrium is shifted, but also the values of K_p and K_c change.

4.6.1 Effect of Temperature Change On Equilibrium

Of the three types of disturbances of the equilibrium of a reaction; like a change in concentration, in pressure, or in temperature—only temperature changes can alter the equilibrium constant (K). Heat of reaction is very important to explain this changes, when an equilibrium is disturbed by a change; in concentration, pressure or volume of gaseous reaction mixture, the composition of the equilibrium mixture changes because the reaction quotient Q_c no longer equals the equilibrium constant K_c . As long as the temperature remains constant, however, concentration, pressure, valume changes donot change the value of the equilibrium constant,

By contrast, a change in temperature nearly always changes the value of the equilibrium constants. For the Haber sythesis of ammonia from N_2 gas and H_2 gas, we get :



Here forward reaction is exothermic (releases heat; $\Delta H < 0$), so the reverse reaction is endothermic (absorbs heat; $\Delta H > 0$). Here at equilibrium, 'heat is considered as a component of the equilibrium system. A rise in temperature "adds" heat to the system and a drop in temperature "removes" heat from the system. As with a change in any other component, the system shifts left or right to reduce the effect of the change. With the figure 4.12 the production of ammonia gas in an exothermic reaction is explained :

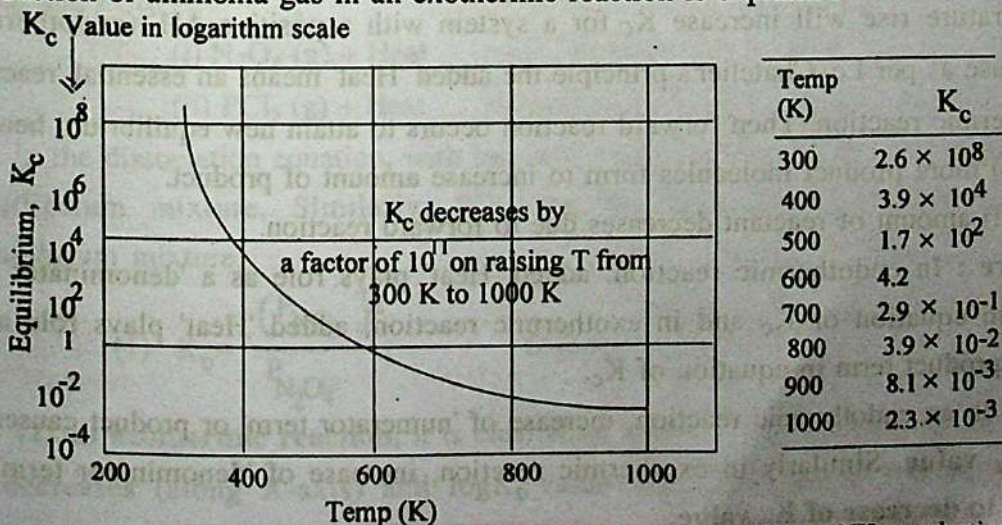
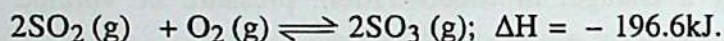


Fig. 4.12 : Temperature dependence of the equilibrium constant, K_c for NH_3 production reaction.

From the curve of equilibrium constant K_c and kelvin temp K , it is clear that the equilibrium constant, K_c decreases by a factor of 10^{11} over the temperature range 300 – 1000 K (fig-4.12).

At low temperature, the equilibrium mixture is rich in NH_3 gas because the value of K_c is large. At high temperatures, the equilibrium shifts to the left, the value of K_c is low, then the reaction mixture contains more N_2 and H_2 with less NH_3 . At 300K temp. for NH_3 production, $K_c = 2.6 \times 10^8$; but at 1000K temp. $K_c = 2.3 \times 10^{-3}$. Similar to NH_3 production in every exothermic reaction, product decreases with increase of temp. In production of H_2SO_4 by Contact Process, oxidation of SO_2 to SO_3 is an exothermic reaction.



So at optimum-conditions in an industry, for NH_3 production in presence of Fe catalyst 500°C or, 773K temp. is used. For SO_3 production in presence of V_2O_5 catalyst 450°C or, 723K temp. is applied.

In general, the temperature dependence of an equilibrium constant (K_c) depends on the negative or positive sign of the enthalpy change ΔH for the reaction.

The effects of temperature on equilibrium are :

* A temperature rise will decrease K_c for a system with a negative ΔH (exothermic reaction). Because as per Le-Chatelier's principle the added 'Heat' acts as 'product-term'. Then backward reaction occurs to get new equilibrium; hence –

- * (i) amount of product decreases due to dissociation of product.
- * (ii) amount of reactant increases due to backward reaction.

* A temperature rise will increase K_c for a system with a positive ΔH (endothermic reaction). Because as per Le-Chatelier's principle the added 'Heat' means an essential 'reactant term' in endothermic reaction. Then forward reaction occurs to attain new equilibrium hence–

- * (i) more product molecules form to increase amount of product.
- * (ii) amount of reactant decreases due to forward reaction.

Know More : In endothermic reaction, added 'Heat' plays role as a 'denominator' or, reactant term in equation of K_c and in exothermic reaction, added 'Heat' plays role as a 'numerator or, product term in equation of K_c .

As a result in an endothermic reaction, increase of 'numerator term' or product causes to **increase of K_c value**. Similarly in exothermic reaction, increase of 'denominator term' or reactant causes to **decrease of K_c value**.

(A) **Van't Hoff Equation : The Effect of T on K** : The Van't Hoff equation shows how the equilibrium constant (K) is affected by changes in temperature. Generally at constant temp. the equilibrium constant (K_c and K_p) of any reaction remains constant. But with change of temp. equilibrium state changes with change in equilibrium constant. Van't Hoff proposed the following equation to explain the affect of temp. on equilibrium constant :

$$\log K_p = \frac{-\Delta H}{2.303R} \times \frac{1}{T} + \text{constant};$$

Here K_p = equilibrium const. (with partial pressure)

R = molar const; T = kelvin temp.

Van't Hoff's equation is similar to linear equation $y = mx + c$. Hence $\log K_p$ vs $\frac{1}{T}$ graph will be a straight line. For endothermic reaction and exothermic reaction, two different straight lines like fig 4.13(a) and 4.13(b) are obtained.

(1) **In endothermic reaction**, it is clear from graph 4.13(a) that when temp. (T) increases $\frac{1}{T}$ decreases (along X axis) and $\log K_p$ value increases (along Y-axis, straight line is upwards).

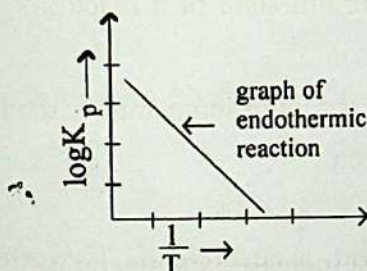


Fig. 4.13(a) : $\log K_p$ vs $\frac{1}{T}$ graph for endothermic reaction

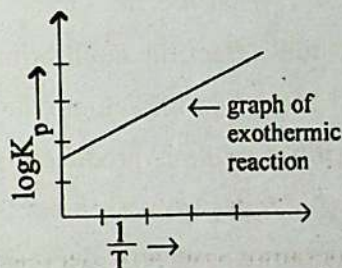
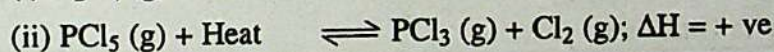
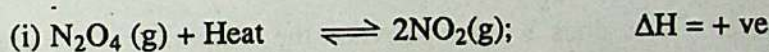


Fig. 4.13(b) : $\log K_p$ vs $\frac{1}{T}$ graph for exothermic reaction

Hence with increase of temp. (T), value of equilibrium constant (K_p) increases in endothermic reaction. Two examples for endothermic reaction are thermal dissociation of N_2O_4 and PCl_5 .



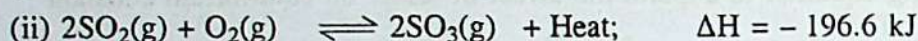
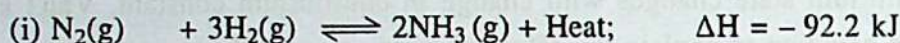
In the dissociation equation, with increase of temp. concentration of NO_2 gas increases in equilibrium mixture. Similarly, PCl_3 and Cl_2 gases concentrations increase in their equilibrium mixture.

$$(1) K_p = \frac{(P_{NO_2})^2}{P_{N_2O_4}};$$

$$(2) K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

(2) **In exothermic reaction**, it is clear from graph 4.13 (b) that when temp. (T) increases $\frac{1}{T}$ decreases (along X-axis) and $\log K_p$ value decreases (along Y-axis, straight line is downwards.). Hence with increase of temp. equilibrium constant value decreases in

exothermic reaction. Example of exothermic reaction is NH_3 production from N_2 and H_2 gases. Here with increase of temp. after equilibrium NH_3 dissociates into N_2 and H_2 hence NH_3 production becomes less. Similarly SO_3 gas production from SO_2 is an exothermic reaction



$$(1) K_p = \frac{(\text{P}_{\text{NH}_3})^2}{\text{P}_{\text{N}_2} \times (\text{P}_{\text{H}_2})^3} \quad (2) K_p = \frac{(\text{P}_{\text{SO}_3})^2}{\text{P}_{\text{SO}_2}^2 \times \text{P}_{\text{O}_2}}$$

Student's Work - 4.5 : Equilibrium Based :

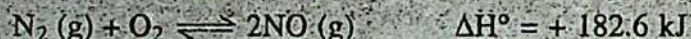
Problem- 4.23(a) : What is chemical equilibrium? [Di. B. 2016]

Problem- 4.23(b) : Chemical equilibrium is dynamic; explain. [Ctg. B. 2015]

Problem- 4.23(c) : Prove dynamic nature of chemical reaction with an example.

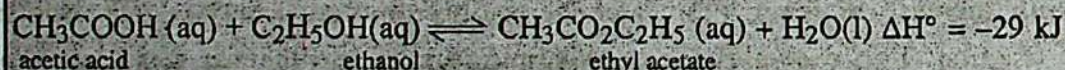
Problem-4.24 : What are the factors that influence equilibrium state of a reaction? And which factor does effect the equilibrium state and how; explain.

Problem - 4.25(a) : In an automobile engine, air is heated at a high temperature, then the air pollutant nitric oxide is produced by the following reaction :



How does the amount of NO gas vary at equilibrium with an increase in temperature?

Problem- 4.25(b) : Ethyl acetate, a solvent used as finger nail-polish remover, is made by the reaction between acetic acid and ethanol :



Does the amount of ethyl acetate in an equilibrium mixture increase or decrease when the temperature is increased? How does K_c change when the temperature is decreased? Justify your answers using Le Chateliers' principle.

4.6.2 Effect of Pressure Change (or Volume Change) on Equilibrium

In general, Le-Chatelier's principle predicts that :

* An increase in pressure by reducing the volume will bring about net reaction in the direction that decreases the number of moles of gas.

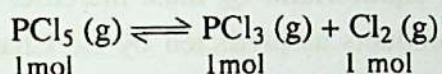
* An decrease in pressure by expanding the volume will bring about net reaction in the direction that increases the number of moles of gas.

Let us discuss the three cases for the effect of pressure change on equilibrium with variation in number of moles of the products.

(i) With increase in number of moles of product :

When in an equilibrium system, number of moles of the product increases than that of reactants, then pressure of the equilibrium gaseous mixture increases in a closed chamber. In that case, with increase of pressure the yield decreases. For example,

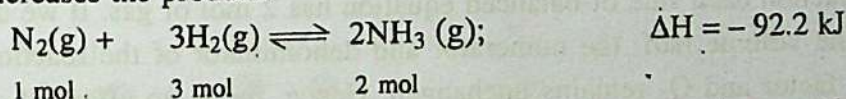
In thermal dissociation of PCl_5 , number of moles of gaseous product increases; that is volume of the gaseous mixture increases. So in a closed chamber, pressure of the reaction mixture increases.



On increasing pressure, the volume of gas mixture decreases; concentration increases. Again, on decreasing pressure, volume of gas mixture increases; concentration decreases. Now, from reaction quotient, $Q_c = \frac{[\text{PCl}_3] \times [\text{Cl}_2]}{[\text{PCl}_5]}$, we know that when the volume is halved, on increasing pressure, then the concentration is double, but the numerator of Q_c is the product of two concentrations, so it quadruples while the denominator only doubles. Thus, Q_c becomes greater than K_c , ($Q_c > K_c$). As a result, to decrease Q_c , the system forms more PCl_5 and a new equilibrium position is reached by backward reaction. Hence in this case, with the increase of pressure the amount of product or yield decreases.

(2) With decrease in number of moles of product :

If in a reaction the number of moles decreases, then increase of pressure on the system in equilibrium will shift the equilibrium in the forward direction, i.e. towards the products. Then, the pressure decreases at constant volume. Hence the forward reaction will diminish the effect of increase of pressure. For this reason very high pressure is used in the manufacture of ammonia, as it increases the product.



The balanced equation for this reaction has 4 mol of gas on the reactant side of the equation and 2 mol on the product side.

Now we shall explain the effect of change in pressure on equilibrium in the light of Le-Chatelier's principle with the value of reaction quotient, Q_c and equilibrium constant, K_c . Let us look again at the reaction quotient for the equilibrium mixture of 0.50 M N_2 , 3.0M H_2 and 1.98 M NH_3 at 700K :

$$\begin{aligned} Q_c &= \frac{[\text{NH}_3]_t^2}{[\text{N}_2]_t \times [\text{H}_2]_t^3} = \frac{(1.98)^2}{(0.50) \times (3.0)^3} \\ &= 0.29 = K_c \end{aligned}$$

MCQ-4.6 : Which one is not a characteristic of chemical equilibrium?

- (a) Stability (b) Reversibility
(c) Reaction rate (d) incompleteness

If we disturb the equilibrium by reducing the volume by a factor 2, with increase of pressure; then concentration of each component like reactant and product becomes double. Then $[\text{NH}_3]_t = 1.98 \times 2 = 3.96$; $[\text{N}_2]_t = 0.5 \times 2 = 1.0$; $[\text{H}_2]_t = 3.0 \times 2 = 6.0$. Now putting these values in reaction quotient expression, Q_c , we get :

$$Q_c = \frac{[\text{NH}_3]_t^2}{[\text{N}_2]_t \times [\text{H}_2]_t^3} = \frac{(3.96)^2}{(1.0) \times (6.0)^3} = 0.0726 < K_c$$

For the system to move to a new state of equilibrium, Q_c must increase. This means that the net reaction must go from reactants to products as predicted by Le Chatelier's principle [Fig-4.14]. In practice, the yield of ammonia in the Haber process is increased by running the reaction at high pressure, typically 130–300 atm.

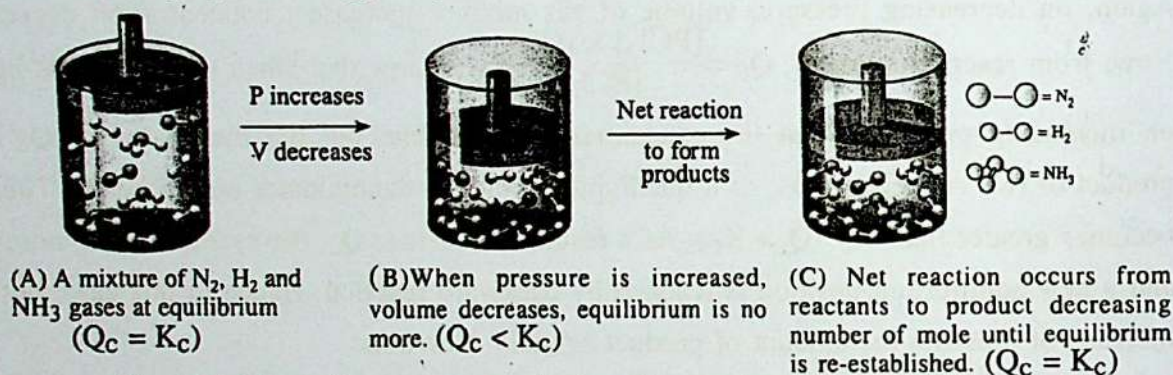
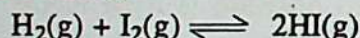


Fig-4.14 :Effect of pressure on production of ammonia

(3) **With no change in moles :** When there is no difference between numbers of moles of reactants and products, no change in volume occurs; hence pressure change has no effect on the gaseous equilibrium. For example, the synthesis of hydrogen iodide and its dissociation :

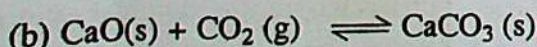
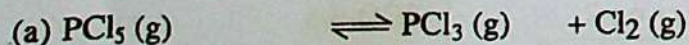


In this reaction each side of balanced equation has 2 mol of gas. If we double the pressure by making the volume half, the numerator and denominator of the reaction quotient change by the same factor and Q_c remains unchanged. Hence, there is no effect of change of pressure on equilibrium :

$$Q_c = \frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]} = \frac{[\text{HI}] \times [\text{HI}]}{[\text{H}_2] \times [\text{I}_2]}$$

Worked Example- 4.10 : Effect of Change in Pressure (Volume) on Equilibrium :

Does the number of moles of reaction products increase, decrease or remain same when each of the following equilibria is subjected to a decrease in pressure by increasing volume?



Strategy : According to Le-Chatelier's principle, the stress of a decrease in pressure is relieved by net reaction in the direction that increases the number of moles of gas.

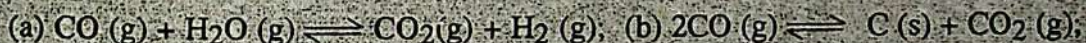
Solution : (A) In decomposition of PCl_5 , here 1 mol of gas converts to 2 mol of product gas; net reaction will go from reactants to products, on decreasing pressure, thus increasing the number of moles of PCl_3 and Cl_2 gas.

(B) According to given balanced equation, there is only 1 mol of gas on the reactant side and no gas on product side; so the stress of a decrease in pressure is relieved by net reaction from products to reactants. The number of moles of CaCO_3 therefore decreases.

(C) According to given balanced equation, there are 4 mol of gas on both sides; so the composition of the equilibrium mixture is unaffected by a change in pressure. The number of moles of Fe_3O_4 and H_2 remains the same.

Students' Work -4.6 : Effect of Pressure on Equilibrium :

Problem 4.26 : Does the number of moles of products increase, decrease or remain the same when each of the following equilibria is subjected to an increase in pressure by decreasing the volume?



4.6.3 Effect of Concentration Change on Equilibrium

To know the effect of changes in concentrations on equilibrium; let us consider the equilibrium that occurs in the Haber process for the synthesis of ammonia from N_2 and H_2 gases :

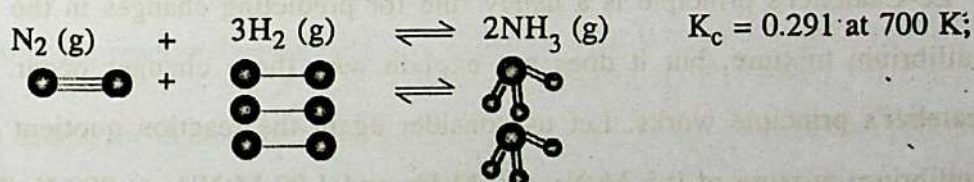


Fig- 4.15 : Equation of NH_3 synthesis with molecular models of reactants and product.

Suppose that we have an equilibrium mixture of 0.5 M N_2 gas, 3.0 M H_2 gas and 1.98 M NH_3 gas at 700 K and that we disturb the equilibrium by increasing the N_2 gas concentration to 1.5 M.

Le-Chatelier's principle tells us that reaction will occur to relieve the stress of the increased concentration of N_2 by converting some of the N_2 to NH_3 . As the N_2 concentration decreases,

the H_2 concentration must also decrease and the NH_3 concentration must increase in accord with the stoichiometry of the balanced equation. These changes are shown in fig-4.16.

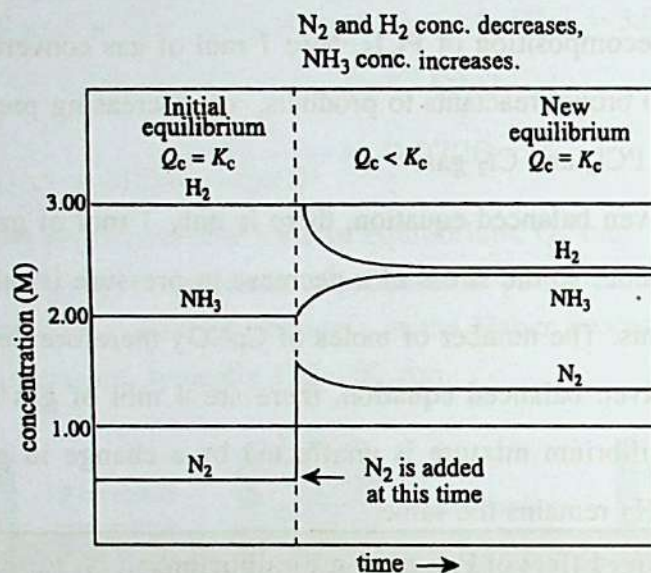


Fig-4.16 : Changes in concentrations when N_2 is added to an equilibrium mixture of N_2 , H_2 and NH_3

In general, when an equilibrium is disturbed by increasing or decreasing of any reactant or product, then Le-Chatelier's principle tells that :

* The concentration stress of an *added* reactant or product is relieved by net reaction in the direction that *consumes* the added substance.

* The concentration stress of a *removed* reactant or product is relieved by net reaction in the direction that *replenishes* (or *refills*) the removed substance.

Le-Chatelier's principle is a handy rule for predicting changes in the composition of an equilibrium mixture, but it does not explain *why* those changes occur. To see why Le-Chatelier's principle works, Let us consider again the reaction quotient Q_c . For the initial equilibrium mixture of 0.5 M N_2 , 3.0 M H_2 and 1.98 M NH_3 at 700 K, Then Q_c equals the equilibrium constant K_c (0.291). Because the system is at equilibrium :

$$Q_c = \frac{[\text{NH}_3]_t^2}{[\text{N}_2]_t \times [\text{H}_2]_t^3}$$

$$= \frac{(1.98)^2}{(0.5) \times (3.0)^3}$$

$$= 0.29 = K_c$$

When the equilibrium is disturbed by adding N_2 to increase concentration to 1.5 M, then denominator of the equilibrium constant expression increases and Q_c decreases to a value less than K_c .

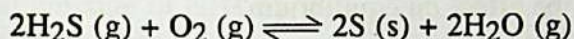
$$Q_c = \frac{[NH_3]_t^2}{[N_2]_t \times [H_2]_t^3} = \frac{(1.98)^2}{(1.5) \times (3.0)^3} = 0.0968 < K_c$$

Hence for the system to establish a new state of equilibrium, Q_c must increase. In other words, the numerator of the equilibrium expression must increase and the denominator must decrease. This implies the net conversion of N_2 and H_2 to NH_3 ; just as predicted by Le-Chatelier's principle. When the new equilibrium is established (fig-4.16), the concentrations are 1.31 M N_2 , 2.43 M H_2 , and 2.36 M NH_3 , and Q_c again equals K_c :

$$Q_c = \frac{[NH_3]_t^2}{[N_2]_t \times [H_2]_t^3} = \frac{(2.36)^2}{(1.31) \times (2.43)^3} = 0.296 = K_c$$

Worked Example-4.11 : Effect of Change in Concentration on Equilibrium :

To improve air quality and obtain a useful product, chemists often remove sulphur from coal and natural gas by treating the fuel contaminant hydrogen sulphide with O_2 :



What happens to : (a) $[H_2O]$, if O_2 is added? (b) $[H_2S]$, if O_2 is added?

(c) $[O_2]$, if H_2S is removed? (d) $[H_2S]$, if sulphur is added

Strategy : We write the reaction quotient to see how Q_c is affected by each disturbance relative to K_c . This effect tells us the direction in which the reaction proceeds for the system to re-attain equilibrium and how each concentration changes.

Solution : Writing the reaction quotient, $Q_c = \frac{[H_2O]^2}{[H_2S]^2 \times [O_2]}$

(a) When O_2 is added, the denominator of Q_c increases, so $Q_c < K_c$. The reaction proceeds to the right until $Q_c = K_c$ again, so $[H_2O]$ **increases**.

(b) As in part (a), when O_2 is added, $Q_c < K_c$. Some H_2S reacts with the added O_2 as the reaction proceeds to the right, so $[H_2S]$ **decreases**.

(c) When H_2S is removed, the denominator of Q_c decreases, so $Q_c > K_c$. As the reaction proceeds to the left to re-form H_2S , more O_2 is produced as well, so $[O_2]$ **increases**.

(d) The concentration of solid S is unchanged as long as some is present, So it does not appear in the reaction quotient. Adding more S has no effect, so $[H_2S]$ is **unchanged**.

Worked Example–4.12 : Effect of Different Factors on Equilibrium.

* (a) $A(g) + B(g) \rightleftharpoons 2C(g)$; this reaction at a particular temp. is in equilibrium. In this reaction, (i) by adding catalyst, or (ii) increasing pressure at constant temp. whether the product (C) can be increased?

Solution : (i) By adding catalyst amount of product (C) can not be increased; because catalyst has no effect on equilibrium. (ii) In this reaction, molar volumes in both sides are equal; hence, pressure has no effect on equilibrium of this reaction. So at constant temp., amount of product can not be increased by increasing pressure.

* (b) $CaCO_3(s) \xrightleftharpoons{\Delta} CaO(s) + CO_2(g)$; this reaction is in a closed chamber. At constant temp. if CO_2 gas is added from outside then what will be effect on equilibrium?

Solution : In this given reaction, $K_p = P_{CO_2}$; because $CaCO_3(s)$ and $CaO(s)$ are solids. If CO_2 gas is added from outside, then partial pressure of CO_2 will be increased. But at constant temp. value of K_p is constant. So added CO_2 gas will react with equi-molar amount of CaO to form $CaCO_3$ till the partial pressure becomes as before.

* (c) $C(s) + O_2(g) \rightleftharpoons CO_2(g)$; this reaction occurs in a closed chamber. If C (s) powder is added in this reaction, what will be effect on equilibrium?

Solution : Here C(s) is a pure solid substance. Such substance has constant 'active mass' and value of 'active mass' does not depend on amount of substance. So by adding C(s), equilibrium of that reaction will not change.

Students' Work - 4.7 : Effect of Concentration on Equilibrium :

Problem – 4.27 : Consider the equilibrium for the water-gas shift reaction :



Use Le-Chatelier's principle to predict how the concentration of H_2 will change when the equilibrium is disturbed by :

(a) Adding CO gas,

(b) Adding CO_2 gas,

(c) Removing H_2O ,

(d) Removing CO_2 ,

Also account for the change using the reaction quotient Q_c .

4.7 Application of Le-Chatelier's Principle on Industrial Productions

There are important applications of Le-Chatelier's Principle in industrial productions. Here two important applications have been discussed.

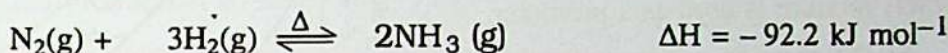
(A) Synthesis of ammonia : In industry, large amount of ammonia is produced from nitrogen and hydrogen using Haber-Bosch process with following reaction :



(1) **Effect of Pressure** : In this reaction the number of moles is reduced from 4 moles to 2 moles. Hence according to Le-Chatelier's Principle an increase in pressure should increase the production of ammonia. Experimentally it has found to be true and a pressure of 200 atm is used in industry to get a reasonable and economically profitable production of ammonia.

Quantitative relation between yield and pressure in synthesis of ammonia

The synthesis of ammonia from N_2 and H_2 gases may be represented as follows :



At initial stage : 1 mol 3 mol 0 mol

At equilibrium : $(1-x)$ mol $(3-3x)$ mol $2x$ mol

According to Le-Chatelier's Principle the higher is the pressure, the higher will be the yield of ammonia. This is found experimentally. Here this will be established mathematically.

The total number of moles at equilibrium = $(1 - x + 3 - 3x + 2x) = (4 - 2x)$ mol

\therefore Equilibrium constant, $K_p = \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3}$; If total pressure on gas mixture is P atm

Partial pressure of NH_3 , $P_{NH_3} = \frac{2x}{(4-2x)} \times P = \frac{2x}{2(2-x)} \times P = \frac{x}{(2-x)} \times P$

Partial pressure of N_2 , $P_{N_2} = \frac{(1-x)}{(4-2x)} \times P$; Partial pressure of H_2 , $P_{H_2} = \frac{(3-3x)}{(4-2x)} \times P$

$$\therefore K_p = \frac{\left(\frac{x}{2-x} \times P\right)^2}{\left(\frac{1-x}{4-2x} \times P\right) \left(\frac{3-3x}{4-2x} \times P\right)^3} = \frac{x^2 \times P^2}{(2-x)^2} \times \frac{2(2-x)}{(1-x) \times P} \times \frac{8(2-x)^3}{27(1-x)^3 P^3} = \frac{16x^2(2-x)^2}{27(1-x)^4 P^2}$$

If $x \ll 1$, then $(2-x) \approx 2$; $(1-x) \approx 1$; So $K_p = \frac{64}{27} \cdot \frac{x^2}{P^2}$; or, $x_2 = \frac{27}{64} \cdot K_p \times P^2$

or, $x = \sqrt{\frac{27 \times K_p}{64}} \times P$; Since K_p is a constant (at a particular temperature),

$\therefore x \propto P$, or the yield of ammonia is directly proportional to the pressure applied.

From the above relation, it is clear that **production of NH_3 increases with increase of pressure**. From experimental data, we know that the favourable conditions for **maximum yield of ammonia** are 130 atm – 300 atm at a temperature range **400°–500°C**

(2) Effect of Temperature :

Ammonia synthesis is an exothermic reaction. So, according to Le-Chatelier's Principle, the lower the reaction temperature is, the higher will be the production of ammonia. But rate

of reaction is slow at lower temperature. Hence to increase the rate of reaction, a favourable temperature is selected, at which the rate of reaction and total production become profitable.

This temperature is known as **optimum temperature**. In Haber's ammonia synthesis process the optimum temperature is then $400^{\circ} - 500^{\circ}\text{C}$ with Fe-powder as catalyst and MgO , SiO_2 and Al_2O_3 mixture is used as a promoter.

As the reaction occurs with decrease of volume of reaction mixture, the percentage yield of ammonia is expected with high pressure, and it is supported by the equation of K_p .

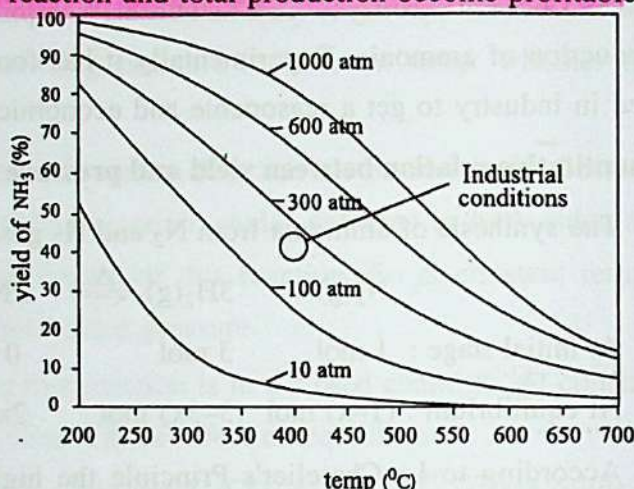


Fig. 4.17 : Percent yield of ammonia Vs. temperature ($^{\circ}\text{C}$) at five different operating pressures.

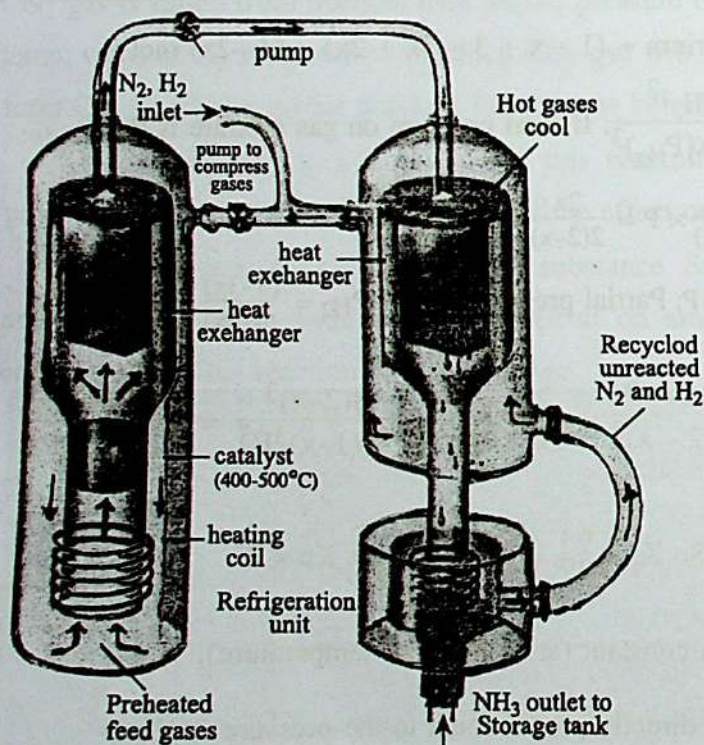
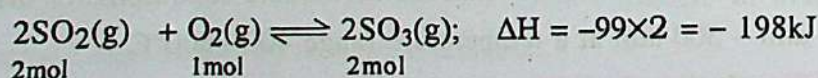
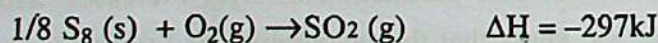


Fig-4.18 : Haber's process for industrial production of ammonia



(1) Since the reaction is exothermic, according to Le Chatelier's Principle the lower the temperature the higher is the production. However since the rate of reaction at lower temperature is very slow, it is necessary to use a high temperature.

So, to extend equipment's life and minimize cost, modern ammonia plants operate mostly at pressures of about 130 atm to 300 atm and temperature of around 400°C ; together with catalyst consisting of 5 mm to 10 mm chunks of iron crystals embedded in a fused mixture of MgO , Al_2O_3 , and SiO_2 .

(B) Oxidation of Sulphur dioxide : In industrial manufacture of sulphuric acid by contact process, an important step is the oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3).

(2) Using V_2O_5 or Pt as catalyst rate of the reaction is increased. Then $400^\circ - 500^\circ\text{C}$ temperature can be used as **optimum temperature**.

(3) Since oxygen from air is easily available and as one reactant large excess of oxygen is introduced in the reaction vessel; then more amount of SO_2 is oxidized to SO_3 .

(4) Since in this reaction the number of moles of product decreases, according to Le Chatelier's Principle the production of SO_3 will increase with increasing pressure. Hence 98–99% SO_2 is oxidized, by applying 1 – 7 atm as **optimum pressure**.

(5) Each of the three steps in manufacture of H_2SO_4 is exothermic; for example, burning of sulphur $\Delta H^\circ = -297\text{kJ/mol}$; oxidising SO_2 , $\Delta H^\circ = -99\text{kJ/mol}$; hydrating SO_3 , $\Delta H^\circ = -132\text{kJ/mol}$. So the heat is a valuable by-product in contact process. Three-quarters of the produced heat is sold as steam, and the rest of it is used to pump gases through the plant.

4.8 Law of Mass Action

In 1864, two Norwegian chemists, Cato Maximilian Guldberg and Peter Waage, studied many reversible reactions in which reactant and product concentrations varied widely. They found that, for a particular system and temperature, the same equilibrium state is obtained regardless of how the reaction is run. Such a reversible reaction is the interconversion of colourless gas dinitrogen tetroxide (N_2O_4) to the dark brown gas nitrogen dioxide (NO_2). Here is an experimental observation data with N_2O_4 – NO_2 system at 25°C .

Table-4.4 : Molar concentration data at 25°C for the reaction : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

Expt. No.	Initial concentration (M)		Equilibrium concentration (M)		Equilibrium-const. Expression
	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$[\text{N}_2\text{O}_4]$	$[\text{NO}_2]$	$K_c = [\text{NO}_2]^2/[\text{N}_2\text{O}_4]$
1	0.04	0.00	0.0337	0.0125	4.64×10^{-3}
2	0.00	0.08	0.0337	0.0125	4.64×10^{-3}
3	0.06	0.00	0.0522	0.0156	4.66×10^{-3}
4	0.00	0.06	0.0246	0.0107	4.65×10^{-3}
5	0.02	0.06	0.0429	0.0141	4.63×10^{-3}

From table-4.4 it is clear that the equilibrium mixtures, in experiments 1 and 2, have identical compositions because the initial concentration of N_2O_4 in expt-1 is half the initial concentration of NO_2 in expt.-2; that is, the **total number of N and O atoms is the same in both experiments**. In expt.-3 to 5, different initial concentrations of N_2O_4 and/or NO_2 give

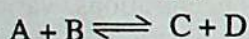
different equilibrium concentrations. In all the experiments, however, the equilibrium concentrations are related. The last column in table-4.4 shows that, at equilibrium, the expression $[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$ has a constant value of approximately 4.64×10^{-3} M. This constant value for the expression $[\text{NO}_2]^2/[\text{N}_2\text{O}_4]$ appears to be related to the balanced equation for the reaction $\text{N}_2\text{O}_4 (\text{g}) \rightleftharpoons 2\text{NO}_2 (\text{g})$ in that the concentration of the product is in the numerator, raised to the power of its coefficient in the balanced equation, and the concentration of the reactant is in the denominator.

On the basis of experimental studies of many reversible reactions, C.M. Guldberg and P. Waage proposed, in 1864, a law known as **Law of Mass Action** regarding the rate of chemical reactions.

The Law of mass action : 'At a constant temperature, the rate of a chemical reaction at any instant is directly proportional to the active masses (i.e., molar concentration or partial pressure) of the reactants at that instant taking part in the reaction.'

(A) **Mathematical expression of equilibrium constant, K_c**

Let us consider following general reversible reaction :



If $[\text{A}]$, $[\text{B}]$ are the molar concentration of reactant A and B, then according to the Law of mass action, the rate of forward reaction, $R_f = k_1 [\text{A}] \times [\text{B}]$; here k_1 = rate constant of the forward reaction. Similarly $[\text{C}]$, $[\text{D}]$ are the molar concentration of product C and D, then rate of backward reaction, $R_b = k_2 [\text{C}] \times [\text{D}]$, here k_2 = rate constant of backward reaction.

At the equilibrium, rate of forward reaction = rate of backward reaction.

So, $R_f = R_b$; $\therefore k_1 [\text{A}] \times [\text{B}] = k_2 [\text{C}] \times [\text{D}]$

$$\text{or, } \frac{k_1}{k_2} = \frac{[\text{C}] \times [\text{D}]}{[\text{A}] \times [\text{B}]}$$

$$\text{or, } K_c = \frac{[\text{C}] \times [\text{D}]}{[\text{A}] \times [\text{B}]} ; \text{ This is called 'Equilibrium Equation'}$$

Here, K_c is called the **molar equilibrium constant** of the reaction and the expression on the right side is called the **equilibrium constant expression**. Values of K_c are generally reported without units because the concentration in the equilibrium constant expression are considered to be concentration ratios in which the molarity of each substance is divided by its molarity (1M) in the thermodynamic standard state. Because the units cancel, the concentration ratios and the values of K_c are dimensionless or Unitless.

For experiment-1 in Table-4.4, for example,

$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{\left(\frac{0.0125\text{M}}{1\text{M}}\right)^2}{\left(\frac{0.0337\text{M}}{1\text{M}}\right)} = 4.64 \times 10^{-3}; \text{ (at } 25^\circ\text{C)}$$

[Thermodynamic standard states are 1M concentration for solution, 1 atm pressure for gas and temp. 25°C are used.]

Here K_c and K_p each represents the ratio of the measurable quantity of substance (molar concentration or partial pressure) to the thermodynamic standard state quantity of the substance]

Equilibrium constants are temperature-dependent, So the temperature must be given when citing a value of K_c . Similarly like K_c , K_p , K_a , K_b , K_w are unitless.

4.9.1 Equilibrium Constant K_c and K_p

Equilibrium constant, K_{eq} : Equilibrium constant, K_{eq} is a ratio of the product of active masses of products obtained in a reversible reaction to the product of the active masses of reactants at equilibrium, each being raised to a power indicating the number of moles of the substances of that reaction. Every reaction has its own equilibrium constant.

The equilibrium constant K_{eq} is expressed in two ways depending on unit of active mass of the reactants :

- (i) When active mass is expressed in molar concentration, then K_{eq} is expressed as K_c .
- (ii) When active mass is expressed in partial pressure, then K_{eq} is expressed as K_p .

The characteristics of K_{eq} :

1. It is independent of the amount of reactants and catalyst.
2. It depends on temperature of the reactions.
3. The greater the value of K_{eq} , the greater is the amount of product obtained in the reaction.
4. Small value of K_{eq} , indicates the small amount of product in the reaction.

Equilibrium constant in molar concentration, K_c : When in a reversible reaction the concentration of reactants and products are expressed in moles per litre, then the equilibrium constant is expressed as K_c .

For a general reaction; $aA + bB \rightleftharpoons cC + dD$

According to Law of Mass action; $K_c = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$

Here $[A]$, $[B]$, $[C]$ and $[D]$ are the molar concentration of A, B, C and D of the reactants and products respectively.

Equilibrium constant in partial pressure, K_p : When in a reversible reaction all the reactants and products are in gaseous state, the equilibrium constant can be expressed in terms of partial pressures, K_p . Here active mass of each substance is its partial pressure. Hence the rate of reaction is directly proportional to the partial pressure.

For a general gaseous equation : $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

According to Law of Mass action, $K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$

Here P_A , P_B , P_C and P_D are the partial pressures of the substances A, B, C and D respectively.

Know More : Is the value of K_c and K_p equal to zero or infinity?

The equilibrium constant K_c or K_p is related to a reversible reaction.

Let us consider a reversible reaction : $A + B \rightleftharpoons C + D$

According to the Law of Mass action, $K_c = \frac{[C] \times [D]}{[A] \times [B]}$

Where $[A]$, $[B]$, $[C]$ and $[D]$ are the molar concentration of A, B, C and D of the substance.

(i) The value of K_c will be zero, when the product of the molar concentrations of the products will be zero i.e., $[C] \times [D] \neq 0$, then $K_c = \frac{0}{[A] \times [B]} = 0$

But, at equilibrium of a reversible reaction, $[C] \times [D]$ can never be zero. So, the value of K_c will never be zero.

Similarly for a reversible reaction

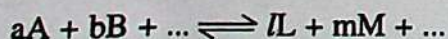
$[A]$ and $[B]$ can not be zero, If $[A] \times [B] = 0$

then $K_c = \frac{[C] \times [D]}{0} = \infty$ (infinity). But it is not possible, because $[A] \times [B]$ is not zero.

Hence the value of K_c is not zero or infinity at any time.

4.9.2 Relation between K_p and K_c

Let us consider a general reversible gaseous reaction as follows :



If molar concentration of A, B, and L, M, etc. at equilibrium are represented by $[A]$, $[B]$ and $[L]$, $[M]$ etc., then molar equilibrium constant K_c is given by :

$$K_c = \frac{[L]^l \times [M]^m \times \dots}{[A]^a \times [B]^b \times \dots}$$

Again if the partial pressures of A, B and L, M etc. at equilibrium are represented by P_A , P_B , P_L and p_M etc., then partial pressure equilibrium constant of the reaction is :

$$K_p = \frac{P_L^l \times P_M^m \times \dots}{P_A^a \times P_B^b \times \dots}$$

We know that if in an ideal gas mixture, the partial pressure of n mole of a gas be p and if the gas occupies a volume V at a temperature T , then we get :

$$pV = nRT; \text{ or, } p = \frac{n}{V} RT = CRT; \text{ where, } C = \frac{n}{V} = \text{molar concentration ... (1)}$$

Putting the value of p from (1) in the following equation for K_p we get :

$$K_p = \frac{P_L^l \times P_M^m \times \dots}{P_A^a \times P_B^b \times \dots} = \frac{(C_L RT)^l \times (C_M RT)^m \times \dots}{(C_A RT)^a \times (C_B RT)^b \times \dots} = \frac{(C_L^l \times C_M^m \times \dots) \times (RT)^{l+m+\dots}}{(C_A^a \times C_B^b \times \dots) \times (RT)^{a+b+\dots}}$$

$$= K_c \times (RT)^{(l+m+\dots) - (a+b+\dots)}$$

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

where, $\Delta n = (l+m+\dots) - (a+b+\dots)$

= (Total mole number of products) – (Total mole number of reactants)
= Change of number of moles in chemical equation of the reaction.

When total number of moles of products is equal to total number of moles of reactants in a chemical equation, then $\Delta n = 0$; so, $K_p = K_c (RT)^0 = K_c \times 1$; or, $K_p = K_c$

How To Solve Equilibrium Problems :

Many kinds of equilibrium problems arise in the real world, as well as on chemistry exams, but we can group most of them into two types :

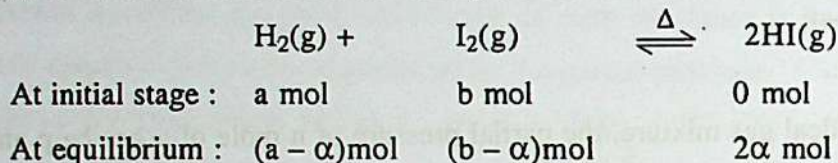
1. In one type, we are given equilibrium quantities (concentrations or partial pressure) and asked to solve for K .
2. In the other type we are given K and initial quantities and asked to solve for the equilibrium quantities.

4.9.3 Application of Law of Mass action to Homogeneous Equilibrium

The reaction equilibrium, in which all reactants and products are in the same physical state or phase, is known as homogeneous equilibrium. To know how much product may be obtained from a certain reaction, the value of K_c and K_p are calculated for the reaction. Some examples of homogeneous equilibrium are given below.

(A) When numbers of moles of reactants and products are equal, then $K_c = K_p$.

(1) Synthesis of hydrogen iodide : Synthesis of hydrogen iodide from hydrogen and iodine is a reversible reaction and it may be shown as follows :



Calculation of K_c : Let us suppose that 'a' mole H_2 and 'b' mole I_2 are taken in a closed flask of volume V L and are allowed to react. At equilibrium, let α mole H_2 and α mole I_2 react to produce 2α moles HI. So at equilibrium the amounts of H_2 and I_2 are $(a - \alpha)$ mole and $(b - \alpha)$ mole respectively.

$$\therefore \text{Molar concentration of } \text{H}_2 = \frac{(a - \alpha)}{V} (\text{molL}^{-1})$$

$$\text{Molar concentration of } \text{I}_2 = \frac{(b - \alpha)}{V} (\text{molL}^{-1})$$

$$\text{Molar concentration of HI} = \frac{2\alpha}{V} (\text{molL}^{-1})$$

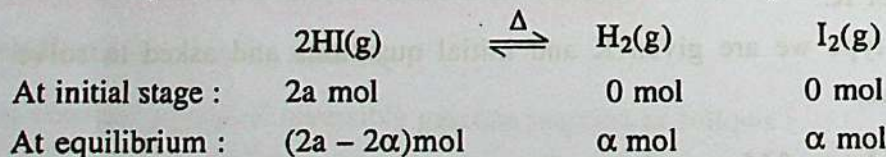
$$\therefore K_c = \frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]} = \frac{\left(\frac{2\alpha}{V}\right)^2}{\left(\frac{a - \alpha}{V}\right) \times \left(\frac{b - \alpha}{V}\right)} = \frac{4\alpha^2}{(a - \alpha)(b - \alpha)}$$

Significance of K_c and K_p :

(1) Since, $K_p = K_c \times (RT)^{\Delta n}$ and since here, $\Delta n = (2 - 2) = 0$, $K_p = K_c (RT)^0 = K_c$

(2) Since here both K_p and K_c are not related to volume V or pressure P, so in this reaction they will remain unchanged, even if V and P are changed.

(2) Dissociation of hydrogen iodide : When hydrogen iodide is heated in a closed flask, it dissociates to H_2 and iodine. It is a reversible reaction and is expressed as follows :



Calculation of K_c : Let us suppose that '2a' mol HI is taken in a flask of V litre and heated. At the equilibrium 2α mol HI is decomposed to produce α mol H_2 and α mol I_2 .

$$\therefore \text{Molar concentration of HI} = \frac{(2a - 2\alpha)}{V} (\text{molL}^{-1})$$

$$\text{Molar concentration of } \text{H}_2 = \frac{\alpha}{V} (\text{molL}^{-1}); \text{ Molar concentration of } \text{I}_2 = \frac{\alpha}{V} (\text{molL}^{-1})$$

$$\therefore \text{Equilibrium constant, } K_c = \frac{\left(\frac{\alpha}{V}\right) \times \left(\frac{\alpha}{V}\right)}{\left(\frac{2a - 2\alpha}{V}\right)^2} = \frac{\alpha^2}{4(a - \alpha)^2}$$

Calculation of K_p : From above equation, we get at equilibrium number of moles of HI, H_2 and I_2 like $(2a - 2\alpha)$, α and α respectively. Therefore total number of moles in mixture = $(2a - 2\alpha) + \alpha + \alpha = 2a$. If total pressure of the gas mixture be P , then at equilibrium,

$$\text{Partial pressure of HI, } P_{HI} = \frac{(2a - 2\alpha)}{2a} \times P$$

$$\text{Partial pressure of } H_2, P_{H_2} = \frac{\alpha}{2a} \times P; \text{ Partial pressure of } I_2, P_{I_2} = \frac{\alpha}{2a} \times P$$

$$\therefore \text{Equilibrium constant, } K_p = \frac{P_{H_2} \times P_{I_2}}{(P_{HI})^2} = \frac{\left(\frac{\alpha \times P}{2a}\right) \times \left(\frac{\alpha \times P}{2a}\right)}{\left(\frac{(2a - 2\alpha) \times P}{2a}\right)^2} = \frac{\alpha^2}{4(a - \alpha)^2}$$

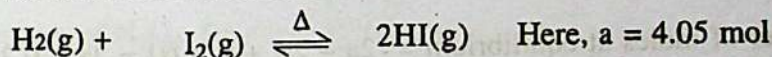
Significance of K_c and K_p :

(1) In this case, $K_p = K_c$

(2) K_p and K_c do not depend on the volume V or total pressure P .

Worked Example-4.12(1) : In a 1L flask 4.05 mol H_2 and 4.65 mol I_2 were heated to 444°C and at equilibrium 6.75 mol HI was produced. Calculate K_c and K_p for the reaction.

Solution : The required reversible reaction is :



At initial stage : a mol b mol 0 mol $b = 4.65$ mol

At equilibrium : $(a - \alpha)$ mol $(b - \alpha)$ mol 2α mol $\alpha = \frac{6.75}{2} \text{ mol} = 3.375 \text{ mol}$

\therefore At equilibrium,

$$V = 1\text{L}$$

$$[H_2] = (a - \alpha) = (4.05 - 3.375) = 0.675 \text{ molL}^{-1}$$

$$[I_2] = (b - \alpha) = (4.65 - 3.375) = 1.275 \text{ molL}^{-1}$$

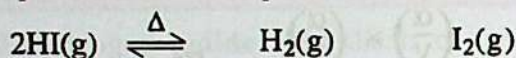
$$[HI] = 2\alpha = 2 \times 3.375 = 6.75 \text{ molL}^{-1}$$

$$\therefore K_c = \frac{[HI]^2}{[I_2] \times [H_2]} = \frac{(6.75)^2}{(1.275) \times (0.675)} = \frac{45.5625}{0.860625} = 52.94$$

Ans. Here number of moles of reactants and products are same, $\therefore K_p = K_c = 52.94$

Worked Example-4.12(2) : 40 g HI was taken in a 2 L flask and heated to 327°C . It is given that for the reaction $2HI \rightleftharpoons H_2 + I_2$; the molar equilibrium constant at 327°C is 0.0559 and the total pressure of gas mixture is 1.5 atm. Calculate concentration and partial pressure of H_2 , I_2 and HI at equilibrium.

Solution : The required reversible equation is :



At initial stage : 2a mol 0 mol 0 mol

At equilibrium : (2a - 2α) mol α mol α mol

40 g HI = $\frac{40}{128}$ mol = 0.312 mol [Molar mass of HI = 128 g]

Here, $a = \frac{0.312}{2} = 0.156$ mol; α = ?

Since volume of flask is 2L, so by dividing mole numbers of HI, I₂ and H₂ by 2L their concentration in molL⁻¹ unit are obtained.

$$\therefore K_c = \frac{[\text{H}_2] \times [\text{I}_2]}{[\text{HI}]^2} = \frac{\left(\frac{\alpha}{2}\right) \times \left(\frac{\alpha}{2}\right)}{\left(\frac{2a - 2\alpha}{2}\right)^2} = \frac{\alpha^2}{(2a - 2\alpha)^2} = \frac{\alpha^2}{(0.312 - 2\alpha)^2}$$

$$\text{or, } 0.0559 = \frac{\alpha^2}{(0.312 - 2\alpha)^2}; [K_c = 0.059]$$

Since α is very small, (0.312 - 2α) may be taken as 0.312

$$\therefore 0.0559 = \frac{\alpha^2}{(0.312)^2}$$

$$\text{or, } \alpha^2 = 0.0559 \times (0.312)^2 = 0.0559 \times 0.097344 = 0.0054415$$

$$\therefore \alpha = \sqrt{0.0054415} = 0.0738$$

Total number of moles at equilibrium = [2a - 2α + α + α] = 2a = 0.312

$$\begin{aligned} \text{Mol fraction of HI} &= \frac{\text{Number of moles of HI}}{\text{Total number of moles}} = \frac{(2a - 2\alpha)}{2a} \\ &= \frac{(0.312 - 2 \times 0.0738)}{0.312} = 0.526923 \end{aligned}$$

$$\begin{aligned} \text{Concentration of HI} &= \left(\frac{2a - 2\alpha}{2}\right) = \frac{(0.312 - 2 \times 0.0738)}{2} \\ &= \frac{(0.312 - 0.1476)}{2} = 0.0822 \end{aligned}$$

$$\text{Concentration of I}_2 = [\text{I}_2] = [\text{H}_2] = \frac{\alpha}{2} = \frac{0.0738}{2} = 0.0369$$

Again partial pressure of HI, P_{HI} = mol fraction of HI × total pressure
= (0.526923 × 1.5) atm = 0.79 atm

Similarly partial pressure of I₂, P_{I₂} = mol fraction of I₂ × total pressure

$$= \frac{\alpha}{2a} \times 1.5 \text{ atm} = \frac{0.0738}{0.312} \times 1.5 \text{ atm} = 0.355 \text{ atm.}$$

Similarly partial pressure of H_2 , $P_{\text{H}_2} = \text{mol fraction of } \text{H}_2 \times \text{total pressure}$

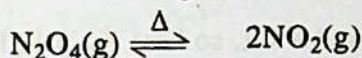
$$= \frac{\alpha}{2a} \times 1.5 \text{ atm} = 0.355 \text{ atm.}$$

Ans. Concentration; $[\text{H}_2] = [\text{I}_2] = 0.0369 \text{ molL}^{-1}$, $[\text{HI}] = 0.0822 \text{ molL}^{-1}$

Partial pressure : $P_{\text{H}_2} = P_{\text{I}_2} = 0.355 \text{ atm}$, $P_{\text{HI}} = 0.73 \text{ atm}$.

(B) When numbers of moles of reactants and products are unequal, then $K_p \neq K_c$

(3) Dissociation of dinitrogen tetroxide : When dinitrogen tetroxide (N_2O_4) is heated in a closed flask, it dissociates to nitrogen dioxide (NO_2). The equation of this reversible reaction:



At initial stage : $a \text{ mol}$ 0 mol

At equilibrium : $(a - \alpha) \text{ mol}$ $2\alpha \text{ mol}$

Calculation of K_p : Let ' a ' mol of N_2O_4 is heated at initial stage and that at equilibrium α mol of N_2O_4 has decomposed. So at equilibrium amount of N_2O_4 is $(a - \alpha)$ mol and that of NO_2 is 2α mol. Total number of mol of gases at equilibrium = $(a - \alpha + 2\alpha) = (a + \alpha)$. If the total pressure of gas mixture be P , then at equilibrium –

$$\therefore \text{The partial pressure of } \text{N}_2\text{O}_4, P_{\text{N}_2\text{O}_4} = \frac{(a - \alpha)}{(a + \alpha)} \times P$$

$$\therefore \text{The partial pressure of } \text{NO}_2, P_{\text{NO}_2} = \frac{2\alpha}{(a + \alpha)} \times P$$

$$\therefore K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2\alpha}{a + \alpha}\right)^2 \times P^2}{\left(\frac{a - \alpha}{a + \alpha} \times P\right)} = \frac{4\alpha^2}{(a + \alpha)^2} \times \frac{(a + \alpha)}{(a - \alpha)} \times P = \frac{4\alpha^2 \times P}{(a^2 - \alpha^2)}$$

Significance of K_p of this reaction : From the following equation it is seen that :

$$K_p = \frac{4\alpha^2 \times P}{(a^2 - \alpha^2)}$$

(1) If α , and P are known, K_p can easily be calculated.

(2) If the pressure P is increased, the amount of dissociation, α will decrease to keep K_p constant. Conversely if P is decreased α will increase.

(3) If the amount of dissociation, α is very small then α^2 may be neglected in comparison to a^2 and the equation is reduced to as follows :

Ans. The partial pressure of $\text{N}_2\text{O}_4 = 12.15 \text{ atm}$ (approx.); that of $\text{NO}_2 = 2.85 \text{ atm}$.

Worked Example-4.12(4) : The partial pressures of N_2O_4 and NO_2 in equilibrium mixture at 25°C are 0.75 atm and 0.25 atm respectively. Calculate K_p and K_c of the dissociation of N_2O_4 .

Solution : The required equation is : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

$$K_p = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}}$$

$$= \frac{(0.25)^2}{0.75} = 0.0833 = 8.33 \times 10^{-2}$$

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

$$\text{or, } 0.0833 = K_c \times (0.082 \times 298)^1 = 24.436 K_c$$

$$\text{or, } K_c = \frac{0.0833}{24.436} = 3.40 \times 10^{-3}$$

$$\text{Ans : } K_p = 8.33 \times 10^{-2}; K_c = 3.40 \times 10^{-3}$$

From question :

$$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$$

$$T = 25^\circ\text{C} = 298 \text{ K}$$

$$\Delta n = (2 - 1) = 1$$

Worked Example - 4.12 (5) : At 298K and 1 atm pressure dinitrogen tetroxide is 18.5% dissociated into nitrogen dioxide. What is the degree of percent dissociation of N_2O_4 at that temperature and 0.5 atm pressure?

Answer : The reaction : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

At initial stage : $a \text{ mol}$ 0 mol

At equilibrium : $(a - \alpha) \text{ mol}$ $2\alpha \text{ mol}$

Let us suppose that 1 mol N_2O_4 has been taken i. e., $a = 1 \text{ mol}$

According to question at 298 K and 1 atm pressure, when $a = 1 \text{ mol}$, $\alpha = 0.185 \text{ mol}$.

$$\text{Here, } \alpha = \frac{1}{2} \sqrt{\frac{K_p}{P}}; \text{ or, } 0.185 = \frac{1}{2} \sqrt{\frac{K_p}{1}}; \text{ or, } K_p = (0.185 \times 2)^2 = 0.1369$$

$$\text{Now putting } P = 0.5 \text{ (in above equation); } \alpha = \frac{1}{2} \sqrt{\frac{K_p}{0.5}}$$

$$\text{or, } \alpha = \frac{1}{2} \sqrt{\frac{0.1369}{0.5}}$$

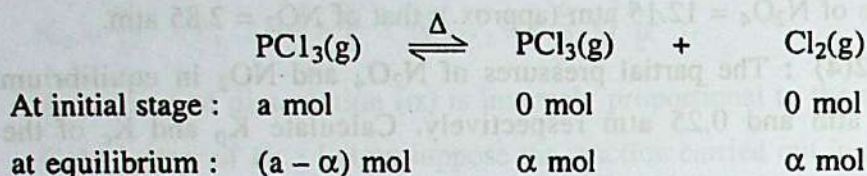
$$\text{or, } \alpha = \frac{1}{2} \times 0.524 = 0.262$$

$$\text{So degree of percent dissociation, } \beta = \frac{\alpha \times 100}{a} = \frac{0.262 \times 100}{1} = 0.262 \times 100 = 26.2\%$$

Ans. At 298 K and 0.5 atm pressure the degree of percent dissociation = 26.2% .

(4) Dissociation of Phosphorus Pentachloride (PCl_5)

On heating, phosphorus pentachloride dissociates reversibly as follows :



Calculation of K_c : Initially 'a' mole PCl_5 is heated in a flask of volume V litre and at equilibrium α mol of PCl_5 dissociates to produce α mol PCl_3 and α mol Cl_2 .

$$\text{Concentration of } \text{PCl}_5, [\text{PCl}_5] = \frac{(a - \alpha)}{V}$$

$$\text{Concentration of } \text{PCl}_3, [\text{PCl}_3] = \frac{\alpha}{V}; \text{Concentration of } \text{Cl}_2, [\text{Cl}_2] = \frac{\alpha}{V}$$

$$\therefore K_c = \frac{[\text{PCl}_3] \times [\text{Cl}_2]}{[\text{PCl}_5]} = \frac{\frac{\alpha}{V} \times \frac{\alpha}{V}}{\frac{(a - \alpha)}{V}} = \frac{\frac{\alpha^2}{V^2}}{\frac{(a - \alpha)}{V}} = \frac{\alpha^2}{(a - \alpha) \times V}$$

Calculation of K_p : At equilibrium of the above reaction, the total number of moles in mixture = $(a - \alpha) + \alpha + \alpha = (a + \alpha)$. If the total pressure be P, then at equilibrium –

$$\text{Partial pressure of } \text{PCl}_5, P_{\text{PCl}_5} = \text{mol fraction of } \text{PCl}_5 \times \text{total pressure} = \frac{(a - \alpha)}{(a + \alpha)} \times P$$

$$\text{Partial pressure of } \text{PCl}_3, P_{\text{PCl}_3} = \frac{\alpha}{(a + \alpha)} \times P; \text{ and Partial pressure of } \text{Cl}_2, P_{\text{Cl}_2} = \frac{\alpha}{(a + \alpha)} \times P;$$

$$\therefore K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{\frac{\alpha}{(a + \alpha)} \times P \times \frac{\alpha}{(a + \alpha)} \times P}{\frac{(a - \alpha)}{(a + \alpha)} \times P} = \frac{\alpha^2 \times P}{(a^2 - \alpha^2)}$$

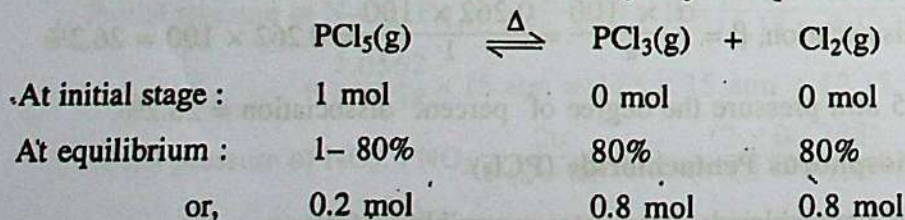
Significance of K_c and K_p of this reaction :

(1) If pressure is reduced, then to keep K_p constant, the amount of dissociation (α) increases.

(2) If the volume of the container is increased, keeping constant initial amount 'a' of PCl_5 , then to keep K_c constant, the amount of dissociation ' α ' increases.

Worked Example – 4.12(6) : At 25°C and 1 atm pressure 80% PCl_5 dissociates in PCl_3 and Cl_2 . Calculate the partial pressures of PCl_5 , PCl_3 , and Cl_2 , K_p and K_c .

Solution : The reversible dissociation of PCl_5 may be represented as follows :



$$\therefore \text{Total number of moles at equilibrium} = (0.2 + 0.8 + 0.8) = 1.8 \text{ mol}$$

Partial pressure of PCl_5 , $P_{\text{PCl}_5} = \frac{0.2}{1.8} \times 1 \text{ atm} = 0.11 \text{ atm}$;

Partial pressure of PCl_3 , $P_{\text{PCl}_3} = \frac{0.8}{1.8} \times 1 \text{ atm} = 0.44 \text{ atm}$ and

partial pressure of Cl_2 , $P_{\text{Cl}_2} = \frac{0.8}{1.8} \times 1 \text{ atm} = 0.44 \text{ atm}$

$$\therefore K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{0.44 \times 0.44}{0.11} = \frac{0.1936}{0.11} = 1.76$$

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

Here, $K_p = 1.76$

$$\therefore 1.76 = K_c (0.082 \times 298)^1 = 24.436 K_c$$

$R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$$\text{or, } K_c = \frac{1.76}{24.436} = 7.20 \times 10^{-2}$$

$T = (273 + 25) \text{ K} = 298 \text{ K}$

$$\therefore K_c = 7.20 \times 10^{-2}$$

$\Delta n = (2 - 1) = 1$

Answer : Partial pressures of PCl_5 , PCl_3 and Cl_2 at equilibrium are 0.11 atm, 0.44 atm and 0.44 atm respectively. The values of K_c and K_p are 7.20×10^{-2} and 1.76 respectively.

Worked Example-4.12 (7) : At 50°C temperature calculate the total pressure needed for 50% dissociation of PCl_5 , when dissociation constant, K_p is 1.8.

Solution : The required reaction : $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$

At initial stage : 1 mol 0 mol 0 mol

At equilibrium : 0.5 mol 0.5 mol 0.5 mol

Let required total pressure be P atm.

At equilibrium total moles = $(0.5 + 0.5 + 0.5) = 1.5 \text{ mol}$.

We know, partial pressure = total pressure \times mole fraction.

$$\text{Partial pressure of } \text{PCl}_5, P_{\text{PCl}_5} = P \times \frac{0.5}{1.5} = \frac{P}{3}$$

$$\text{Partial pressure of } \text{PCl}_3, P_{\text{PCl}_3} = P \times \frac{0.5}{1.5} = \frac{P}{3}$$

$$\text{Partial pressure of } \text{Cl}_2, P_{\text{Cl}_2} = P \times \frac{0.5}{1.5} = \frac{P}{3}$$

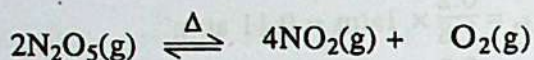
$$\text{Now, from Law of mass action } K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{\frac{P}{3} \times \frac{P}{3}}{\frac{P}{3}} = \frac{P}{3}$$

From question, $K_p = 1.8$, $\therefore 1.8 = \frac{P}{3}$; or, $P = 1.8 \times 3 \text{ atm}$, or, $P = 5.4 \text{ atm}$.

Ans. Total pressure needed = 5.4 atm.

(5) Dissociation of Nitrogen Pentoxide (N_2O_5)

On heating, Nitrogen Pentoxide dissociates reversibly as follows :



At initial stage : 2a mol 0 mol 0 mol.

At equilibrium : (2a - 2α) mol 4α mol α mol

Calculation of K_p : Initially '2a' mol N_2O_5 is heated in a flask of volume V litre and at equilibrium '2α' mol of N_2O_5 dissociates to produce 4α mol NO_2 and α mole O_2 gas. At equilibrium total number of mol in the gas mixture = (2a - 2α + 4α + α) = (2a + 3α). If the total pressure of gas mixture be P, then at equilibrium –

$$\text{Partial pressure of } \text{N}_2\text{O}_5, P_{\text{N}_2\text{O}_5} = \frac{(2a - 2\alpha) \times P}{(2a + 3\alpha)}$$

$$\text{Partial pressure of } \text{NO}_2, P_{\text{NO}_2} = \frac{4\alpha \times P}{(2a + 3\alpha)}$$

$$\text{Partial pressure of } \text{O}_2, P_{\text{O}_2} = \frac{\alpha \times P}{(2a + 3\alpha)}$$

$$\text{Equilibrium constant, } K_p = \frac{(P_{\text{NO}_2})^4 \times P_{\text{O}_2}}{(P_{\text{N}_2\text{O}_5})^2} = \frac{\left[\frac{4\alpha P}{(2a + 3\alpha)} \right]^4 \left[\frac{\alpha P}{(2a + 3\alpha)} \right]}{\left[\frac{(2a - 2\alpha) \times P}{(2a + 3\alpha)} \right]^2}$$

$$\text{or, } K_p = \frac{256\alpha^5 P^5 \times (2a + 3\alpha)^2}{(2a + 3\alpha)^5 \times 4(a - \alpha)^2 P^2} = \frac{64\alpha^5 P^3}{(2a + 3\alpha)^3 (a - \alpha)^2}$$

Significance of K_p : Here if pressure is increased, then to maintain K_p constant dissociation amount α will be decreased.

Calculation of K_c : Suppose the reaction is performed in V litre flask. At equilibrium–

Concentration of N_2O_5 , $[\text{N}_2\text{O}_5] = \frac{(2a - 2\alpha)}{V}$; concentration of NO_2 , $[\text{NO}_2] = \frac{4\alpha}{V}$,

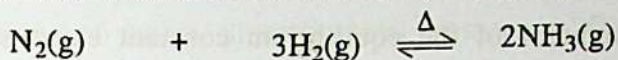
concentration of O_2 , $[\text{O}_2] = \frac{\alpha}{V}$

$$\therefore \text{Equilibrium constant, } K_c = \frac{[\text{NO}_2]^4 \times [\text{O}_2]}{[\text{N}_2\text{O}_5]^2} = \frac{\left(\frac{4\alpha}{V} \right)^4 \times \frac{\alpha}{V}}{\left(\frac{2a - 2\alpha}{V} \right)^2} = \frac{256\alpha^5}{V^5} \times \frac{V^2}{4(a - \alpha)^2}$$

$$\text{or, } K_c = \frac{64\alpha^5}{(a - \alpha)^2 V^3}$$

Significance of K_c : $K_p = K_c (RT)^{\Delta n}$ and here $\Delta n = (5 - 2) = 3$; So $K_p = K_c (RT)^3$

(6) **NH₃ Manufacture** : Manufacture of ammonia from N₂ and H₂ is as follows :



At initial stage : a mol 3b mol 0 mol

At equilibrium : (a - α) mol (3b - 3α) mol 2α mol

Calculation of K_c : Suppose in V litre flask 'a' mol N₂ gas and 3b mol N₂ gas are taken. After their reaction 2α mol NH₃ is produced at equilibrium. So at equilibrium (a - α) mol N₂ and (3b - 3α) mol H₂ are present in reaction mixture. Then concentration of N₂, [N₂] = $\frac{(a - \alpha)}{V}$; Concentration of H₂, [H₂] = $\frac{(3b - 3\alpha)}{V}$ and concentration of NH₃, [NH₃] = $\frac{2\alpha}{V}$.

$$\therefore \text{Equilibrium constant; } K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{2\alpha}{V}\right)^2}{\left(\frac{a - \alpha}{V}\right) \times \left(\frac{3b - 3\alpha}{V}\right)^3} = \frac{4\alpha^2 V^2}{27(a - \alpha)(b - \alpha)^3}$$

Calculation of K_p : At equilibrium, according to above NH₃ production reaction, total moles in equilibrium mixture = (a - α + 3b - 3α + 2α) = (a + 3b - 2α). Total pressure of gas mixture is P, then—

$$\text{Partial pressure of N}_2, P_{\text{N}_2} = \frac{(a - \alpha) \times P}{(a + 3b - 2\alpha)}$$

$$\text{Partial pressure of H}_2, P_{\text{H}_2} = \frac{(3b - 3\alpha) \times P}{(a + 3b - 2\alpha)}$$

$$\text{Partial pressure of NH}_3, P_{\text{NH}_3} = \frac{2\alpha \times P}{(a + 3b - 2\alpha)}$$

$$\therefore \text{Equilibrium constant, } K_p = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2}) \times (P_{\text{H}_2})^3} = \frac{\left[\frac{2\alpha P}{(a + 3b - 2\alpha)}\right]^2}{\frac{(a - \alpha) P}{(a + 3b - 2\alpha)} \times \left[\frac{(3b - 3\alpha) P}{(a + 3b - 2\alpha)}\right]^3}$$

$$\text{or, } K_p = \frac{4\alpha^2(a + 3b - 2\alpha)^2}{27(a - \alpha)(b - \alpha)P^2}$$

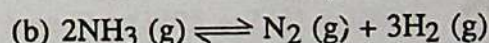
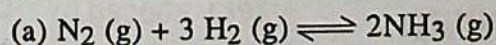
Significance of K_p & K_c : (i) $K_p = K_c(RT)^{\Delta n}$; here $\Delta n = (2 - 4) = -2$.

$$\therefore K_p = K_c(RT)^{-2}, \text{ or, } K_c = K_p \times (RT)^2$$

(2) From relation of K_p with P (pressure), at equilibrium if pressure is increased, amount of product (α) increases to keep K_p value constant.

Worked Example-4. 13 : Writing Equilibrium Equations :

Write the equilibrium equation for each of the following reactions :



Strategy : Putting concentrations of the reaction products in the numerator and that of the reactants in the denominator of the equilibrium constant expression; then raise the concentration of each substance to the power of its coefficient in the balanced equation.

Solution : (a) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \times [\text{H}_2]^3}$$

(b) $2\text{NH}_3(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$

$$K'_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}; \text{ Here } K'_c = \frac{1}{K_c}$$

MCQ-4.7 : In which reaction values of K_p and K_c are equal?

(a) $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

(b) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$

(c) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

(d) $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$

Because the balanced equation in part (b) is the reverse of that in part (a); the equilibrium constant expression in part (b) is the reciprocal of the expression in part (a) and the equilibrium constant K'_c is the reciprocal of K_c .

Worked Example-4.14 : Calculating Equilibrium Constant K_c :

At 500 K, the following concentrations are measured for an equilibrium mixture : $[\text{N}_2] = 3.0 \times 10^{-2} \text{ M}$; $[\text{H}_2] = 3.7 \times 10^{-2} \text{ M}$; $[\text{NH}_3] = 1.6 \times 10^{-2} \text{ M}$. Calculate the equilibrium constant at 500 K for each of the reactions in worked Example-4.13.

Strategy : To calculate the value of the equilibrium constant, substitute the equilibrium concentrations into the equilibrium equation.

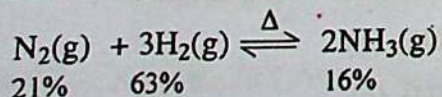
$$\text{Solution : (a) } K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2] \times [\text{H}_2]^3} = \frac{(1.6 \times 10^{-2})^2}{(3.0 \times 10^{-2}) \times (3.7 \times 10^{-2})^3} = 1.7 \times 10^2$$

$$\text{(b) } K'_c = \frac{[\text{N}_2] \times [\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{(3.0 \times 10^{-2}) (3.7 \times 10^{-2})^3}{(1.6 \times 10^{-2})^2} = 5.9 \times 10^{-3}$$

Note that K'_c is the reciprocal of K_c . That is, $5.9 \times 10^{-3} = \frac{1}{1.7 \times 10^2}$

Worked Example – 4.14 (1) : At 700 K and 20 atm pressure at the equilibrium state of the ammonia synthesis reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$; 21% N_2 and 16% NH_3 are present in the gas mixture. Calculate K_p and K_c of the reaction.

Solution : According to the question in the gas mixture 21% N_2 and 16% NH_3 are present. So amount of $\text{H}_2 = (100 - 21 - 16)\% = 63\%$



Let us suppose that there are in total 100 moles in the gas mixture. So, amount of N_2 , H_2 and NH_3 are 21, 63 and 16 moles. Since the total pressure is 20 atm. we can easily calculate their partial pressures.

$$\therefore P_{H_2} = \frac{63}{100} \times 20 \text{ atm} = 12.6 \text{ atm}; P_{NH_3} = \frac{16}{100} \times 20 \text{ atm} = 3.2 \text{ atm};$$

$$P_{N_2} = \frac{21}{100} \times 20 \text{ atm} = 4.2 \text{ atm}$$

$$\begin{aligned} \therefore K_p &= \frac{(P_{NH_3})^2}{(P_{N_2}) \times (P_{H_2})^3} \\ &= \frac{(3.2)^2}{(4.2) \times (12.6)^3} = \frac{10.24}{8401.6} = 1.2 \times 10^{-3} \end{aligned}$$

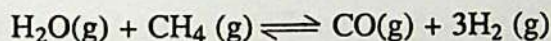
We know, $K_p = K_c (RT)^{\Delta n}$; Here $\Delta n = 2 - (1 + 3) = -2$, $R = 0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}$

$$\begin{aligned} \text{or, } K_c &= \frac{K_p}{(RT)^{\Delta n}}; \text{ or, } K_c = \frac{1.2 \times 10^{-3}}{(0.082 \times 700)^{-2}} = 1.2 \times 10^{-3} \times (0.082 \times 700)^2 \\ &= 1.2 \times 10^{-3} \times 3294.76 = 3.9537 \end{aligned}$$

Ans. $K_p = 1.2 \times 10^{-3}$ and $K_c = 3.9537$

Worked Example-4.15 : Relating Equilibrium Constants K_p and K_c :

Hydrogen is produced industrially by the steam-hydrocarbon re-forming process. The reaction that takes place in the first step of this process is :



(a) If $K_c = 3.8 \times 10^{-3}$ at 1000K; what is the value of K_p at the same temperature?

(b) If $K_p = 6.1 \times 10^4$ at 1125°C; what is the value of K_c at 1125°C

Strategy : To calculate K_p from K_c or vice versa, use the equation, $K_p = K_c \times (RT)^{\Delta n}$, where R must be in units of $(\text{L.atm})/(\text{K.mol})$, T is in kelvin, and Δn is the number of moles of gaseous products minus the number of moles of gaseous reactants.

Solution :

(a) For this reaction, $\Delta n = (1+3) - (1+1) = 2$.

$$\begin{aligned} K_p &= K_c \times (RT)^{\Delta n} = K_c \times (RT)^2 \\ &= (3.8 \times 10^{-3}) \times (0.08206 \times 1000)^2 = 2.6 \end{aligned}$$

(b) Here solving the equation $K_p = K_c \times (RT)^2$,

we get the value of K_c :

$$K_c = \frac{K_p}{(RT)^2} = \frac{6.1 \times 10^4}{(0.08206 \times 1398)^2} = 4.6$$

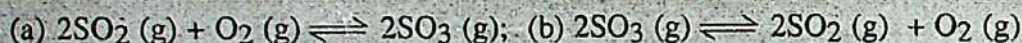
Note that, here $T = (1125 + 273) = 1398\text{K}$

MCQ-4.8 : On heating 4.25 mol H_2 with 4.75 mol I_2 , then equilibrium mixture of H_2 , I_2 and HI have 0.86, 1.36 and 6.78 mol L^{-1} respectively. What is value of K_c ?

(a) 36 (b) 32.67 (c) 33.5 (d) 39.3

Students' Work - 4.8 : Law of Mass Action Based :

Problem-4.28 : The oxidation of sulphur dioxide to give sulphur trioxide is an important step in the industrial process for the synthesis of sulphuric acid. Write the equilibrium equation for each of the following reactions :



Problem- 4.29 : At 800K, the following equilibrium concentrations were measured : $[\text{SO}_2] = 3.0 \times 10^{-3} \text{ M}$; $[\text{O}_2] = 3.5 \times 10^{-3} \text{ M}$; $[\text{SO}_3] = 5.0 \times 10^{-2} \text{ M}$.

Calculate the equilibrium constant at 800 K for each of the reactions in Problem – 4.28.

[Ans : (a) 7.9×10^4 ; (b) 1.3×10^{-5}]

Problem-4.30 : (a) Equilibrium constants K_p and K_c have no-unit; explain why.

(b) Establish relation between K_p and K_c .

(c) $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g})$; for this stem reaction establish relation between K_p and K_c . [Ctg. B. 2015]

(d) $2\text{A}_2\text{O}_5(\text{g}) \rightleftharpoons 4\text{AO}_2(\text{g}) + \text{O}_2(\text{g})$; for this stem reaction deduce expression for K_p . [C. B. 2015]

(e) Deduce expression for K_p of N_2O_4 dissociation. [R. B. 2015]

(f) Value of K_c can never be zero; explain why? [C. B. 2015; Di. B-2015]

Problem-4.31 : In the industrial synthesis of hydrogen, mixtures of CO and H_2 are enriched in H_2 by allowing the CO to react with steam. The chemical equation for this so-called water gas shift reaction is : $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}_2(\text{g}) + \text{H}_2(\text{g})$

What is the value of K_p at 700 K if partial pressures in an equilibrium mixture at 700 K are 1.31 atm of CO, 10.0 atm of H_2O , 6.12 atm of CO_2 , and 20.3 atm of H_2 ? [Ans : 9.48]

Problem-4.32 : In Ostwald process for the industrial synthesis of nitric acid, nitric oxide reacts with oxygen to give nitrogen dioxide : $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

(a) If $K_c = 6.9 \times 10^5$ at 227°C , what is the value of K_p at 227°C ? [Ans. $K_p = 1.68 \times 10^4$;

(b) If $K_p = 1.3 \times 10^{-2}$ at 1000 K, what is the value of K_c at 1000K? [Ans. $K_c = 1.066$]

4.9.4 Significance of K_c

Knowing the value of the equilibrium constant for a chemical reaction we get the following benefits :

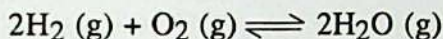
- (1) Judging the extent of reaction,
- (2) Predicting the direction of reaction.
- (3) Calculating the equilibrium concentrations

MCQ-4.9 : As per $\text{A} + \text{B} \rightleftharpoons 3\text{D}$ equation, relation of K_p and K_c will be :

- (a) $K_p = K_c (RT)$, (b) $K_p = K_c \times (RT)^{-1}$
 (c) $K_c = K_p (RT)$, (d) $K_c = K_p \times (RT)^2$

1. Judging the Extent of Reaction : The numerical value of the equilibrium constant for a reaction indicates the extent to which reactants are converted to products; it means how far the reaction, proceeds before the equilibrium state is reached. A large value of K_c means that

the equilibrium ratio of products to reactants is very large. In other words, the reaction proceeds nearly to completion. For example, the reaction of H_2 with O_2 forms H_2O ; here at 500K (227°C), the value of equilibrium constant of the reaction is very large, $K_c = 2.4 \times 10^{47}$ at 500 K.



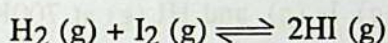
$$\therefore \text{For forward reaction (at 500K), } K_c = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_2]^2 \times [\text{O}_2]} = 2.4 \times 10^{47}$$

$$\therefore \text{For backward reaction (at 500K), } K'_c = \frac{[\text{H}_2]^2 \times [\text{O}_2]}{[\text{H}_2\text{O}]^2} = \frac{1}{K_c} = \frac{1}{2.4 \times 10^{47}} = 4.2 \times 10^{-48}$$

Here the value 4.2×10^{-48} is very negligible; that is actually H_2O does not dissociate to give H_2 and O_2 . Hence it is an irreversible reaction.

Now let us judge two reversible reactions like (i) Synthesis of HI and (ii) dissociation of N_2O_4 with their equilibrium constant values.

(i) At 700K, H_2 gas and I_2 vapour react to form HI and here $K_c = 57$



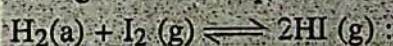
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]} = 57.0 \text{ (at 700K)}$$

If the equilibrium concentrations of H_2 and I_2 are both 0.01M, then the concentration of HI at equilibrium is 0.075 M from the following calculation :

$$[\text{HI}]^2 = K_c \times [\text{H}_2] \times [\text{I}_2]$$

$$\begin{aligned} [\text{HI}] &= \sqrt{K_c \times [\text{H}_2] \times [\text{I}_2]} \\ &= \sqrt{(57.0) \times (0.01) \times (0.01)} \\ &= 0.075\text{M} \end{aligned}$$

MCQ-4.10 : At equilibrium state of reaction



(i) it is dynamic, (ii) at constant system reaction does not end, (iii) product does not increase.

Which is correct?

(a) i, ii (b) ii, iii (c) i, iii (d) i, ii and iii.

Thus, the concentrations of both reactants and products such as 0.07M and 0.07M are appreciable and calculable.

(ii) The gas-phase decomposition of N_2O_4 to NO_2 is another reaction with a value of equilibrium constant $K_c = 4.64 \times 10^{-3}$ (at 25°C), which is neither large nor small. Accordingly, equilibrium mixtures contain appreciable concentrations of both $[\text{N}_2\text{O}_4] = 0.0337$ and $[\text{NO}_2] = 0.125$, as shown previously in Table-4.4.

General Conclusions : We can make the following generalizations concerning the composition of equilibrium mixtures :

(i) If K_c is in the range 10^{-3} to 10^3 , then appreciable concentrations of both reactants and products are present.

(ii) If $K_c > 10^3$, then products predominate over reactants. If K_c is very large, the reaction proceeds nearly to completion.

(iii) If $K_c < 10^{-3}$, then reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.

These points are illustrated in Figure -4.19 :

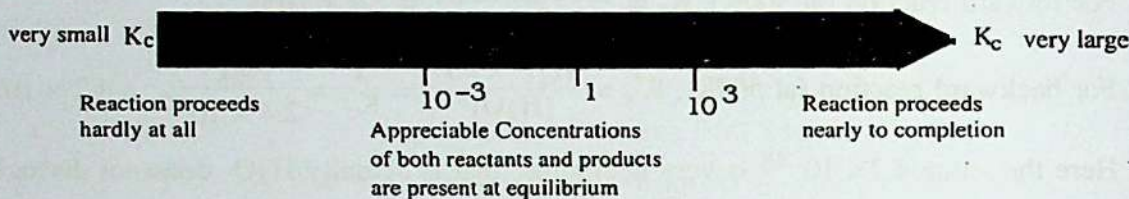
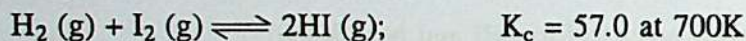


Fig. 4.19 : Judging the extent of reaction with the value of K_c .

2. Predicting the Direction of Reaction :

Let us look again at the gaseous reaction of hydrogen and iodine :



Suppose that we have a mixture of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$ at 700K with concentrations after time t , from the reaction starts :

$[\text{H}_2]_t = 0.1\text{M}$; $[\text{I}_2]_t = 0.2\text{M}$, and $[\text{HI}]_t = 0.4\text{M}$. At this time the reaction is not yet at equilibrium.

If we substitute these concentrations into the equilibrium constant expression, we get a value called the reaction quotient, Q_c .

$$\therefore \text{Reaction Quotient, } Q_c = \frac{[\text{HI}]_t^2}{[\text{H}_2]_t \times [\text{I}_2]_t} = \frac{(0.4)^2}{(0.1) \times (0.2)} = 8.0$$

The reaction quotient Q_c is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values.

From the above calculation, the numerical value of Q_c (8.0) does not equal K_c (57.0), so the mixture of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$ is not at equilibrium. As time passes, though, reaction will occur, changing the concentrations and thus changing the value of Q_c in the direction of K_c . After a sufficiently long time, an equilibrium state will be reached and then $Q_c = K_c$.

Thus the reaction quotient Q_c is useful because it lets us predict the direction of reaction by comparing the values of Q_c and K_c .

Thus, we can make the following generalizations concerning the direction of the reaction :

- (i) If $Q_c < K_c$, net reaction goes from left to right (reactants to products).
- (ii) If $Q_c > K_c$, net reaction goes from right to left (products to reactants).
- (iii) If $Q_c = K_c$, no net reaction occurs.

Worked Example. 4.16 : Predicting the Direction of Reaction :

A mixture of 1.57 mol of N_2 , 1.92 mol of H_2 , and 8.13 mol of NH_3 is introduced into a 20L reaction vessel at 500K. At this temperature, the equilibrium constant K_c for the reaction:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2 . Is the reaction mixture at equilibrium? If not what is the direction of the net reaction?

Strategy : Calculating value of Q_c and then compare it with equilibrium constant K_c .

Solution : Initial molar concentration of N_2 , $[N_2] = 1.57 \text{ mol}/20\text{L} = 0.0785\text{M}$

Similarly, $[H_2] = 1.92 \text{ mol}/20\text{L} = 0.096\text{M}$; $[NH_3] = 8.13 \text{ mol}/20\text{L} = 0.406 \text{ M}$. Substituting these concentrations into the equilibrium constant expression, we get;

$$Q_c = \frac{[NH_3]_t^2}{[N_2]_t \times [H_2]_t^3} = \frac{(0.406)^2}{(0.0785) \times (0.096)^3} = 2.37 \times 10^3.$$

(ii) Because Q_c is greater than K_c , then net reaction will proceed from right to left, decreasing the concentration of NH_3 and increasing the concentrations of N_2 and H_2 until $Q_c = K_c = 1.7 \times 10^2$.

3. Calculating Equilibrium Concentrations from Initial concentrations :

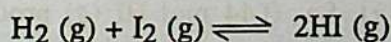
Worked Example-4.17 : The equilibrium constant K_c for the reaction of H_2 with I_2 at 700K is 57.0. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$; $K_c = 57.0$ at 700K. If 1.0 mol H_2 and 1.0 mol I_2 react in a 10L reaction vessel at 700K; what are the concentrations of H_2 , I_2 , and HI at equilibrium? What is composition of equilibrium mixture in moles?

Solution : It will be solved in following 5 steps.

Step-1 : The balance equation is : $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Step-2 : The initial concentrations are : $[H_2] = [I_2] = 1.0 \text{ mol}/10\text{L} = 0.10 \text{ M}$.

Suppose, after time t , $x \text{ mol/L}$ H_2 and $x \text{ mol/L}$ I_2 react to produce $2x \text{ mol/L}$ HI . Then concentrations of H_2 and I_2 reduce to $(0.1-x) \text{ mol/L}$ each.



Initial concentration (M): 0.1 0.1 0

Change in concentration (M): -x -x + 2x

Equilibrium concentration (M): $(0.1-x)$ $(0.1-x)$ +2x

Step - 3 : Substituting the values of concentrations into the equilibrium equation :-

$$Q_c = K_c = 57 = \frac{[HI]^2}{[H_2] \times [I_2]} = \frac{(2x)^2}{(0.1-x) \times (0.1-x)} = \frac{4x^2}{(0.1-x)^2}$$

Taking square root of both sides : $\sqrt{57} = \pm 7.55 = \frac{2x}{(0.1-x)}$

Taking positive value :

$$+ 7.55 = \frac{2x}{(0.1-x)}$$

$$\text{or, } 7.55 \times (0.1-x) = 2x$$

$$\text{or, } 0.755 = 2x + 7.55x$$

$$\text{or, } x = 0.755/9.55 = 0.0791\text{M.}$$

Taking negative value :

$$-7.55 = \frac{2x}{(0.1-x)}$$

$$\text{or, } -7.55 \times (0.1-x) = 2x$$

$$\text{or, } -0.755 = 2x - 7.55x$$

$$\text{or, } x = (-0.755)/(-5.55) = 0.136\text{ M}$$

Because initial concentrations of H_2 and I_2 are 0.10 M, x can not exceed 0.10M. So discard $x = 0.136\text{M}$ as chemically unreasonable and choose value $x = 0.0791\text{M}$.

Step-4 : Calculate the equilibrium concentrations from the calculated value of x :

$$[\text{H}_2] = [\text{I}_2] = (0.10 - x) = (0.1 - 0.0791) = 0.021\text{M}$$

$$[\text{HI}] = 2x = 2 \times 0.0791 = 0.158\text{M}$$

Step - 5 : Check the results by substituting them into the equilibrium equation.

$$K_c = 57.0 = \frac{[\text{HI}]^2}{[\text{H}_2] \times [\text{I}_2]} = \frac{(0.158)^2}{(0.021) \times (0.021)} = 57.0$$

Calculation of number of moles of each substance in equilibrium mixture :

Mole number = Molarity \times Volume of reaction vessel in litre

$$\therefore \text{Moles of } \text{H}_2 = \text{Moles of } \text{I}_2 = (0.021 \text{ mol/L}) \times 10\text{L} = 0.21\text{mol.}$$

$$\text{Moles of HI} = (0.158 \text{ mol/L}) \times 10\text{L} = 1.58 \text{ mol}$$

Worked Example-4.18 : In a closed vessel at 440°C , 2 mol HI (g) is heated till it goes to about 22% HI dissociation at equilibrium. Calculate equilibrium constant of it.

Solution : Equation of dissociation : $2\text{HI(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{I}_2\text{(g)}$; From question, 22% of 2 mol HI (g) = $2 \times 0.22 \text{ mol} = 0.44 \text{ mol}$ HI dissociates. So undissociated amount in equilibrium mixture = $(2 - 0.44) \text{ mol} = 1.56 \text{ mol}$ HI. From equation, 2 mol HI (g) produces 1 mol H_2 (g) and 1 mol I_2 (g). So 0.44 mol HI (g) produces 0.22 mol H_2 (g) and 0.22 mol I_2 (g). If volume of closed vessel be V litre, then molar concentration of each component will be as follows :

$$[\text{HI}] = \frac{1.56}{V} \text{ molL}^{-1}; [\text{H}_2] = [\text{I}_2] = \frac{0.22}{V} \text{ molL}^{-1}$$

$$\therefore K_c = \frac{[\text{H}_2] \times [\text{I}_2]}{[\text{HI}]^2} = \frac{\frac{0.22}{V} \times \frac{0.22}{V}}{\left(\frac{1.56}{V}\right)^2} = 0.018$$

Worked Example – 4.19 : At 470°C, compound AB(g) dissociates 45% as :

$2AB(g) \rightleftharpoons A_2(g) + B_2(g)$. Calculate equilibrium constant of it.

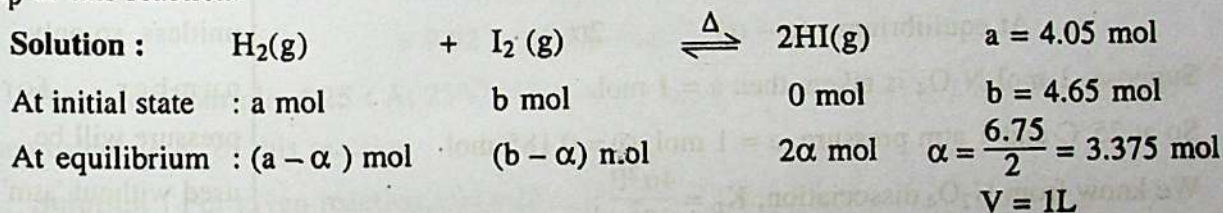
Solution : Related equation : $2AB(g) \rightleftharpoons A_2(g) + B_2(g)$

From question, 45% AB dissociates; then as per equation, from 2 mol AB (g), $2 \times 0.45 = 0.90$ mol AB (g) dissociates. So undissociated amount in equilibrium mixture = $(2 - 0.90) = 1.10$ mol. From equation, 2 mol AB (g) produces 1 mol $A_2(g)$ and 1 mol $B_2(g)$. So 0.90 mol AB (g) produces 0.45 mol $A_2(g)$ and 0.45 mol $B_2(g)$. If volume of closed vessel be V litre, then molar concentration of each component in equilibrium will be :

$$\begin{array}{l} \text{At equilibrium, concn. (M)} \quad \frac{1.10}{V} \quad \frac{0.45}{V} \quad \frac{0.45}{V} \\ \therefore \text{Equilibrium constant, } K_c = \frac{[A_2] \times [B_2]}{[AB]^2} = \frac{\frac{0.45}{V} \times \frac{0.45}{V}}{\left(\frac{1.10}{V}\right)^2} = 2.066 \times 10^{-3} \end{array}$$

$$\therefore K_c = 2.066 \times 10^{-3}$$

Worked Example – 4.20 : At 444°C, 4.05 mol $H_2(g)$ and 4.65 mol $I_2(s)$ are heated in 1.0L flask producing 6.75 mol HI (g). as $H_2(g) + I_2(g) \xrightarrow{444^\circ C} 2HI(g)$. Calculate K_c and K_p of this reaction.



$$\text{At equilibrium, } [H_2] = (a - \alpha) = (4.05 - 3.375) = 0.675 \text{ (M)}$$

$$[I_2] = (b - \alpha) = (4.65 - 3.375) = 1.275 \text{ (M)}$$

$$[HI] = 2\alpha = 2 \times 3.375 = 6.75 = 6.75 \text{ (M)}$$

For K_c calculation, molar concentration of each component is divided by 1M.

$$\therefore K_c = \frac{[HI]^2}{[I_2][H_2]} = \frac{(6.75)^2}{(1.275)(0.675)} = \frac{45.5625}{0.860625} = 52.94$$

Mole no. of reactants and product are same; so $\Delta n = 0$, $\therefore K_p = K_c = 52.94$

Worked Example – 4.21 : At 298K, in equilibrium mixture of N_2O_4 dissociation, partial pressure of $N_2O_4(g)$ is 0.8 atm and K_p of the reaction is 0.008. Calculate K_c and partial pressure of $NO_2(g)$.

Solution : Related equation : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

$$K_p = \frac{(\text{PNO}_2)^2}{\text{PN}_2\text{O}_4}; \text{ or } (\text{PNO}_2)^2 = K_p \times \text{PN}_2\text{O}_4 \text{ [by cross-multiplication]}$$

$$(\text{PNO}_2)_2 = 0.008 \times 0.8 \text{ atm} = 0.0064 \text{ atm}$$

$$\therefore \text{PNO}_2 = \sqrt{0.0064} = 0.08 \text{ atm}$$

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

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

$$K_c = \frac{0.008}{(0.082\text{K}^{-1} \times 298\text{K})^1}$$

$$K_c = \frac{0.008}{24.436} = 3.274 \times 10^{-4}$$

$$\therefore K_c = 3.274 \times 10^{-4}$$

$$\text{Here, } K_p = 0.008$$

$$K_c = ?$$

$$\text{Here, } R = \frac{0.082 \text{ L atm K}^{-1} \text{ mol}^{-1}}{\text{L mol}^{-1} \text{ atm}}$$

$$T = 298\text{K}$$

$$\Delta n = (2 - 1) = 1$$

[Note : In equations of K_c & K_p related component is divided by related 1M and 1atm term; because K_c and K_p are unitless.]

Worked Example- 4.22 : At 25°C and 1atm pressure N_2O_4 dissociates 18.5% into products (NO_2). Calculate K_p of it. What will be degree of dissociation at 25°C and 0.5 atm?

Solution : Related equation : $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

At equilibrium : $(a - \alpha) \quad 2\alpha$

Suppose, 1 mol N_2O_4 is taken, then $a = 1$ mol.

So at 25°C and 1 atm pressure, $a = 1$ mol, $\alpha = 0.185$ mol

We know from N_2O_4 dissociation, $K_p = \frac{4\alpha^2 P}{a^2}$;

$$\therefore \alpha = \frac{a}{2} \sqrt{\frac{K_p}{P}}; \text{ or, } 0.185 = \frac{1}{2} \sqrt{\frac{K_p}{1}}; \text{ or, } K_p = (0.18 \times 2)^2 = 0.1369$$

$$\text{At } P = 0.5, \text{ amount of dissociation, } \alpha = \frac{1}{2} \sqrt{\frac{K_p}{0.5}}; \text{ or, } \alpha = \frac{1}{2} \sqrt{\frac{0.1369}{0.5}}$$

$$\text{or, } \alpha = \frac{1}{2} \times 0.524 = 0.262$$

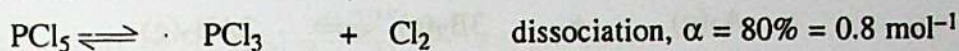
$$\therefore \text{Degree of dissociation, } \beta = \frac{\alpha}{a} = \frac{0.262}{1}; \beta = 0.262 = 26.2\%$$

$$\therefore \text{at } 25^\circ\text{C} \text{ and } 0.5 \text{ atm degree of dissociation, } \beta = 26.2\%$$

Worked Example-4.23 : At 25°C and 3.0 atm. pressure PCl_5 dissociates 80% to PCl_3 and Cl_2 . Calculate K_p and partial pressure of PCl_3 and Cl_2 .

Note : K_p is unitless, so only number for pressure will be used without 'atm'

Solution : Related reaction :



At initial stage : 1 mol 0 0 $P = 3.0 \text{ atm}$; Equiv. const., $K_p = ?$

At equilibrium : $(1-0.8) \text{ mol}$ 0.8 mol 0.8 mol Partial pressure of PCl_3 , $P_{\text{PCl}_3} = ?$

Total mole no. at equilibrium = $(0.20 + 0.8 + 0.8) = 1.8$

Partial Pressure of PCl_5 , $P_{\text{PCl}_5} = \frac{0.20}{1.8} \times 3 \text{ atm} = \frac{0.33 \text{ atm}}{1 \text{ atm}} = 0.33$

Partial Pressure of PCl_3 , $P_{\text{PCl}_3} = \frac{0.8}{1.8} \times 3 \text{ atm} = 1.332 \text{ atm} = \frac{1.332 \text{ atm}}{1 \text{ atm}} = 1.332$

Partial Pressure of Cl_2 , $P_{\text{Cl}_2} = \frac{0.8}{1.8} \times 3 \text{ atm} = 1.332 \text{ atm} = \frac{1.332 \text{ atm}}{1 \text{ atm}} = 1.332$

\therefore Equilibrium constant, $K_p = \frac{P_{\text{PCl}_3} \times P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{1.332 \times 1.332}{0.33} = 5.33$

$\therefore K_p = 5.33$, Partial pressure of $\text{PCl}_3 = 1.332 \text{ atm}$, Partial pressure of $\text{Cl}_2 = 1.332 \text{ atm}$.

Worked Example- 4.24 : At a particular temp. for reaction $2\text{A} + \text{B} \rightleftharpoons 2\text{C}$, the equilibrium constant, $K_c = 8.0 \times 10^{-4}$. If rate constant of backward reaction $= 1.24 \text{ L mol}^{-1} \text{ s}^{-1}$; then calculate rate constant of forward reaction.

Solution : Equilibrium constant, $K_c = \frac{\text{rate constant of forward reaction}}{\text{rate constant of backward reaction}}$

\therefore Rate constant of forward reaction $= K_c \times \text{rate constant of backward reaction}$

$$= 8 \times 10^{-4} \times 1.24 \text{ L. mol}^{-1} \text{ s}^{-1}$$

$$= 9.92 \times 10^{-4} \text{ L. mol}^{-1} \text{ s}^{-1}$$

Worked Example-4.25 : At 25°C , $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$; if its $K_p = 3 \times 10^{24}$; then calculate K_c of this reaction.

Solution : For given reaction, $\Delta n = [2 - (2 + 1)] = -1$.

From question, $K_p = 3 \times 10^{24}$, and $T = (25 + 273)\text{K} = 298\text{K}$

Here, $R = \frac{0.082 \text{ L.atm. mol}^{-1} \text{ K}^{-1}}{\text{L.atm.mol}^{-1}}$

$\therefore K_p = K_c \times (RT)^{\Delta n}$; putting the values, we get :

$$\text{or, } 3 \times 10^{24} = K_c (0.082 \text{ K}^{-1} \times 298 \text{ K})^{-1}$$

$$\therefore K_c = (3 \times 10^{24}) \times (0.082 \times 298)$$

$$= 7.33 \times 10^{25}$$

Worked Example - 4.26 : $\text{A}_2(\text{g}) + 3\text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}_3(\text{g})$; if at 650K temp. and 25 atm pressure, the equilibrium mixture of this reaction contains $22\%\text{A}_2$ and $17\%\text{AB}_3$; calculate K_p and K_c of this reaction.

Solution : Here total pressure, $P = 25$ atm.



From question, $\text{B}_2 = (100 - 22 - 17)\% = 61\%$

$$\text{Partial pressure of A}_2, P_{\text{A}_2} = \frac{22}{100} \times 25 \text{ atm} = 5.5 \text{ atm} = \frac{5.5 \text{ atm}}{1 \text{ atm}} = 5.5$$

$$\text{Partial pressure of B}_2, P_{\text{B}_2} = \frac{61}{100} \times 25 \text{ atm} = 15.25 \text{ atm} = \frac{15.25 \text{ atm}}{1 \text{ atm}} = 15.25$$

$$\text{Partial pressure of AB}_3, P_{\text{AB}_3} = \frac{17}{100} \times 25 \text{ atm} = 4.25 \text{ atm} = \frac{4.25 \text{ atm}}{1 \text{ atm}} = 4.25$$

$$\therefore K_p = \frac{(P_{\text{AB}_3})^2}{P_{\text{A}_2} \times (P_{\text{B}_2})^3} = \frac{(4.25)^2}{5.5 \times (15.25)^3} = 9.25 \times 10^{-4}$$

We know, $K_p = K_c (RT)^{\Delta n}$ (i)

$$\text{Here, } K_p = 9.25 \times 10^{-4}, T = 650\text{K}, \Delta n = 2 - (1 + 3), = -2, R = \frac{0.082 \text{ Latm mol}^{-1} \text{K}^{-1}}{\text{Latm mol}^{-1}}$$

$$K_p = K_c (RT)^{-2}$$

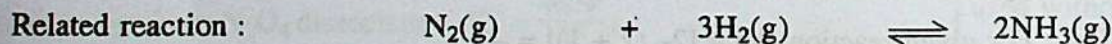
$$\therefore K_c = K_p (RT)^2 = 9.25 \times 10^{-4} \times (0.082 \times 650)^2; \text{ or, } K_c = 2.6278;$$

$$\therefore K_p = 9.25 \times 10^{-4} \text{ and } K_c = 2.6278$$

[Note : In equation of K_p and K_c , every related term is to divide by 1M for concentration and 1 atm for pressure term, to make K_p and K_c unitless.]

Worked Example – 4.27 : At 400°C on heating 0.326 mol N_2 and 0.439 mol H_2 in a 1.0L vessel, in equilibrium total mole obtained = 0.657 mol. Calculate K_c of this reaction.

Solution : Suppose x mol N_2 reacts with $3x$ mol H_2 to produce $2x$ mol NH_3 .



$$\text{Initial mole number :} \quad 3.326 \quad 0.439 \quad 0$$

$$\text{Change in mole number :} \quad -x \quad -3x \quad 2x$$

$$\text{At equilibrium (mole) :} \quad (0.326 - x) \quad (0.439 - 3x) \quad 2x$$

From question, total mole number in equilibrium :

$$(0.326 - x) + (0.439 - 3x) + 2x = 0.657$$

$$\text{or, } 0.765 - 2x = 0.657$$

$$\text{or, } 0.765 - 0.657 = 2x; \text{ or, } x = 0.054$$

$$\therefore \text{At equilibrium mole no. of N}_2 = (0.326 - 0.054) = 0.272 \text{ mol}$$

$$\therefore \text{At equilibrium molarity of N}_2, [\text{N}_2] = \frac{0.272 \text{ mol}}{1\text{L}} = 0.272(\text{M})$$

At equilibrium mole number of $H_2 = (0.439 - 0.054 \times 3) = 0.275 \text{ mol}$;

At equilibrium molarity of H_2 , $[H_2] = \frac{0.275 \text{ mol}}{1L} = 0.275 (M)$

At equilibrium mole number of $NH_3 = 2 \times 0.054 = 0.108 \text{ mol}$

At equilibrium molarity of NH_3 $[NH_3] = \frac{0.108 \text{ mol}}{1L} = 0.108(M)$

$$\therefore K_c = \frac{[NH_3]^2}{[H_2][H_2]^3} = \frac{(0.108)^2}{0.272 \times (0.275)^3} = \frac{0.01665}{0.00567} = 2.057$$

[Note : In equation of K_c , every molarity term is divided by 1M, because K_c is unitless.]

Students' Work – 4.9 Calculation of K_p and K_c Based :

Problem-4.33 : For reversible reaction, explain the significance of K_p and K_c .

Problem-4.34 : At 427°C , in a reaction vessel, $[H_2] = 0.10M$ and $[I_2] = 0.20 M$ are mixed. At that temperature, the reaction such as $H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$ has equilibrium constant $K_c = 57.0$. Calculate concentrations of H_2 , I_2 , and HI in equilibrium mixture.

[Ans. $[H_2] = 0.006M$; $[I_2] = 0.106M$; $[HI] = 0.189M$]

Problem – 4.35(a) : At 25°C , Calculate the equilibrium concentrations of N_2O_4 and NO_2 of the reaction $N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$ in a vessel that contains an initial N_2O_4 concentration of $0.05 M$. The equilibrium constant K_c for that reaction is 4.64×10^{-3} .

[Ans. $[N_2O_4] = 0.0429M$; $[NO_2] = 0.0141M$]

Problem – 4.35(b) : At 25°C , in equilibrium mixture of N_2O_4 dissociation, the partial pressure of N_2O_4 is 0.8 atm and $K_p = 0.008$. Calculate K_c of the reaction and partial pressure of NO_2 .

[Ans. $K_c = 3.274 \times 10^{-4}$; $P_{NO_2} = 0.08 \text{ atm}$.]

Problem – 4.35(c) : Calculate the equilibrium concentrations at 25°C , for the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2 (g)$; if the initial concentrations are $[N_2O_4] = 0.02 M$ and $[NO_2] = 0.03M$. Here $K_c = 4.64 \times 10^{-3}$ at 25°C

[Ans. $[N_2O_4] = 0.0292M$; $[NO_2] = 0.0116M$]

Problem – 4.35(d) : At 30°C and 1 atm pressure, for dissociation of N_2O_4 gas $K_p = 0.50$; then calculate the percent amount of its dissociation.

[Ans. 33.33%]

Problem-4.36(a) : An inorganic chemist studying the dissociation reaction of phosphorus halide, mixes 0.105 mol of PCl_5 with 0.045 mol of Cl_2 and 0.045 mol of PCl_3 in a $0.50L$ flask at 250°C : $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$; $K_c = 4.2 \times 10^{-2}$. In which direction will the reaction proceed?

[Ans. In forward direction;]

Problem-4.36(b) : If $[PCl_5] = 0.2065 M$ at equilibrium in problem-4.36(a); what are the equilibrium concentrations of other components?

[Ans. $[PCl_3] = [Cl_2] = 0.093M$]

Problem 4.37(a) : An inorganic chemist studying the decomposition reaction of PCl_5 , takes 1 mol PCl_5 in a reaction vessel at 250°C and 1 atm pressure. At this conditions, 80%

PCl_5 dissociates. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$. Calculate partial pressures of PCl_3 and Cl_2 , K_p and K_c of this reaction.

[Ans. $K_c = 4.1 \times 10^{-2}$; $K_p = 1.76$; Partial pressure of $\text{PCl}_3 = 0.44 \text{ atm}$.]

Problem – 4.37(b) : At 30°C and 1.5 atm pressure, 15.6% PCl_5 dissociates. Calculate the value of K_p of this reaction. [Ans. $K_p = 0.0374$]

Problem – 4.37(c) : At 250°C and 3 atm pressure, 80% PCl_5 dissociates into PCl_3 and Cl_2 . Calculate partial pressure of PCl_3 and Cl_2 gas and K_p . [Ans. 1.33 atm , $K_p = 5.36$]

Problem – 4.38 (a) : At 450°C and $1.01 \times 10^5 \text{ Nm}^{-2}$ pressure, in 1.0L flask 1mol H_2 and 1 mol I_2 mixture is allowed to react. In equilibrium mixture, 1.56 mol HI is present; deduce K_p of this reaction. [Ans. $K_p = 50.37$]

Problem – 4.38(b) : At 425°C 4.25 mol H_2 is heated with 4.75 mol I_2 in 1.0L flask; then 6.70 mol HI is produced ($\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$). Calculate K_c and K_p of this reaction.

[Ans. $K_c = K_p = 35.627$]

Problem – 4.38(c) : At 445°C temp. 41.14 g H_2 and 1325.88g I_2 mixture is heated in a 1.0L flask; then 1308.16g HI is produced. Calculate equilibrium constants of this reaction.

[Ans. $K_c = K_p = 85.61$]

Problem–4.38 (d) : At 425°C temp. 15 mol H_2 and 5.2 mol I_2 mixture is heated in a 1.0L flask, then 10 mol HI is produced. Calculate equilibrium constants of this reaction.

[Ans. $K_c = K_p = 50$]

Problem– 4.38(e) : At 37°C , 35% HI dissociates. Calculate K_p and K_c of this reaction.

[Ans. $K_p = 0.7248$; $K_c = 0.07248$]

Problem–4.39 : At a particular temp. and 1atm pressure, in 2.0L flask the reaction, $\text{X}_2(\text{g}) + \text{Y}_2(\text{g}) \rightleftharpoons 2\text{XY}(\text{g})$ occurs with initial concentration of 2 mol X_2 and 2 mol Y_2 . At equilibrium mixture 3.12 mol product is produced. Calculate K_c and K_p of this reaction.

[Ans. $K_p = K_c = 50.28$] [B.B. 2015]

Worked Example-4.28 : Calculating Equilibrium Partial Pressures :

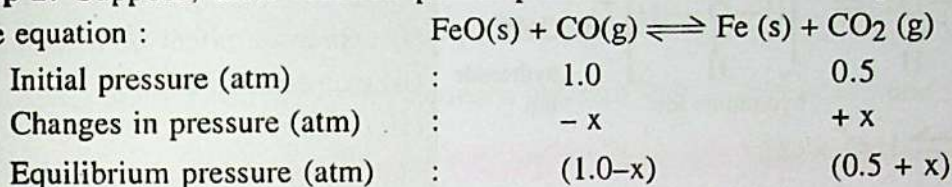
During steel production from iron ore, iron (II) oxide is reduced by CO gas to give iron metal and CO_2 . The equilibrium constant K_p for the reaction at 1000 K is 0.259 .

$\text{FeO}(\text{s}) + \text{CO}(\text{g}) \rightleftharpoons \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$. What are the equilibrium partial pressures of CO and CO_2 at 1000K , if the initial partial pressures are $P_{\text{CO}} = 1.0 \text{ atm}$ and $P_{\text{CO}_2} = 0.5 \text{ atm}$?

Strategy : Calculate equilibrium partial pressures from initial partial pressures and K_p .

Solution : Step–1 : Balanced equation : $\text{FeO}(\text{s}) + \text{CO}(\text{g}) \rightleftharpoons \text{Fe}(\text{s}) + \text{CO}_2(\text{g})$

Step-2: Suppose, after reaction partial pressure of CO reduces by x atm. Then from balance equation :



Step-3 : Putting the equilibrium partial pressures in the equilibrium equation for K_p .

$$K_p = 0.259 = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{(0.5+x)}{(1.0-x)}; [\text{solid FeO, Fe terms excluded}]$$

$$\text{or, } 0.259 - 0.259x = 0.5 + x; \text{ or, } x = -0.241/1.259 = -0.191$$

Step-4 : Putting value of x into equilibrium partial pressure expressions :

$$P_{\text{CO}} = 1.0 - x = 1.0 - (-0.191) = 1.191 \text{ atm.}$$

$$P_{\text{CO}_2} = 0.5 + x = 0.5 + (-0.191) = 0.309 \text{ atm.}$$

Step - 5 : Check the results by substituting them into the equilibrium equation :

$$K_p = 0.259 = \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{0.309}{1.191} = 0.259$$

A negative value of x means that the reaction goes from products to reactants to reach equilibrium. This makes sense because the initial reaction quotient, $Q_p = 0.5/1.0 = 0.5$, is greater than the equilibrium constant $K_p = 0.259$. When $Q_p > K_p$, then the net reaction always goes from products to reactants (right to left).

Students' Work - 4.10 : Partial Pressure Calculation Based :

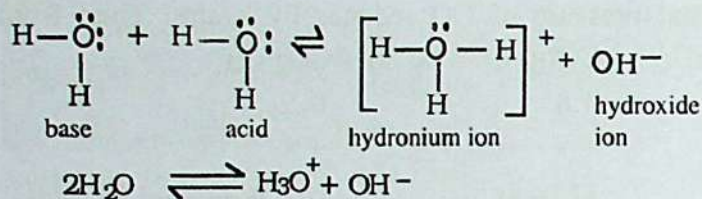
Problem-4.40 : The equilibrium constant K_p for water gas production reaction :

$\text{C(s)} + \text{H}_2\text{O(g)} \rightleftharpoons \text{CO(g)} + \text{H}_2\text{(g)}$; is 2.44 at 1000 K. What are the equilibrium partial pressures of $\text{H}_2\text{O(g)}$, CO and H_2 ; if the initial partial pressures are $P_{\text{H}_2\text{O}} = 1.2 \text{ atm}$, $P_{\text{CO}} = 1.0 \text{ atm}$, and $P_{\text{H}_2} = 1.4 \text{ atm}$? [Ans : $P_{\text{H}_2\text{O}} = 0.9 \text{ atm}$; $P_{\text{CO}} = 1.3 \text{ atm}$; $P_{\text{H}_2} = 1.7 \text{ atm}$]

Problem - 4.41(a) : In reaction, $2\text{SO}_2\text{(g)} + \text{O}_2\text{(g)} \rightleftharpoons 2\text{SO}_3\text{(g)}$; at a particular temp : $K_p = 4.75$. In equilibrium, partial pressure of SO_2 and SO_3 are respectively 0.25 atm and 0.45 atm. Calculate partial pressure of $\text{O}_2\text{(g)}$. [Ans. 0.6821 atm].

4.10.1 Ionic Product of Water : Auto-Ionization of Water

In 1894 Kohlrausch and Heydweiller showed that very pure water conducts electricity to a very small amount. Hence, water is a weak electrolyte. The reason is that water itself dissociates into positive ions such as hydronium ions (H_3O^+) and negative ion such as hydroxyl ion (OH^-) in an equilibrium process. This process is known as **autoionization** (or self-ionization) of water. Here water molecules can act as proton donor or acid and proton acceptor or base both. One molecule of water acting as acid, donates proton to other molecule of water, acting as a base :



According to the chemical equilibrium we get :

$$K = \frac{[\text{H}_3\text{O}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

MCQ-4.11 : Significances of K_c are :

- (i) expresses extent of reaction
- (ii) expresses direction,
- (iii) concn. of components at equilibrium can be calculated from its initial concn.

Which is correct?

- (a) i, ii
- (b) ii, iii,
- (c) i, iii
- (d) i, ii and iii

However due to slight ionization of water, the concentration of water does not change. So molar concentration of water $[\text{H}_2\text{O}]$ may be taken as constant.

$$\therefore [\text{H}_3\text{O}^+] \times [\text{OH}^-] = K \times [\text{H}_2\text{O}]^2 = K_w = \text{constant}$$

$$\therefore K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$$

Here K_w is called the **ionic product of water**. Its value changes slightly with change of temperature. At 25°C its value is taken as 1×10^{-14} .

There are **two important aspects** of the dynamic equilibrium in the dissociation of water.

★ **First**, the forward and reverse reactions are rapid : H_2O molecules, H_3O^+ ions and OH^- ions continually interconvert as protons transfer quickly from one species to another.

★ **Second**, the position of the equilibrium lies far to the left. At any given instant, only a tiny fraction of the water molecules are dissociated into H_3O^+ ions and OH^- ions. The vast majority of the water molecules are undissociated.

From the experimental calculation, it is found that H_3O^+ ions concentration in pure water is $1.0 \times 10^{-7} \text{ M}$ at 25°C . Since the dissociation of water produces equal concentrations of H_3O^+ ions and OH^- ions; hence

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M at } 25^\circ\text{C}$$

Further more, we know that molar concentration of pure water, calculated from its density and molar mass, is 55.5 M at 25°C .

$$[\text{H}_2\text{O}] = \frac{1000 \text{ g/L}}{18 \text{ g mol}^{-1}} = 55.5 \text{ mol/L at } 25^\circ\text{C}$$

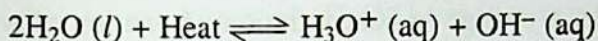
From these facts; we conclude that the ratio of dissociated to undissociated water molecules is about $(1.0 \times 10^{-7})/55.5 \text{ M} = 1.8 \times 10^{-9}$

(A) Characteristics of Ionic Product of Water (K_w) :

(1) **Application of Equation of K_w :** The equation $K_w = [H_3O^+] \times [OH^-]$ is applicable to pure water and any other type of aqueous solution like neutral, acidic or alkaline solution.

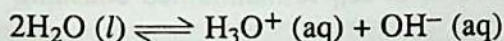
So at a particular temp. in pure water or in any aqueous solution, the product of molar concentrations of H_3O^+ ion and OH^- ion is constant and it is equal to value of K_w .

(2) **Effect of Temp. on K_w :** Like other equilibrium constants, value of K_w is constant at a particular temperature and with change of temp. value of K_w also changes. Auto ionisation of water is an endothermic process.



Hence with increase of temp. molar concentration of H_3O^+ and OH^- ions increases i. e. K_w increases. At different temp. different values of K_w are shown below : [Table-4.4(a)]

Temperature ($^{\circ}C$)	10 $^{\circ}C$	25 $^{\circ}C$	30 $^{\circ}C$	50 $^{\circ}C$	100 $^{\circ}C$
Value of K_w	0.292×10^{-14}	1.0×10^{-14}	1.465×10^{-14}	5.474×10^{-14}	8.7×10^{-14}

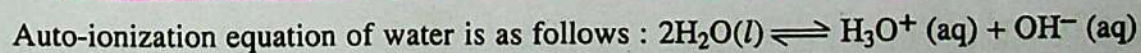
(3) Relation between Auto-ionization constant (K_d) and Ionic Product (K_w) :

$$\text{Here } K_d = \frac{[H_3O^+] \times [OH^-]}{[H_2O]^2} = \frac{K_w}{[H_2O]^2}; \therefore K_w = K_d \times [H_2O]^2$$

Hence auto-ionization constant (K_d) of water and ionic product (K_w) are not same.

Now in 1L pure water, mole-number of H_2O , $[H_2O] = \frac{1000g}{18g \text{ mol}^{-1}} = 55.55 \text{ mol}$; [density of water $1g \cdot cm^{-3}$]. Molar concentration of pure water, $[H_2O] = 55.55 \text{ molL}^{-1}$

$\therefore K_w = K_d \times (55.55)^2$; this is the relation of auto-ionization of water (K_d) and ionic product K_w of water.

(4) Molar Concentration of H_3O^+ ion and OH^- ion of pure water :

It is clear that the number of H_3O^+ ion and OH^- ion or their molar concentration, produced from auto-ionization of very small number of H_2O molecules are same. Hence.

$$[H_3O^+] = [OH^-]. \text{ Hence } K_w = [H_3O^+] \times [OH^-] = [H_3O^+]^2 = [OH^-]^2$$

So in pure water, $[H_3O^+] = [OH^-] = \sqrt{K_w}$

(i) At 25°C temp. $K_w = 10^{-14}$; \therefore at 25°C, in pure water

$[H_3O^+] = [OH^-] = \sqrt{10^{-14}} = 10^{-7}$ M. Here in 1 crore or 10 millions litre pure water, 1 mol H_3O^+ ion and 1 mol OH^- ion are present,

(ii) At 100°C temp. $K_w = 8.7 \times 10^{-14}$; [from table-4.4(a)]

\therefore at 100°C, in pure water $[H_3O^+] = [OH^-] = \sqrt{8.7 \times 10^{-14}} = 2.95 \times 10^{-7} \text{ mol L}^{-1}$.

(B) Auto-ionization of Water and Acid-Base Relation :

Relation between H_2O and OH^- ions in aqueous solution : Auto-ionization of water has two major cosequences for aqueous acid-base chemistry :

(1) According to **Le Chatelier's principle**, a change in concentration of one ion of weak electrolyte like water remaining in dynamic equilibrium, will shift the equilibrium position; but it does not change the equilibrium constant. Therefore, if some acid is added, then $[H_3O^+]$ ions increase, and so $[OH^-]$ ions must decrease, if some base is added then OH^- ions increase and so $[H_3O^+]$ ions must decrease. However, the addition of H_3O^+ or OH^- ions merely lead to the formation of H_2O molecule, so the value of K_w is maintained constant.

* A change in $[H_3O^+]$ causes an inverse change in $[OH^-]$ and vice versa :

Higher $[H_3O^+] \Rightarrow$ Lower $[OH^-]$ and Higher $[OH^-] \Rightarrow$ Lower $[H_3O^+]$

(2) Both ions, like H_3O^+ and OH^- , are present in all aqueous systems. Thus all acidic solutions contain a low concentration of OH^- ions, and all basic solutions contain a low concentration of H_3O^+ ions. The equilibrium nature of autoionization allows us to define 'acidic' or 'basic' solutions in terms of relative magnitudes of $[H_3O^+]$ and $[OH^-]$ ions.

In an 'Acidic Solution', $[H_3O^+] > [OH^-] > \sqrt{K_w}$

In a 'Neutral Solution', $[H_3O^+] = [OH^-] = \sqrt{K_w}$

In a 'Basic Solution', $[H_3O^+] < [OH^-] < \sqrt{K_w}$

(3) **Calculation of molar concentrations of H_3O^+ and OH^- ion in aqueous solution :** If we know the value of K_w at a particular temperature and concentration of one of the two ions, we can calculate concentration of other ion by solving for it from K_w expression :

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} \text{ and } [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]}; \text{ For example, at } 25^\circ\text{C} \text{ when any one of } [\text{H}_3\text{O}^+]$$

and $[\text{OH}^-]$ is known, then other can be calculated from K_w ; such as

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w = 1.0 \times 10^{-14}$$

$$[\text{H}_3\text{O}^+] = \frac{1.0 \times 10^{-14}}{[\text{OH}^-]}; \text{ and } [\text{OH}^-] = \frac{1 \times 10^{-14}}{[\text{H}_3\text{O}^+]}$$

Worked Example – 4.29 : Calculating $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ From K_w :

The concentration of $[\text{H}_3\text{O}^+]$ ion in a sample of lemon juice is 2.5×10^{-3} M. Calculate the concentration of OH^- ion, and classify the solution as acidic, neutral, or basic.

Strategy : $[\text{H}_3\text{O}^+]$ is known, then $[\text{OH}^-] = K_w / [\text{H}_3\text{O}^+]$

$$\text{Solution : } [\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14}}{2.5 \times 10^{-3}} = 4.0 \times 10^{-12} \text{ M}$$

Because $[\text{H}_3\text{O}^+] > [\text{OH}^-]$, the solution is acidic.

Students' Work– 4.11 : Ionic- Product Based :

Problem–4.42 : At 25°C , Calculate the ratio of dissociated water molecules and undissociated water molecules from ionic product of water (K_w) and its molar concentration.

Problem-4.43 : The concentration of $[\text{OH}^-]$ ion in a sample of sea water is 5.0×10^{-6} M. Calculate the concentration of $[\text{H}_3\text{O}^+]$ ion, and classify the solution as acidic, neutral, or basic. [Ans. 2.0×10^{-9} M; Solution is basic]

Problem–4.44(a) : At 50°C the value of K_w is 5.5×10^{-14} . What are the concentrations of H_3O^+ and OH^- ions in a neutral solution at 50°C ? [Ans. 2.345×10^{-7} M]

Problem – 4.44 (b) : At 25°C , the concentration of OH^- ion in aqueous solution is 2×10^{-5} M. Calculate concentration of H_3O^+ ion in that solution. [Ans. 5×10^{-10} M]

Problem–4.45(a) : At 50°C the value of ionic-product (K_w) of water is more than that at 25°C ; explain. [Ans. Rise of temp. ionization of H_2O increases]

Problem – 4.45 (b) : Why concentration of OH^- ion increases with rise of temperature; explain, whether water becomes alkaline or not. [Ans : not alkaline, H_3O^+ , OH^- ions equal]

4.10.2 Relation between Degree of Dissociation and Concentration of Acid and Base : Ostwald's Dilution Law

Strong acids and bases are almost completely dissociated in aqueous solutions. But weak acids and bases are partially ionised. The fraction of the amount of a substance dissociated in a solution is called degree of dissociation of that substance.

Definition of degree of dissociation of acid and base : The fraction of mole number of acid or base dissociated in aqueous solution is called the degree of dissociation of acid or base. It is denoted by α (alpha).

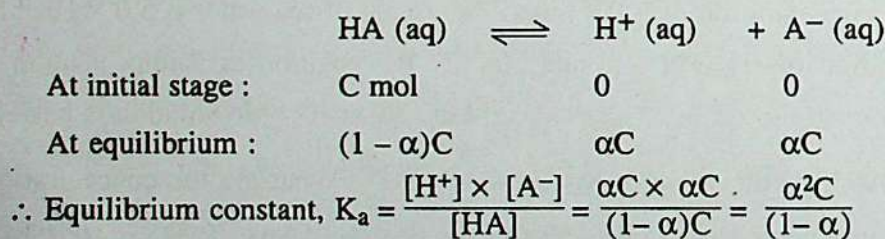
$$\therefore \text{Degree of dissociation, } \alpha = \frac{\text{number of mole of substance dissociated in solution}}{\text{total number of mole of substance in solution}}$$

For example, 0.1 M acetic acid is about 5% dissociated. Hence degree of dissociation of acetic acid in 0.1 M solution = 5% or $(0.1 \times 0.05) = 0.005 \text{ molL}^{-1}$. Degree of dissociation of weak acids and bases depends on concentration and increases with dilution.

The quantitative relation between degree of dissociation and concentration of weak electrolyte-like weak acid and base was established by Ostwald and the relation is known as **Ostwald's Dilution Law**.

Ostwald's Dilution Law : The degree of dissociation of weak electrolytes like weak acid and base is inversely proportional to the square root of concentration of that electrolyte.

Let us suppose that HA is a weak acid and its molar concentration in a solution be C and its degree of dissociation be α . So in 1 L solution from C mole of HA only αC mole HA will dissociate to produce αC mole H^+ and αC mole A^- ion and $(1-\alpha) C$ mole HA will remain as undissociated.



For weak acids the value of α is very small and hence $(1 - \alpha)$ may be taken as 1.

$$\text{Then, } K_a = \alpha^2 C; \text{ or, } \alpha^2 = \frac{K_a}{C}; \text{ or, } \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a} \times \frac{1}{\sqrt{C}}$$

or, $\alpha \propto \frac{1}{\sqrt{C}}$. Since K_a is constant and hence $\sqrt{K_a}$ is also constant.

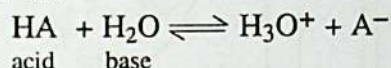
Similarly for a weak base, $\alpha = \sqrt{K_b} \times \frac{1}{\sqrt{C}}$; Therefore, $\alpha \propto \frac{1}{\sqrt{C}}$.

This is the mathematical relation of Ostwald's Dilution Law.

Applicability : (i) Ostwald's dilution law is applicable for weak acid, weak base and weak electrolyte. (ii) Applicability increases with increase of dilution. (iii) At infinite dilution, complete dissociation occurs, then no equilibrium exists and application of Ostwald's dilution law is not applicable.

4.10.3 Acid Dissociation Constant, K_a

According to Bronsted-Lowry acid-base concept, the equilibrium expression for a general weak acid (HA) in water is :



$$\text{At equilibrium, } K_c = \frac{[\text{H}_3\text{O}^+] \times [\text{A}^-]}{[\text{HA}] \times [\text{H}_2\text{O}]}$$

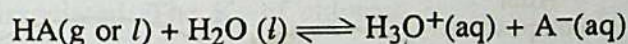
In general, the concentration of water, $[\text{H}_2\text{O}]$, is so much larger than $[\text{HA}]$ that it changes negligibly when HA dissociates; thus it is treated as a constant.

$$\therefore K_c \times [\text{H}_2\text{O}] = K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{A}^-]}{[\text{HA}]}$$

Here equilibrium constant K_a is called acid-dissociation constant (or acid-ionisation constant, K_a is unitless. [Note article 4.8, K_c]

Acid Dissociation Constant : The fraction of the number of mole of an acid dissociated in per litre aqueous solution is known as acid dissociation constant, K_a .

We know that strong electrolyte ionizes in aqueous solution in hundred percent; but weak electrolyte ionizes partly. Similarly strong acid dissociates about completely producing maximum hydronium ion (H_3O^+) and anions. For example,



For all strong acids, no undissociated acid molecule (HA) is present in aqueous solution. Hence $[\text{H}_3\text{O}^+] = [\text{HA}]$ (initial). In otherwards, $[\text{HA}]_{\text{eq}} \approx 0$ (zero)

$$\therefore Q_c = \frac{[\text{H}_3\text{O}^+] [\text{A}^-]}{[\text{HA}] \times [\text{H}_2\text{O}]} ; \quad \text{then } Q_c = K_c \gg 1$$

For all weak acids, very small number of molecules of HA ionize in water. Then $[\text{H}_3\text{O}^+] \ll [\text{HA}]$; and at equilibrium $Q_c = K_c \ll 1$

So weak acids dissociates very slightly into ions in water. Thus the stronger the acid, the higher the $[\text{H}_3\text{O}^+]$ at equilibrium, and larger the K_a value.

Stronger acid \Rightarrow Higher $[\text{H}_3\text{O}^+] \Rightarrow$ Larger K_a

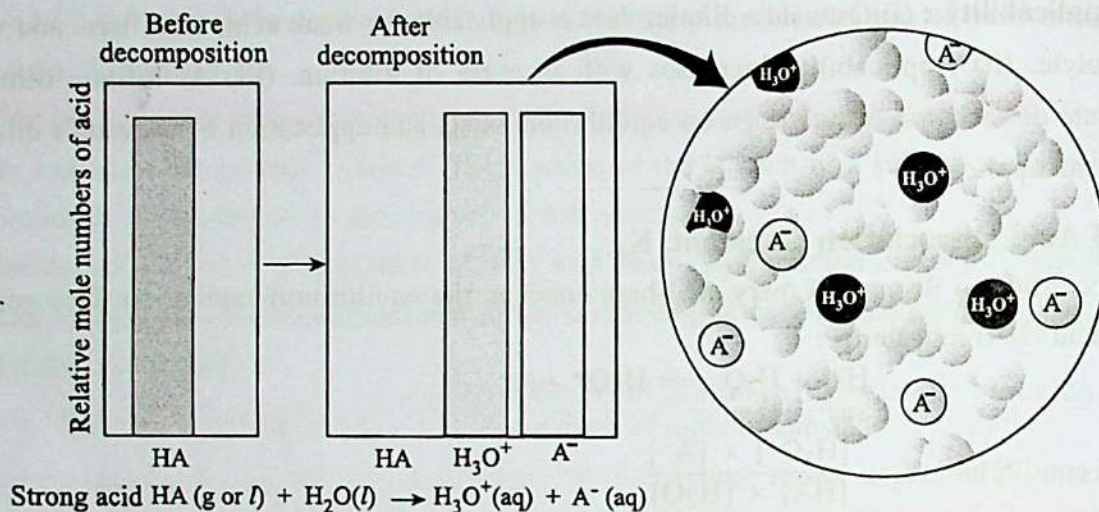


Fig-4.20 : The extent of dissociation of strong acids

In addition to K_a , another useful unit of the strength of a weak acid is the **percent dissociation**. Percent dissociation is defined as the concentration of the acid that dissociates divided by the initial concentration of the acid times 100%.

$$\text{Percent dissociation} = \frac{[\text{HA}]_{\text{dissociated}} \times 100\%}{[\text{HA}]_{\text{initial}}}$$

For example 1.0M CH_3COOH solution has $[\text{H}_3\text{O}^+] = 4.2 \times 10^{-3} \text{ M}$. Because $[\text{H}_3\text{O}^+]$ equals the concentration of CH_3COOH that dissociates, the percent dissociation in 1.0M CH_3COOH is 0.42%.

$$\begin{aligned} \text{Percent dissociation} &= \frac{[\text{CH}_3\text{COOH}] \times \text{dissociated} \times 100\%}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \\ &= \frac{4.2 \times 10^{-3} \text{ M} \times 100\%}{1.0 \text{ M}} = 0.42\% \end{aligned}$$

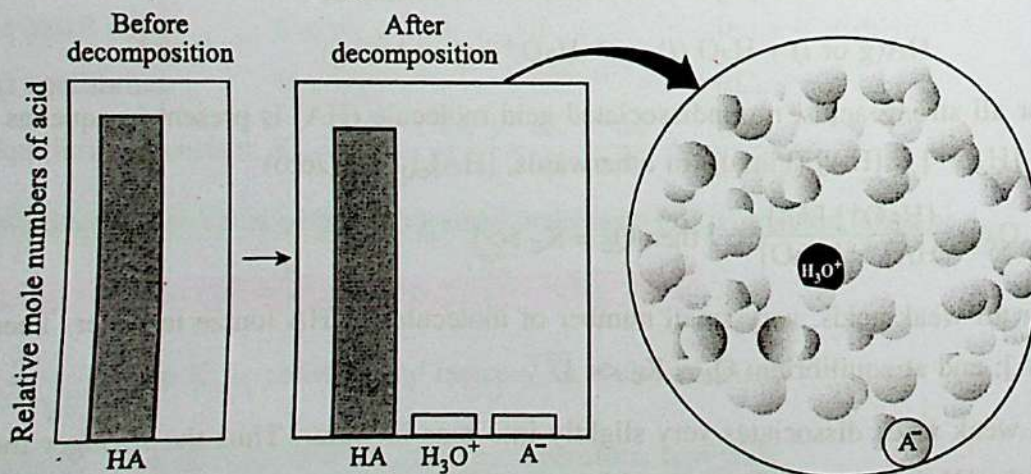
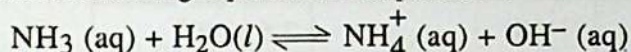


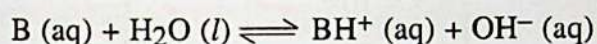
Fig-4.21 : Extent of dissociation of weak acids

4.10.4 Base -Dissociation Constant, K_b

According to Bronsted-Lowry acid-base concept, weak bases, such as ammonia (NH_3), accept a proton from water to give the conjugate acid ammonium ion (NH_4^+) and hydroxide ion (OH^-) with the following equilibrium expression :



The equilibrium reaction of any base 'B' with water is characterized by the following equilibrium equation. Here base 'B', accepts a proton from water molecule to produce conjugate acid BH^+ ion and OH^- ion. In this reaction H_2O acts as a proton donor or acid :



At equilibrium, $K_c = \frac{[\text{BH}^+] \times [\text{OH}^-]}{[\text{B}] \times [\text{H}_2\text{O}]}$; here $[\text{H}_2\text{O}]$ remains constant almost.

$$\therefore K_c \times [\text{H}_2\text{O}] = K_b = \frac{[\text{BH}^+] \times [\text{OH}^-]}{[\text{B}]}$$

Here the equilibrium constant, K_b is called the base-dissociation constant. K_b has no unit. [Note article-4.8, K_c]

Hence, the fraction of the number of mole of a base dissociated in per litre aqueous solution is known as base-dissociation constant, K_b . Here K_b has no unit.

4.11 Dissociation Constants and Acid-Base strength

Importance of K_a : The range of values for the K_a of typical weak acids give a general idea of the fraction of HA molecules that dissociate into ions :

(1) For a weak acid with a relatively high K_a ($\sim 10^{-2}$), a 1M solution has $\sim 10\%$ of the HA molecules dissociated. The K_a of chlorous acid (HClO_2) is 1.1×10^{-2} and 1M HClO_2 is 10% dissociated.

(2) For a weak acid with a moderate K_a ($\sim 10^{-5}$), a 1M solution has $\sim 0.3\%$ of the HA molecules dissociated. The K_a of acetic acid is 1.8×10^{-5} , and 1M CH_3COOH is 0.42% dissociated.

(3) For a weak acid with a relatively low K_a ($\sim 10^{-10}$), a 1M solution has $\sim 0.001\%$ of the HA molecules dissociated. The K_a of HCN is 6.2×10^{-10} , and 1M HCN is 0.0025% dissociated.

* Thus, for solutions of the same initial HA acid concentration, the smaller the K_a , the lower is the percent dissociation of HA acid.

Smaller $K_a \Rightarrow$ Lower % dissociation of HA \Rightarrow Weaker acid.

Table-4.5 lists K_a values of some acids in water with name, formula :

Table -4.5 : K_a values of some acids at 25°C

Name, formula	Structural formula	K_a
1. Hydrochloric acid, HCl	H-Cl	2.5×10^7
2. Phosphorous acid, H_3PO_3	$HPO(OH)_2$	3×10^{-2}
3. Sulphurous acid, H_2SO_3	$O=S(OH)_2$	1.4×10^{-2}
4. Phosphoric acid, H_3PO_4	$O=P(OH)_3$	7.2×10^{-3}
5. Nitrous acid, HNO_2	$O=N-OH$	4.5×10^{-4}
6. Hydrofluoric acid, HF	H-F	6.8×10^{-4}
7. Formic acid, HCO_2H	$\begin{array}{c} O \\ \\ H-C-OH \end{array}$	1.8×10^{-4}
8. Acetic acid, CH_3CO_2H	$\begin{array}{c} O \\ \\ CH_3-C-OH \end{array}$	1.8×10^{-5}

Stronger acid



Weaker acid

Fig- 4.22 : Acids' strength

Factors that affect the strength of acids :

The strength of strong acids depend on following factors :

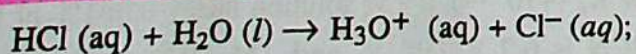
- Dissociation constant of acid (K_a)
- Size of negative ion,
- Oxidation number of central atom,
- Size of the central atom and
- Nature of solvent.

MCQ- 4.12 : Which acid is most strong?

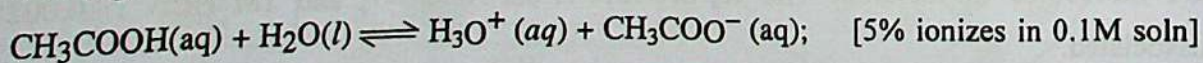
- (a) H_2SeO_3 (b) H_2SO_4
(c) $HClO_4$ (d) HIO_4

(1) **Acid-dissociation constant (K_a)** : The more the value of K_a of an acid the more the acid is strong. In aqueous solution HCl, HBr, HI, HNO_3 , H_2SO_4 etc. dissociate about completely (i.e. 99–100%); these acids are called **strong acid**. They have very large value of K_a . For example, HCl ($K_a = 2.5 \times 10^7$); HBr ($K_a = 3.2 \times 10^9$); HI ($K_a = 1.0 \times 10^{10}$); H_2SO_4 ($K_{a1} = 1.0 \times 10^3$).

On the otherhand, 0.1M CH_3COOH dissociates only 5% and its $K_a = 1.8 \times 10^{-5}$. So acetic acid is a **weak acid**.



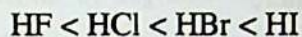
[100% ionizes in 0.1M soln]



[5% ionizes in 0.1M soln]

(2) **Size of negative ion** : The strength of hydric acids depends mainly on the size of the anion or conjugate base. The larger the conjugate base, the weaker base it is and hence the

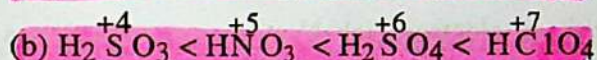
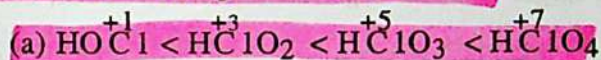
stronger is the acid. For this reason the strength of hydrides of elements in group 7A (17) are as follows :



Hydrides : Hydrides are those acids which contain hydrogen and some other nonmetal element generally except oxygen e. g. HCl, HBr, H₂S etc.

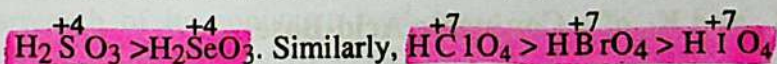
Oxoacids : Oxoacids are those acids which contain hydrogen, oxygen and some other nonmetal element generally. e.g., H₂SO₄, HClO₄ etc.

(3) Oxidation state of oxoacid : The strength of oxoacid depends mainly on two factors – (i) oxidation state or oxidation number of the central element and (ii) electronegativity of the central element. The higher is the oxidation state, the stronger is the acid. For example the strength of the following acids are as follows :



(4) Size of the Central Atom : When the oxidation state of the central element of different oxoacids are same, then only the smaller size or more electronegativity of the central element determines the comparative acid strength. The more smaller atomic size of the element in a group or higher the electronegativity of central atom, the stronger is the acid. For example, in HNO₃ and H₃PO₄ the oxidation state of both same group elements N and P are +5. Since N is smaller in size or more electronegative than P, hence HNO₃ is a stronger acid than H₃PO₄ acid. Similarly, $\text{H}\overset{+3}{\text{N}}\text{O}_2 > \text{H}_3\overset{+3}{\text{P}}\text{O}_3$

Besides this, between sulfurous acid (H₂SO₃) and selenous acid (H₂SeO₃),



Among the weak acids K_a of HIO₃ = 1.7×10^{-1} ; K_a of CH₃COOH = 1.8×10^{-5} . First K_a of H₂S = 9.1×10^{-8} . These values of K_a indicate the acidic power.

(5) Nature of solvent : The acid can ionize more in a solvent which has more power to accept proton or more basic. For example in water acetic acid is a weak acid., But in ammonia solution, acetic acid acts as a strong acid. On the other hand, opposite relation appears for bases. That is with the increase power of proton acceptance of a base, the dissociation of dissolved base (to produce OH⁻ ions) decreases. As a result the power of a base decreases.

Factors that affect the strength of bases :

The strength of bases depend on following factors :

- (i) Solubility of metal oxides and hydroxides in water,
- (ii) Dissociation constant of base (K_b),
- (iii) Lone pair electron release capacity.

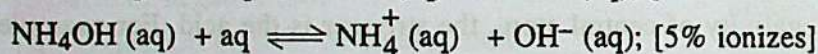
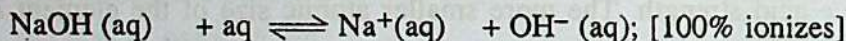
More water soluble metal oxides and hydroxides are strong bases and less water soluble metal oxides and hydroxides are weak bases.

***Strong bases :** Water-soluble compounds containing O^{2-} or OH^- ions are strong bases. The cations are usually those of the most active metals :

- (a) M_2O or MOH , where M = Group IA (1) metal (Li, Na, K, Rb, Cs)
- (b) MO or $M(OH)_2$, Where M = Group 2A (2) metal (Ca, Sr, Ba)

The metal oxides and hydroxides have larger value of K_b . $NaOH$, KOH , $CsOH$, etc, ionize % in water. So they are strong bases having highest K_b values.

*** Weak bases :** Many compounds with an electron rich N-atom are weak bases. These have capacity to release lone pair of electrons to accept protons. These bases have lower K_b values. For example, NH_4OH solution ionizes in aqueous solution near about 5% only; but $NaOH$ ionizes 100% in aqueous solution.

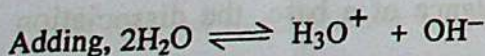
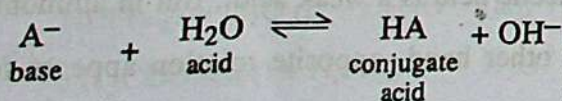
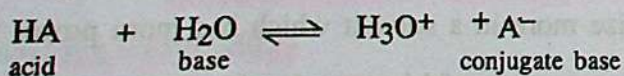


Three weak bases like NH_4OH , NH_2OH (hydroxyl amine) and hydrazine (NH_2-NH_2) have their K_b values as 1.79×10^{-5} , 1.07×10^{-8} , and 1.7×10^{-6} respectively. Similarly K_b of CH_3NH_2 (methylamine), $K_b = 3.7 \times 10^{-4}$, K_b of dimethyl amine $(CH_3)_2NH$ is :

$K_b = 5.4 \times 10^{-4}$, These values of K_b indicate the basic strength.

4.11.1 Relation between K_a and K_b of a Conjugate Acid-Base

An important relation exists between the K_a of acid HA and the K_b of conjugate base A^- ion, which we can see by treating two dissociation reactions as a reaction sequence and then adding them together :



Know More : In all aqueous solutions more or less H_3O^+ and OH^- ions are present.

* In pure water, number of H_3O^+ and OH^- ion or their concentrations remain equal.

* In acidic solution, number of H_3O^+ ions is more than that of OH^- ions.

The sum of the two dissociation reactions here is the auto-ionization of water.

From the equations of K_a and K_b of conjugate acid-base, we get :

$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+] \times [\text{A}^-]}{[\text{HA}] \times [\text{H}_2\text{O}]} \times \frac{[\text{HA}] \times [\text{OH}^-]}{[\text{A}^-] \times [\text{H}_2\text{O}]} \\ = \frac{[\text{H}_3\text{O}^+] \times [\text{OH}^-]}{[\text{H}_2\text{O}] \times [\text{H}_2\text{O}]} = K_w$$

$$\therefore K_a \times K_b = K_w$$

* In alkali solution, number of OH^- ions is more than that of H_3O^+ ions.
* From $K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$ equation it is clear that none of H_3O^+ or OH^- ions may be zero value.

This relation is valid for any conjugate acid-base pair. Taking logarithm of both sides and putting a negative sign on all values, we get.

$$-\log K_a - \log K_b = -\log K_w = -\log (1.0 \times 10^{-14})$$

$$\text{or, } \text{p}K_a + \text{p}K_b = \text{p}K_w = 14; \therefore \text{p}K_a = 14 - \text{p}K_b.$$

This relationship ($K_a \times K_b = K_w$) allows us to find K_a of the acid in a conjugate pair given K_b of the base, and vice versa. Let us see this relationship to obtain a key piece of data for solving equilibrium problems. For example K_b for F^- ion can be calculated from the dissociation constant of HF acid, $K_a = 6.8 \times 10^{-4}$ (from Appendix Table-1)

So, we have (K_a of HF) \times (K_b of F^- ion) = K_w

$$\text{or, } K_b \text{ of } \text{F}^- \text{ ion} = \frac{K_w}{K_a \text{ of HF}} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

Notice that, K_a of acid HF = 6.8×10^{-4}

But, K_b of conjugate base of acid HF, $K_b = 1.5 \times 10^{-11}$

From this solving problem, we can say – as the strength of an acid increases (larger K_a) the strength of its conjugate base decreases (smaller K_b), because the product $K_a \times K_b$ remains constant at 1.0×10^{-14} (K_w)

Problem Solved : Dissociation (α), K_a , K_b , $\text{p}K_a$, $\text{p}K_b$ Based :

Worked Example – 4.30 : Calculate percent dissociation of 0.02 M CH_3COOH acid; ($K_a = 1.8 \times 10^{-4}$).

Solution : We know equilibrium constant, $K_a = \frac{\alpha^2 C}{(1-\alpha)}$; in case of weak electrolyte $(1-\alpha) = 1$

$$\therefore K_a = \alpha^2 C \therefore \alpha = \sqrt{\frac{K_a}{C}} = \left(\frac{1.8 \times 10^{-4}}{0.02\text{M}} \right)^{\frac{1}{2}} = 9.4868 \times 10^{-2} \text{ mol}^{-1}$$

$$\text{Here, } K_a = 1.8 \times 10^{-4} \\ C = 0.02\text{M}$$

$$\therefore \text{Percent dissociation} = 9.4868 \times 10^{-2} \times 100 = 9.4868\%$$

Worked Example–4.31 : At 25°C, dissociation constant of a weak monobasic acid (HA) is 1.6×10^{-4} . What is the amount of dissociation (α) of that acid in 0.1M solution?

Solution : Dissociation of weak acid (α) = $\sqrt{\frac{K_a}{C}}$; Here, $K_a = 1.6 \times 10^{-4}$ and $C = 0.1M$

$$\therefore \text{Amount of dissociation } (\alpha) = \sqrt{\frac{1.6 \times 10^{-4}}{0.1M}} = 0.04 \text{ mol}^{-1}.$$

$$\therefore \text{Percent dissociation of acid} = 0.04 \times 100 = 4\%$$

Worked Example–4.32 : At 25°C 0.1M CH_3COOH dissociates 1.34% in solution. What is its dissociation constant?

Solution : Equilibrium constant of weak acid, $K_a = \frac{\alpha^2 C}{(1-\alpha)}$;

$$\therefore K_a = \frac{\alpha^2 C}{(1-\alpha)}; \quad \text{or, } K_a = \frac{(1.34 \times 10^{-2}) \times 0.1}{(1-1.34 \times 10^{-2})} \quad \text{Here, } C = 0.1M$$

$$\text{or, } K_a = 1.8199 \times 10^{-5}$$

$$\alpha = \frac{1.34}{100} = 1.34 \times 10^{-2}$$

Worked Example–4.33 : At 25°C 0.01M CH_3COOH dissociates 4.2% in aqueous solution. What is molar concentration of hydronium ion (H_3O^+) in acid solution?

Solution : CH_3COOH is a weak acid. For weak acid $[\text{H}_3\text{O}^+] = \alpha C$. Here α is amount of acid dissociation and C is molar concentration.

From question, present dissociation = 4.2%

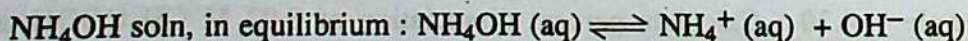
$$\therefore \alpha = \frac{4.2}{100} = 4.2 \times 10^{-2}; \text{ and } C = 0.01M$$

$$\therefore \text{In } 0.01M \text{ } \text{CH}_3\text{COOH} \text{ solution, } [\text{H}_3\text{O}^+] = \alpha C = 4.2 \times 10^{-2} \times 0.01 = 4.2 \times 10^{-4} \text{ molL}^{-1}$$

Worked Example–4.34 : At 30°C in $1.5 \times 10^{-2} M$ NH_4OH solution 3.5% NH_4OH dissociates. Calculate dissociation constant of NH_4OH in solution

Solution : Molar concentration of NH_4OH , $C = 1.5 \times 10^{-2} M$

$$\text{NH}_4\text{OH dissociation amount, } \alpha = \frac{3.5}{100} = 0.035$$



Equilibrium with concentration : $C(1-\alpha) \qquad C\alpha \qquad C\alpha$

$$\begin{aligned} \text{Molar concentration of } \text{NH}_4\text{OH, } [\text{NH}_4\text{OH}] &= C(1-\alpha) = 1.5 \times 10^{-2} \times (1-0.035) \\ &= 1.4475 \times 10^{-2}M \end{aligned}$$

$$\text{Molar concentration of } \text{NH}_4^+, [\text{NH}_4^+] = C\alpha = 1.5 \times 10^{-2} \times 0.035 = 5.25 \times 10^{-4}M$$

$$\text{Molar concentration of } \text{OH}^-, [\text{OH}^-] = C\alpha = 1.5 \times 10^{-2} \times 0.035 = 5.25 \times 10^{-4}M$$

$$\text{NH}_4\text{OH dissociation constant, } K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]} \\ = \frac{[5.25 \times 10^{-4}] \times [5.25 \times 10^{-4}]}{[1.4475 \times 10^{-2}]} = 1.90414 \times 10^{-5}$$

Worked Example – 4.35 : In 1.0 M CH_3COOH acid solution H^+ ion concentration is 4.2×10^{-3} M. Calculate % dissociation, dissociation constant (K_a) and pK_a of the acid.

Solution : $\text{CH}_3\text{COOH} (\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{CH}_3\text{COO}^- (\text{aq})$

$$\therefore \% \text{ dissociation} = \frac{\text{dissociated mole no} \times 100}{\text{total moles in solution}} = \frac{4.25 \times 10^{-3} \times 100}{1.0} = 0.425\%$$

\therefore In solution 0.425% CH_3COOH dissociates.

$$\text{So for 1.0M } \text{CH}_3\text{COOH, } K_b = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$\text{Here, } [\text{H}^+] = 4.25 \times 10^{-3} \text{ M}$$

$$K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{CH}_3\text{COO}^-] = 4.25 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 1.0$$

$$\text{or, } K_a = \frac{4.25 \times 10^{-3} \times 4.25 \times 10^{-3}}{(1 - \alpha)} \quad (1 - \alpha) = (1 - 0.00425) \text{ M}$$

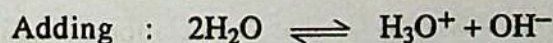
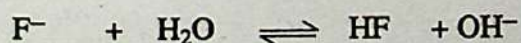
$$\text{or, } K_a = \frac{1.806 \times 10^{-5}}{(1.0 - 0.00425)} = \frac{1.806 \times 10^{-5}}{0.99575} = 1.814 \times 10^{-5}$$

$$\text{We know } pK_a = -\log K_a$$

$$\text{or, } pK_a = -\log (1.814 \times 10^{-5}) = 4.74$$

Worked Example – 4.36 : HF is a weak acid; its $K_a = 6.8 \times 10^{-4}$ and its conjugate base is F^- ion. Calculate its K_b and pK_b . From these values explain the relation of strength of acid and its conjugate base.

Solution :



From above equations, we get K_w from K_a and K_b :

$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+] \times [\text{F}^-]}{[\text{HF}]} \times \frac{[\text{HF}] \times [\text{OH}^-]}{[\text{F}^-]}, [\text{H}_2\text{O}] \text{ is excluded}$$

$$\therefore K_a \times K_b = [\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w$$

$$\therefore K_a \times K_b = K_w$$

$$\text{Here for } F^- \text{ ion, } K_b = \frac{K_w}{K_a \text{ of HF}} = \frac{1.0 \times 10^{-14}}{6.8 \times 10^{-4}} = 1.5 \times 10^{-11}$$

K_a of HF acid is 6.8×10^{-4} and conjugate base of HF is F^- ion and its $K_b = 1.5 \times 10^{-11}$. From both the values of K_a and K_b , it is clear that conjugate base of HF acid has K_b with very low value. So the more the acid strong the more weak its conjugate base. Again pK_a of HF will be $-\log K_a = -\log (6.81 \times 10^{-4}) = 3.17$ and pK_b of conjugate base F^- ion is $-\log K_b = -\log (1.5 \times 10^{-11}) = 10.82$. So it is clear from values of pK_a and pK_b that value of pK_b of weak conjugate base will be more than pK_a value of strong acid.

Students' Work – 4.12 : K_a , K_b , pK_a , pK_b Based :

Problem–4.46(a) : HF is weak acid; but HCl strong acid; explain [R. B. 2015]

Problem–4.46(b) : K_b for trimethylamine is 6.5×10^{-5} . Calculate K_a for trimethyl ammonium ion $(CH_3)_3NH^+$ ion. [Ans. 1.5×10^{-10}]

Problem–4.46(c) : K_a of HCN acid is 4.9×10^{-10} . Calculate K_b for CN^- ion.

[Ans. 2×10^{-5}]

Problem–4.46(d) : Pyridine (C_5H_5N), an organic solvent, has $pK_b = 8.74$. What is the value of pK_a for pyridinium ion $C_5H_5NH^+$? [Ans. 5.26]

Problem–4.46(e) : K_a of formic acid ($HCOOH$) is 3.74. Calculate pK_b of formate ion ($HCOO^-$). [Ans. 10.26]

Problem – 4.46 (f) : At $25^\circ C$ in aqueous solution of NH_3 , the equilibrium mixture contains NH_3 , NH_4^+ and OH^- ions with their molar concentration like $9.6 \times 10^{-3} M$, $4.0 \times 10^{-4} M$ and $4.0 \times 10^{-4} M$ respectively Calculate the dissociation constant of NH_4OH at $25^\circ C$. [Ans. $K_b = 1.67 \times 10^{-5}$]

Problem– 4.46 (g) : At $25^\circ C$ 0.1M CH_3COOH dissociates 1.34% in solution. Calculate dissociation constant (K_a) of the acid. [Ans. 1.82×10^{-5}]

Problem – 4.46 (h) : At $25^\circ C$ weak monobasic acid HA has dissociation constant value $K_a = 1.6 \times 10^{-4}$ at that temp. What will be dissociation amount (α) of that acid?

[Ans. 0.04]

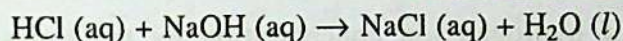
Problem – 4.46 (i) : At a particular temp. 3 weak acids HA, HB, HC have dissociation constants 4.0×10^{-5} , 5.2×10^{-4} and 8.6×10^{-3} respectively Arrange those acids as per their strength if their molar concentrations in aqueous solutions are same and explain its cause.

[Ans. $HA < HB < HC$]

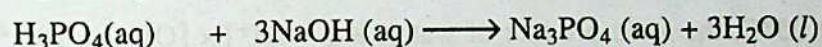
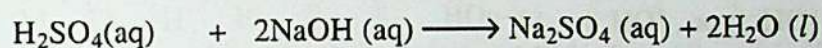
4.11.2 Basicity of an Acid & Acidity of a Base

Basicity of an Acid : Basicity of an acid is the number of mole of monoprotic base or monoacidic base (like NaOH, KOH etc.) required to neutralise completely one mole of that acid. For example,

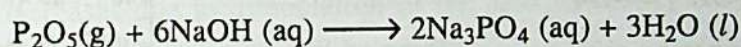
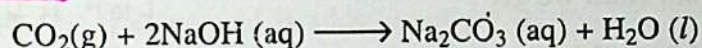
(i) 1 mol HCl neutralises 1 mol NaOH; so **basicity of HCl is 1.0**.



(ii) Similarly, **basicity of H_2SO_4 is 2; basicity of H_3PO_4 is 3**. But **basicity of H_3PO_3 is 2**, because in molecule of H_3PO_3 , two H atoms are as two $-\text{OH}$ groups from which H^+ ion dissociates in solution.

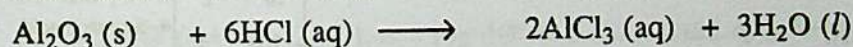
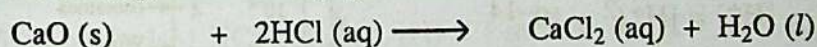
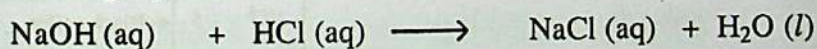


(iii) Like acids, acidic oxides have their basicity. For example, **basicity of CO_2 is 2; basicity of P_2O_5 is 6**. Note the mole number of NaOH in following equations :



Acidity of a Base : Acidity of a base is the number of mole of monoprotic acid or monobasic acid (like HCl acid) required to neutralise completely one mole of that base. For example,

(i) 1 mol NaOH neutralises 1 mol HCl; **so acidity of NaOH is 1.0**. Similarly **acidity of CaO is 2; acidity of Al(OH)_3 is 3 and acidity of Al_2O_3 is 6**. Note the mole number of HCl acid in following equations :



4.12 pH of a Solution and pH Scale

In different experimental works related to biology, biochemistry and medical science, dilute solutions of acids and bases like decimolar ($10^{-1} \text{ molL}^{-1}$) solution and even less concentration of solutions are used. Again ionic product of water is $K_w = 1.0 \times 10^{-14}$. But to express concentrations of H^+ and OH^- ions with negative power of 10 is a troublesome method. In aqueous solutions $[\text{H}_3\text{O}^+]$ can vary from 1M to 10^{-15} M . To handle numbers with negative exponents, **Sorensen, a Scandinavian chemist in 1909, introduced a new unit called pH scale to express H^+ ion concentration.**

Definition of pH : The negative logarithm of the molar concentration of hydrogen ions in a solution is called pH of that solution.

$$\text{pH} = -\log [\text{H}^+]; \text{ or, } [\text{H}^+] = 10^{-\text{pH}}$$

The higher the concentration of hydrogen ions, the lower is pH. The decrease of pH by one unit means the increase of hydrogen ion concentration by ten times. Similarly an increase of pH by one unit means the decrease of hydrogen ion concentration by 10 times.

Similarly the concentration of hydroxide ions may be expressed by pOH.

$$\text{pOH} = -\log [\text{OH}^-]; \text{ or, } [\text{OH}^-] = 10^{-\text{pOH}}$$

pH scale : At 25°C, the ionic product of water, $K_w = [\text{H}^+] \times [\text{OH}^-] = 10^{-14}$.

$$\therefore [\text{H}^+] \times [\text{OH}^-] = 10^{-14}$$

Taking logarithm on both sides we get :

$$\text{or, } \log [\text{H}^+] + \log [\text{OH}^-] = -14$$

$$\text{or, } -\log [\text{H}^+] - \log [\text{OH}^-] = 14$$

$$\text{or, } \text{pH} + \text{pOH} = 14$$

In case of pure water H^+ and OH^- ions are produced from water only. Since from one molecule of water, one H^+ ion and one OH^- ion are produced, in pure water their concentration are equal.

$$\text{i.e., } [\text{H}^+] = [\text{OH}^-]$$

$$\therefore [\text{H}^+] \times [\text{OH}^-] = [\text{H}^+] \times [\text{H}^+] = [\text{H}^+]^2 = 10^{-14}$$

$$\therefore [\text{H}^+] = 10^{-7}$$

$$\text{or, } -\log [\text{H}^+] = -\log 10^{-7} = 7$$

(i) If some acid is added to water, the concentration of hydrogen ions increases due to dissociation of the acid; hence pH of that solution decreases below 7; then the solution will be **acidic**.

If you use a calculator to find the pH from the H_3O^+ concentration, your answer will have more decimal places than proper number of significant figures.

For example, the pH of the lemon juice of $[\text{H}_3\text{O}^+] = 2.5 \times 10^{-3} \text{ M}$ is found on a calculator to be : $\text{pH} = -\log (2.5 \times 10^{-3}) = 2.60206$

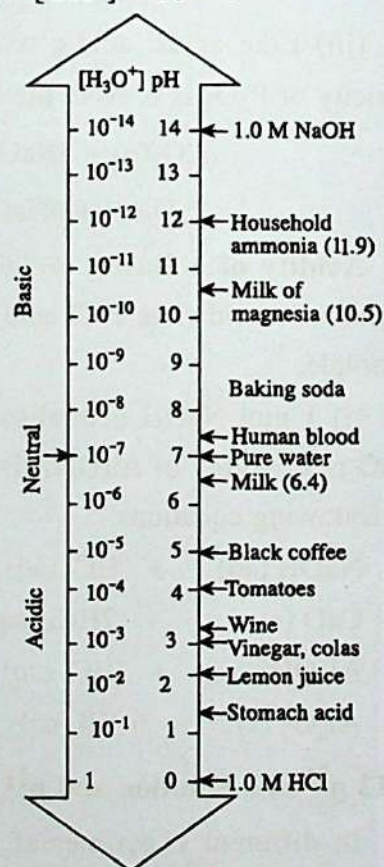


Fig-4.23 : pH scale and pH values of some common substances.

This result should be rounded to pH 2.60 (two significant figures) because $[H_3O^+]$ has only two significant figures.

In figure 4.24, pH scale is shown :

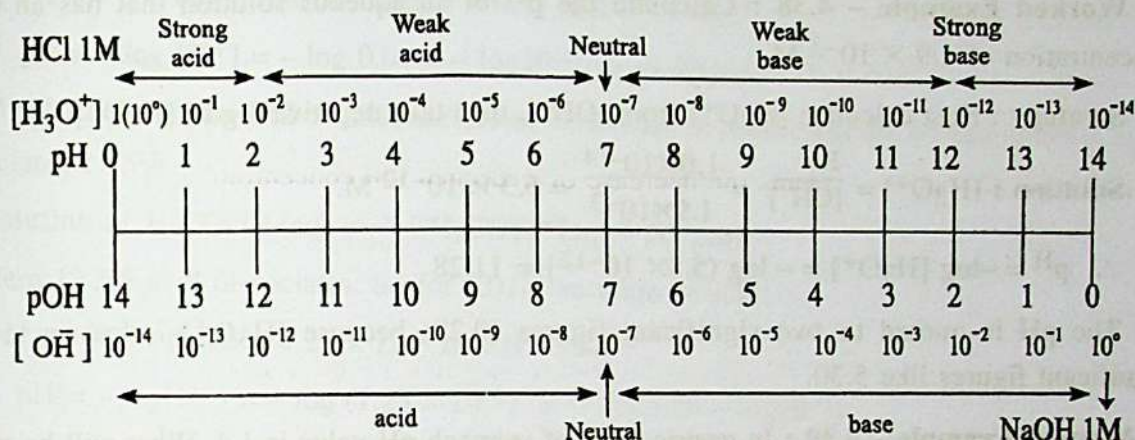


Fig-4.24 : pH scale from 0 –14.

Know More : (i) If some acid is added to water having pH value 7, the concentration of hydrogen ions increases due to dissociation of the acid molecules, hence pH of that solution decreases below 7; then the solution will be **acidic**.

(ii) On the other hand if some base is added to water, the concentration of OH^- ions increases, hence according to chemical equilibrium concentration of H^+ ion decreases, so pH of that solution increases to above 7 and the solution will be **basic**.

∴ If pH of a solution is equal to 7 ($pH = 7$), it is **neutral**.

If pH of a solution is lower than 7 ($pH < 7$), it is **acidic**.

If pH of a solution is higher than 7 ($pH > 7$), it is **basic**.

We know in 1 M HCl solution, $[H] = 1 \text{ mol } H^+ \text{ ion L}^{-1}$.

So the pH of 1M HCl solution will be :

$$pH = -\log [H^+] = -\log 1 = -\log 10^0 = 0. \text{ Since pH of 1M HCl} = 0. \text{ then, } pOH = 14$$

Again pOH of 1M NaOH solution = 0; then the pH of 1M NaOH solution = 14.

Generally in laboratory, the solutions more than 1M concentration are not used. So, the values of pH and pOH of any dilute aqueous solution remains in between 0 and 14. The pH and pOH of different solutions are shown in Fig-4.24 of pH scale.

Worked Example – 4.37 : Calculating H_3O^+ concentration from the pH.

Acid rain is a matter of serious concern because most species of fish die in waters having a pH lower than 4.5 – 5.0. Calculate the H_3O^+ concentration in a lake water that has a pH of 4.5.

MCQ-4.13 : Which solution having the following pH values has more H^+ ion concentration?

(a) 9.5 (b) 7.4

(c) 2.3 (d) 5.5

Strategy : Calculate the $[H_3O^+]$ by taking the antilog of negative of pH.

Solution : $[H_3O^+] = \text{antilog}(-pH) = 10^{-pH} = 10^{-4.5} = 3 \times 10^{-5} \text{ M}$

Worked Example – 4.38 : Calculate the pH of an aqueous solution that has an OH^- concentration of $1.9 \times 10^{-3} \text{ M}$.

Strategy : First calculate $[H_3O^+]$ from $[OH^-]$, then take negative log of $[H_3O^+]$.

Solution : $[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.9 \times 10^{-3}} = 5.3 \times 10^{-12} \text{ M}$.

$\therefore pH = -\log [H_3O^+] = -\log (5.3 \times 10^{-12}) = 11.28$

The pH is quoted to two significant figures (0.28) because $[H_3O^+]$ is known to two significant figures like 5.30.

Worked Example – 4.39 : In gastric juice of stomach pH value is 1.4. What will be molar concentration of H^+ ion or H_3O^+ ion in that juice?

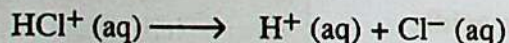
Solution : Taking antilog of negative pH value gives molar concentration of H_3O^+ ion.

$\therefore [H_3O^+] = \text{antilog}(-pH) = 10^{-pH} = 10^{-1.4} = 0.04 \text{ M}$.

\therefore Concentration of H^+ ion in gastric juice = 0.04 M

Worked Example–4.40 : Calculate pH of (a) 0.1M HCl, (b) 0.2M HCl, (c) 0.01M HCl soln.

Solution : (a) 0.1M HCl ionises completely, so 0.1M HCl = 0.1 mol H^+ ion L^{-1} .



0.1.mol

0.1,mol

$\therefore pH = -\log [H^+] = -\log 0.1 = -\log 10^{-1} = 1$

(b) In 0.2 M HCl solution, $[H^+] = 0.2 \text{ molL}^{-1}$.

$\therefore pH = -\log [H^+] = -\log (0.2) = -(-0.699) = 0.699$

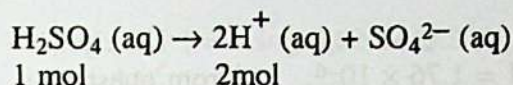
(c) In 0.01M HCl solution, $[H^+] = 0.01 \text{ molL}^{-1}$

$\therefore pH = -\log [H^+] = -\log (0.01) = -\log 10^{-2} = 2$

(*) Note when more acid is in solution, then its pH value is less.

Worked Example–4.41 : What is pH of 0.005M H_2SO_4 acid?

Solution : In aqueous solution 0.005M H_2SO_4 acid ionises completely to produce double H^+ ion as per molarity.



$$\therefore [\text{H}^+] = 2 \times 0.005 \text{ mol H}^+ \text{ ionL}^{-1} = 0.01 \text{ mol H}^+ \text{ ionL}^{-1}$$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log 0.01 = -\log 10^{-2} = -(-2) = 2$$

Worked Example-4.42 : Calculate pH of 0.01M acetic acid solution. In this solution acid dissociates 12.5%.

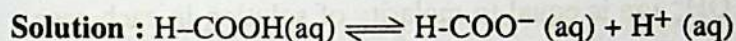


Here 12.5% acid dissociates. So for 0.01M solution of acid

$$[\text{H}^+] = 0.01 \times 0.125 = 1.25 \times 10^{-3} \text{ mol H}^+ \text{ ionL}^{-1}$$

$$\begin{aligned} \therefore \text{pH} &= -\log [\text{H}^+] = -\log (1.25 \times 10^{-3}) = (-\log 1.25 - \log 10^{-3}) \\ &= (-0.097 + 3) = 2.903 \end{aligned}$$

Worked Example-4.43 : Calculate dissociation constant (K_a) of 1.0×10^{-2} M formic acid (H-COOH). pH of this solution is 2.90.



$$K_a = \frac{[\text{H}^+] \times [\text{HCOO}^-]}{[\text{H-COOH}]}; \text{ here, } [\text{H}^+] = [\text{HCOO}^-]$$

$$= \frac{[\text{H}^+] \times [\text{H}^+]}{[\text{H-COOH}]} = \frac{[\text{H}^+]^2}{[\text{HCOOH}]}$$

$$\text{Given, } [\text{HCOOH}] = 1.0 \times 10^{-2} \text{ M}$$

$$\text{pH} = 2.90$$

$$[\text{H}^+] = ?$$

$$K_a = ?$$

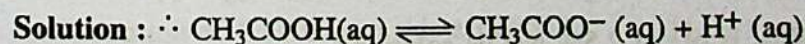
We know, $[\text{H}^+] = \text{antilog} (-\text{pH})$

$$\text{or, } [\text{H}^+] = 10^{-\text{pH}} = 10^{-2.9} = 1.2589 \times 10^{-3} \text{ M}$$

$$\therefore K_a = \frac{[\text{H}^+]^2}{[\text{H-COOH}]} = \frac{(1.2589 \times 10^{-3})^2}{1.0 \times 10^{-2}} = 1.5848 \times 10^{-4}$$

$$\therefore K_a = 1.5848 \times 10^{-4}$$

Worked Example- 4.44 : Calculate pH of 0.1M ethanoic acid at 25°C . [$K_a = 1.76 \times 10^{-5}$].



$$\therefore K_a = \frac{[\text{CH}_3\text{COO}^-] \times [\text{H}^+]}{[\text{CH}_3\text{COOH}]}; \text{ Here, } [\text{CH}_3\text{COO}^-] = [\text{H}^+]$$

Ethanoic acid is a weak acid; it ionises in small amount. So undissociated CH_3COOH concentration is about to 0.1 molL^{-1} .

$$\text{Then } K_a = \frac{[\text{CH}_3\text{COO}^-] \times [\text{H}^+]}{[\text{CH}_3\text{COOH}]} = \frac{[\text{H}^+]^2}{0.1}$$

$$[H^+]^2 = K_a \times 0.1 = (1.76 \times 10^{-5}) \times 0.1 = 1.76 \times 10^{-6}; \quad \text{from question :}$$

$$\therefore [H^+] = \sqrt{1.76 \times 10^{-6}} = 1.33 \times 10^{-3} \text{ molL}^{-1} \quad K_a = 1.76 \times 10^{-5}$$

$$\therefore \text{pH} = -\log (1.33 \times 10^{-3}) = 2.88$$

Worked Example-4.45 : In an aqueous solution concentration of H^+ ion is $3 \times 10^{-5} \text{ molL}^{-1}$. What is its pH ? What is the nature of that solution alkaline or acidic?

Solution : From question, $[H^+] = 3 \times 10^{-5} \text{ molL}^{-1}$

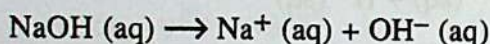
$$\therefore \text{pH} = -\log [H^+] = -\log (3 \times 10^{-5})$$

$$= -[\log 3 - 5 \times \log 10] = -0.4771 + 5 = 4.52$$

\therefore pH of solution = 4.52 which is less than 7; so solution is acidic.

Worked Example-4.46 : Calculate pH of (a) 1M NaOH; (b) 0.1M NaOH; (c) 0.02M NaOH; (d) 0.001 M NaOH solution.

Solution : Here NaOH is a strong alkali. So in all the given dilute solutions NaOH ionises completely. Hence concentration of OH^- ion is equal to molarity of solution in each case.



(a) In 1M NaOH soln, $[OH^-] = 1 \text{ molL}^{-1}$;

$$\therefore \text{pOH} = -\log [OH^-] = -\log 1 = 0;$$

$$\therefore \text{pH} = 14 - \text{pOH} = (14 - 0) = 14$$

(b) In 0.1M NaOH soln, $[OH^-] = 0.1 \text{ molL}^{-1}$

$$\therefore \text{pOH} = -\log [OH^-] = -\log 0.1 = 1; \quad \therefore \text{pH} = (14 - \text{pOH}) = (14 - 1) = 13$$

(c) In 0.02M NaOH soln, $[OH^-] = 0.02 \text{ molL}^{-1}$ $\therefore \text{pOH} = -\log [OH^-] = -\log 0.02 = 1.7$;

$$\therefore \text{pH} = (14 - \text{pOH}) = (14 - 1.7) = 12.3$$

(d) In 0.001M NaOH soln, $[OH^-] = 10^{-3} \text{ mol OH}^- \text{ ionL}^{-1}$

$$\therefore \text{pOH} = -\log [OH^-] = -\log 10^{-3} = 3; \quad \therefore \text{pH} = (14 - \text{pOH}) = (14 - 3) = 11$$

Worked Example - 4.47 : What is pH of 2.5% NaOH solution?

Solution : In 2.5% NaOH solution, NaOH ionises completely. Here 100 mL 2.5% NaOH contains 2.5g NaOH.

$$\therefore 1000 \text{ mL contains NaOH} = (2.5 \times 10) \text{g} = 25 \text{g NaOH}$$

$$\text{Again gram mol. mass of NaOH} = 40 \text{g mol}^{-1}; \quad \therefore 25 \text{g NaOH} = \frac{25 \text{g}}{40 \text{g mol}^{-1}} = 0.625 \text{ mol.}$$

$$\therefore \text{In } 0.625 \text{M NaOH solution, } [OH^-] = 0.625 \text{ mol OH}^- \text{ ionL}^{-1}$$

$$\therefore p^{OH} = -\log [OH^-] = -\log 0.625 = 0.204$$

$$\therefore pH = (14 - p^{OH}) = (14 - 0.204) = 13.796$$

Worked Example-4.48 : Concentration of OH^- ion in a solution is $8.2 \times 10^{-4} \text{ molL}^{-1}$, What is its p^H ?

Solution : From question, $[OH^-] = 8.2 \times 10^{-4} \text{ molL}^{-1}$

$$\therefore p^{OH} = -\log [OH^-] = -\log (8.2 \times 10^{-4})$$

$$= -[\log 8.2 - 4 \log 10] = (-0.9138 + 4) = 3.09$$

$$\therefore pH = (14 - p^{OH}) = (14 - 3.09) = 10.91$$

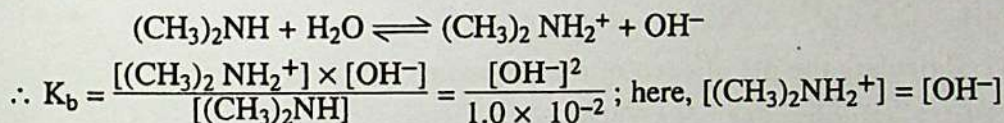
Worked Example-4.49 : Conjugate acid of NH_3 is NH_4^+ ion, its $K_a = 5.8 \times 10^{-10}$, then calculate K_b of NH_3 base.

Solution : From relation of conjugate acid-base, $K_a \times K_b = 10^{-14}$

$$\text{From question, } K_a = 5.8 \times 10^{-10}; \therefore K_b = \frac{10^{-14}}{5.8 \times 10^{-10}} = 1.72 \times 10^{-5}$$

Worked Example- 4.50 : At 25°C temp. organic base dimethyl amine aqueous solution of $1.0 \times 10^{-2} \text{ molL}^{-1}$ concentration has $pH = 7.64$. Calculate K_b of this base.

Solution : Equation for ionisation of this base.



$$\text{From question, } pH = 7.64; \therefore p^{OH} = (14.0 - 7.64) = 6.36$$

$$\therefore [OH^-] = \text{antilog } (-6.36) = 4.37 \times 10^{-7} \text{ molL}^{-1}$$

$$\therefore K_b = \frac{(4.37 \times 10^{-7})^2}{(1.0 \times 10^{-2})} = 1.91 \times 10^{-11}$$

Worked Example-4.51 : At 25°C , p^H of a solution is 5.50. What is the molar concentration of OH^- ion of this solution?

Solution : We know $p^H + p^{OH} = 14.00$

$$\therefore p^{OH} = 14.00 - p^H$$

$$\text{Given, } p^H = 5.50$$

$$\text{or, } p^{OH} = (14.00 - 5.50) = 8.50$$

$$[OH^-] = ?$$

$$\text{or, } -\log [OH^-] = 8.50 \text{ or, } \log [OH^-] = -8.50$$

$$\text{or, } [OH^-] = \text{antilog } (-8.50) = 3.16 \times 10^{-9} \text{ M}$$

Worked Example – 4.52 : Concentration of H^+ ion in the juice of a fruit is $3.3 \times 10^{-2} M$. What is pH of it? Whether the juice is acidic or alkaline?

Solution : We know, $pH = -\log [H^+]$;

From question :

$$\therefore pH = -\log (3.3 \times 10^{-2}) = 1.48$$

$$[H^+] = 3.3 \times 10^{-2} M$$

$\therefore pH$ of fruit juice is 1.48 and it is less than 7; hence fruit juice is acidic.

Worked Example–4.53 : Two solutions of $pH = 3$ and $pH = 6$ are given. Which solution is more acidic and how much times more acidic than other; explain.

Solution : We know, $pH = -\log [H_3O^+]$

$$\therefore [H_3O^+] = 10^{-pH}$$

$$\text{When, } pH = 3, \text{ then } [H_3O^+] = 10^{-3}$$

$$\text{When, } pH = 6, \text{ then } [H_3O^+] = 10^{-6}$$

\therefore Between two solutions of $pH = 3$ and $pH = 6$; the 1st solution with $pH = 3$ has more concentration of H_3O^+ ion than other solution of $pH = 6$. So 1st solution is more acidic,

From calculation, it is clear that the concentration of H_3O^+ ion in solution of $pH 3$ is more than that of 2nd solution and it is $\frac{10^{-3}}{10^{-6}} = 10^3$ times more acidic. So strength of 1st solution is 1000 times more acidic.

Students' Work– 4.13 : pH , K_a , K_b Based :

Problem–4.47. Calculate the pH of each of the following solutions :

(a) A sample of sea-water has OH^- concentration of $1.58 \times 10^{-6} M$. [Ans. 8.20]

(b) A sample of acid rain that has an H_3O^+ concentration of $6.0 \times 10^{-5} M$. [Ans. 4.22]

(c) Calculate the pH of 0.05 M H_2SO_4 solution. [Ans. 1]

(d) What is the pH of 0.01M HCl solution? [Ans. 2]

(e) What is the pH of 0.1M CH_3COOH at $25^\circ C$? Here, $K_a = 1.76 \times 10^{-5}$. [Ans. 2.88]

Note : Here $[H^+] = [CH_3COO^-]$; $\therefore [H^+] \times [CH_3COO^-] = [H^+]^2$

(f) What is the pH of 0.2M NaOH solution? [Ans. 13.3]

(g) Calculate the pH of 2.5% NaOH solution. [Ans. 13.79]

(h) If the dissociation amount of CH_3COOH is 12.5%, then calculate pH of 0.01M

CH_3COOH [Ans. 0.903]

Note : 12.5% dissociated 0.01M acid has $[H^+] = 0.01 \times 12.5M$

Problem – 4.48 : Calculate the concentrations of H_3O^+ ions and OH^- ions in each of the following solutions :

- (a) Human blood $\text{pH} = 7.40$. [Ans. $[\text{H}_3\text{O}^+] = 4.0 \times 10^{-8} \text{ M}$; $[\text{OH}^-] = 2.5 \times 10^{-7} \text{ M}$]
 (b) A cola beverage of $\text{pH} = 2.8$. [Ans. $[\text{H}_3\text{O}^+] = 1.58 \times 10^{-3}$; $[\text{OH}^-] = 6.3 \times 10^{-12} \text{ M}$]
 (c) Orange juice has $\text{pH} = 3.80$. What are the H_3O^+ , OH^- ions concentration in it?
 [Ans. $1.58 \times 10^{-4} \text{ M}$; $6.31 \times 10^{-11} \text{ M}$]

Problem- 4.49 : In an art restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO_3 to -

- (a) 2.0M (b) 0.30M. Calculate $[\text{H}_3\text{O}^+]$, pH , $[\text{OH}^-]$ and pOH of the two solutions at 25°C .
 [Ans. (a) $[\text{H}_3\text{O}^+] = 2.0\text{M}$, $\text{pH} = -0.30$; $[\text{OH}^-] = 5.0 \times 10^{-15}\text{M}$, $\text{pOH} = 14.30$.
 (b) $[\text{H}_3\text{O}^+] = 0.30\text{M}$, $\text{pH} = 0.52$; $[\text{OH}^-] = 3.3 \times 10^{-14} \text{ M}$, $\text{pOH} = 13.48$]

Problem - 4.49 (c) : A soft drink has $\text{pH} = 4.80$; calculate molar concn. of H_3O^+ ion and OH^- ion of it. [Ans. $[\text{H}_3\text{O}^+] = 1.5848 \times 10^{-5} \text{ M}$; $[\text{OH}^-] = 6.309 \times 10^{-10} \text{ M}$]

- (d) A sample HCl soln. has $\text{pH} = 3$; What is its molarity? [Ans. $1.0 \times 10^{-3} \text{ M}$]
 (e) A sample NaOH soln. has $\text{pH} = 11$; What is its molarity? [Ans. $1.3 \times 10^{-3} \text{ M}$]
 (f) What is pH of $10.8 \times 10^{-2} \text{ M}$ HCl solution? [Ans. 0.97]
 (g) What is pH of $2.5 \times 10^{-2} \text{ M}$ H_2SO_4 solution? [Ans. 1.30]
 (h) A sample acid solution has $\text{pH} = 3.60$. What are H_3O^+ ions molarity and number of H_3O^+ ions in it? [Ans : $[\text{H}_3\text{O}^+] = 2.512 \times 10^{-4} \text{ M}$; Number of H_3O^+ ion = 15.127×10^{19}]
 (i) A sample acid solution has $\text{pH} = 5.65$. What are OH^- ions molarity and number of OH^- ions in it? [Ans : $[\text{OH}^-] = 4.47 \times 10^{-9} \text{ M}$; Number of OH^- ion = 2.692×10^{15}]
 (j) At 25°C , what is pH of 0.5M methyl amine (CH_3NH_2)? [$K_b = 4.8 \times 10^{-4}$] [Ans. 12.04]
 (k) At 25°C , 0.25M CH_3COOH solution has $\text{pH} = 2.68$. What is K_a of this acid?
 [Ans. 1.746×10^{-5}]
 (l) 0.25M HCN solution has $\text{pH} = 5$. What is dissociation constant (K_a) of it?
 [Ans. 4.0×10^{-10}]
 (m) At 25°C concentration of NH_4OH solution is 0.25M. Dissociation constant (K_b) of it is 1.76×10^{-5} ; What is its pH ? [Ans. 11.32]

Know More : Whether pH of a solution may be less than 0 (zero) or, more than 14?

Yes, pH of a solution may be less than 0 (zero) and more than 14. Because, pH scale is established on following two basic points; such as 1M HCl solution's $\text{pH} = 0$ and 1M NaOH solution's $\text{pH} = 14 - \text{pOH} = 14 - 0 = 14$.

So for more than 1M HCl solution such as 2M HCl solution $[\text{H}_3\text{O}^+] = 2 \text{ mol } \text{H}_3\text{O}^+ \text{ ion}$, $\text{pH} = -\log 2 = -0.30$. similarly, for 2M NaOH solution. $\text{pH} = (14 - \text{pOH}) = [14 - (-0.3)] =$

14.3. The concept of pH scale was to express the concentration of more dilute solutions such as 0.01M in simple term. So pH term is used to mean very dilute acid or alkali solutions.

4.13. Buffer Solutions

In the previous article-4.12 we have known that when a few drops of acid or base solutions are added to neutral water, then pH changes in noteable range. But there are many chemical, industrial and biological processes where the restoration of pH of the related solutions are very essential. For example, how does blood maintain a constant pH of 7.4 in contact with countless cellular acid-base reactions? How can a chemist sustain a nearly constant $[H_3O^+]$ in reactions that consume or produce H_3O^+ or OH^- ions? The pH of human blood is carefully controlled at a value very close to 7.4 by conjugate acid-base pairs, primarily H_2CO_3 and its conjugate base HCO_3^- . The oxygen carrying ability of blood depends on control of the pH to within 0.1 pH unit. When pH of blood changes beyond 0.5 pH unit from its normal range (pH 7.0 ~ pH 7.8 by any cause, then life will be in danger. For this reason, chemists use solutions which contain weak acid and its conjugate base, are called buffer solutions because they resist drastic or more changes in pH.

Definition of Buffer Solution : The solution, whose pH remains unaltered, even after addition of smal amount of base or acid, is called buffer solution.

The strength of a solution to prevent the change of pH is called **buffer capacity** of the solution. The mechanism of prevention in change of pH value even after addition of acid or base is called **buffer action**.

Buffer solutions are of two classes : such as – (i) **acidic buffer solutions** and (2) **basic buffer solutions**. Acidic buffer solution contain a weak acid and its conjugate base solutions. But basic buffer solution contains a weak base its conjugate acid solutions. Examples,

Acidic buffer solution :

[Weak acid + conjugate base]

(i) $CH_3COOH + CH_3COO^-$ ion.

(ii) $H_2PO_4^- + HPO_4^{2-}$ ion

Preparation of buffer solutions :

(i) **Acidic Buffer Solution :** By dissolving a weak acid and salt of that acid with a strong base, an acidic buffer solution is prepared. For example, An acidic buffer solution can be prepared by dissolving acetic acid and sodium acetate salt in water.

Basic buffer solution :

[Weak base + conjugate acid]

(i) $Na_2CO_3 + HCO_3^-$ ion

(ii) $NH_4OH + NH_4^+$ ion

(ii) **Basic Buffer Solution** : By dissolving a weak base and salt of that base with a strong acid, a basic buffer solution is prepared. For example, A basic buffer solution can be prepared by dissolving NH_4OH and NH_4Cl salt in water.

Buffer solutions of different pH can be prepared by the application of **Henderson Hasselbach equation**.

(A) Henderson-Hasselbach Equation for Acidic Buffer Solution :

Let us take the acetic acid sodium acetate buffer as an example of acid buffer solution. In this solution weak acetic acid dissociates as follows partly :



Using the Law of Mass Action we can write the equilibrium constant :

$$K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}_3\text{O}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

MCQ. 4.14 : What is pH of 0.05 M H_2SO_4 ?

(a) 0.5 (b) 1.0 (c) 1.5 (d) 2.0

Acetic acid is a weak acid, hence it dissociates to a small amount. The degree of its dissociation decreases even more in presence of strong electrolyte sodium acetate. So the concentration of undissociated acetic acid remains almost equal to the initial concentration of acetic acid. But the concentration of acetate ion is equal to the concentration of the sodium acetate salt (strong electrolyte). Hence the above equation may be written as follows :

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]}, \text{ Taking log on both sides we get :}$$

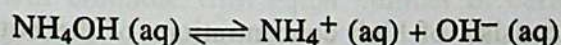
$$\text{or, } \log [\text{H}_3\text{O}^+] \text{ or, } -\text{pH} = -\text{p}K_a - \log \frac{[\text{salt}]}{[\text{acid}]} \quad [\therefore \log \frac{A}{B} = -\log \frac{B}{A}]$$

$$\text{or, } \text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} ; \text{ It is Henderson-Hasselbach Equation of acidic buffer.}$$

Using this equation pH of acid buffer solution can be calculated.

(B) Henderson-Hasselbach Equation for Basic Buffer Solution :

Let us take ammonium hydroxide (NH_4OH) and ammonium chloride (NH_4Cl) buffer as an example of basic buffer solution. In this solution weak base NH_4OH ionises partly :



$$\text{Here equilibrium constant, } K_b = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]} ; [\text{OH}^-] = K_b \times \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

$$\text{Now taking log on both sides, } \log [\text{OH}^-] = \log K_b + \log \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$$

Now multiplying by -1 , we get, $-\log [\text{OH}^-] = -\log K_b - \log \frac{[\text{NH}_4\text{OH}]}{[\text{NH}_4^+]}$

$$\text{or, } p^{\text{OH}} = pK_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_4\text{OH}]} ; \text{ or, } (14 - \text{pH}) = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\therefore \text{pH} = 14 - pK_b - \log \frac{[\text{salt}]}{[\text{base}]} ; \text{ It is Henderson-Hasselbach Equation of basic buffer.}$$

Using this equation pH of basic buffer solution can be calculated.

Uses of Henderson Equation :

- (1) Henderson equation tells us how to prepare a buffer solution with a given pH.
- (2) Henderson equation may be used to calculate pH of a prepared buffer solution.
- (3) This equation may be used to calculate the proportion of acid and salt needed to prepare a buffer solution of definite pH.
- (4) Generally the weak acid whose pK_a value is very close to pH of the required buffer solution is selected. Then the ratio of $[\text{salt}]/[\text{acid}]$ is calculated from the Henderson equation. For example,
 - (i) To prepare a buffer having a pH near to 7, we might use the $\text{H}_2\text{PO}_4^- - \text{HPO}_4^{2-}$ conjugate acid-base pair, because the pK_a for H_2PO_4^- is $-\log (6.2 \times 10^{-8}) = 7.21$
 - (ii) Similarly a mixture of NH_4Cl and NH_3 would be a good choice for a buffer having a pH near to 9, because the pK_a for NH_4^+ is $-\log (5.6 \times 10^{-10}) = 9.25$. As a rule of thumb, the pK_a of the weak acid component of a buffer should be within ± 1 pH of the desired pH.
- (5) Because buffer solutions are widely used in the laboratory and in medicine, pre-packaged buffers having a variety of precisely known pH values are commercially available. The manufacturer prepares these buffers by choosing a buffer system having an appropriate pK_a value and then adjusting the amounts of the ingredients so that the $[\text{base}]/[\text{acid}]$ ratio has the proper value.

4.13.1 Mechanism of Buffer Solution or Buffer Action

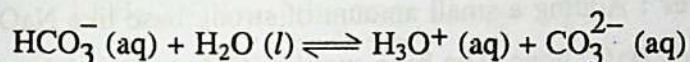
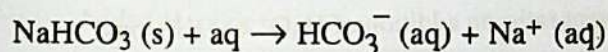
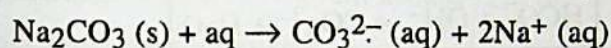
Buffer Action : The mechanism of prevention of change of pH of a solution even after addition of small amount of acid or base is called its buffer action.

★ The essential feature of a buffer is that it consists of high concentrations of the both weak acid (HA) and its conjugate base (A^-). When small amounts of H_3O^+ or OH^- ions are added to the buffer, they cause a small amount of one buffer-component to convert into the other, which changes the relative concentrations of the two components.

★ As long as the amount of H_3O^+ or OH^- ions added is much smaller than the amounts of HA and A^- present originally, the added ions have little effect on the pH, because they are consumed by one or other buffer component : the A^- ion consumes added H_3O^+ , and the HA consumes added OH^- ion.

Let us consider the alkaline buffer prepared from sodium bicarbonate (NaHCO_3) and sodium carbonate (Na_2CO_3) to explain the buffer mechanism. In this buffer, weak base is carbonate (CO_3^{2-}) ions and its conjugate acid is bicarbonate (HCO_3^-) ions.

Here Na_2CO_3 and NaHCO_3 being strong electrolytes (ionic salts) dissociate completely in aqueous solutions. But bicarbonate (HCO_3^-) ion, being a weak electrolyte, dissociates partly with reversible process.



MCQ-4.15 : When a solution has $[\text{OH}^-] = 3.4 \times 10^{-1} \text{ M}$, then its pH will be :
 (a) 9.53 (b) 7.53
 (c) 8.93 (d) 13.53

The equilibrium constant (K_a) of acidic bicarbonate (HCO_3^-) ion is as follows :

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}, [\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} \dots\dots (1)$$

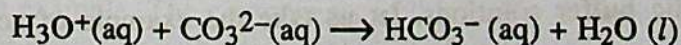
Note that because K_a is constant, the $[\text{H}_3\text{O}^+]$ of the solution depends directly on the buffer-component concentration ratio, $[\text{HCO}_3^-]/[\text{CO}_3^{2-}] = [\text{HA}]/[\text{A}^-]$.

(i) If the ratio $[\text{HA}]/[\text{A}^-]$ goes up, $[\text{H}_3\text{O}^+]$ goes up.

(ii) If the ratio $[\text{HA}]/[\text{A}^-]$ goes down, $[\text{H}_3\text{O}^+]$ goes down.

Now we add a small amount of strong acid (HCl) or strong base (NaOH) and observe the change of pH of the buffer, if any, with explanation of the changes.

(a) Addition of H_3O^+ ions to a Buffer : When a small amount of strong acid like HCl is added to this NaHCO_3 and Na_2CO_3 buffer, then H_3O^+ ions produced from given HCl acid will combine with equal number of carbonate (CO_3^{2-}) ions from the buffer to form more bicarbonate (HCO_3^-) ions.



As a result, $[\text{CO}_3^{2-}]$ ions goes down by that amount of added H_3O^+ ions and $[\text{HCO}_3^-]$ ions goes up by that amount, which increases the buffer component ratio $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$, as we can see in Figure- 4.25, also increases but very slightly

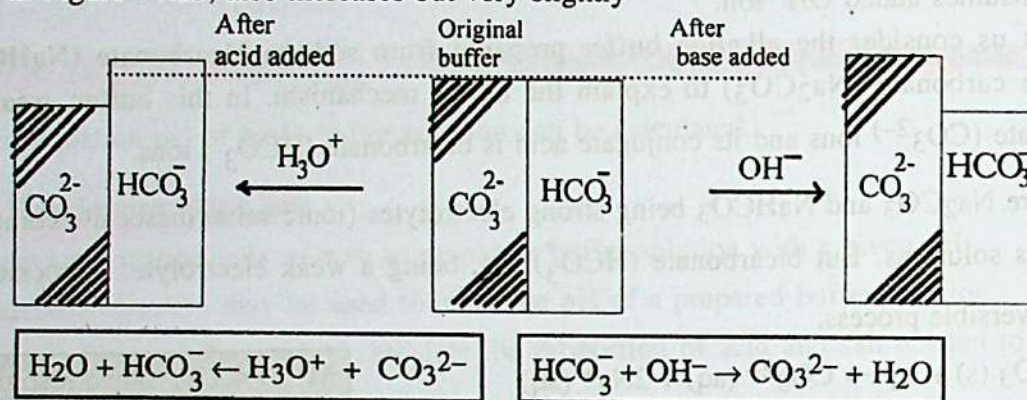
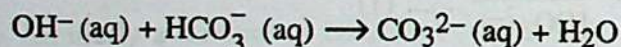
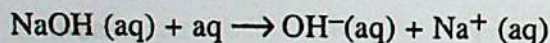


Fig – 4.25 : Change of buffer-component ratio on addition of H_3O^+ or OH^- ions.

(b) Addition of OH^- ions to a Buffer : Adding a small amount of strong base like NaOH produces the opposite result of addition of H_3O^+ ions. The base supplies OH^- ions which will combine with equal number of bicarbonate (HCO_3^-) ions to form CO_3^{2-} ions and water.



As a result, $[\text{CO}_3^{2-}]$ ions goes up by that amount of added OH^- ions and $[\text{HCO}_3^-]$ ions goes down, which decreases the buffer-component ratio $[\text{HCO}_3^-]/[\text{CO}_3^{2-}]$ in equation (1), also see fig-4.25. The change is very slight in both the cases.

Thus, the buffer components consume virtually all the added H_3O^+ ions or OH^- ions. Because the concentration ratio [weak acid]/[conjugate base] remains close to its original value, so the change of pH of the buffer is very negligible and practically remains constant.

[For example, according to bicarbonate buffer system of human blood, at normal condition pH value of blood is 7.4; but blood pH value may be more or less by $\text{pH} \pm 5$ for different causes.]

Alternate Method : Mechanism of Buffer Action :

In old or classical method, buffer action of a buffer solution is explained below :

(1) Mechanism of acidic buffer solution

To explain the mechanism of acidic buffer solutions, let us take the example of acetic acid-acetate buffer. The two components of this buffer dissociate in solution as follows :

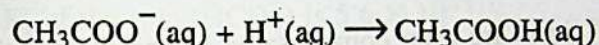
$\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$ [It is a weak acid it dissociates slightly]

$\text{CH}_3\text{COONa}(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{Na}^+(\text{aq})$ [It is a ionic salt, it dissociates completely]

So, in this buffer solution, three ions like CH_3COO^- ion, H^+ ion and Na^+ ion are present.

(A) Removal of added small amount of H^+ ions :

When a small amount of strong acid like HCl acid i.e. H^+ ions are added to this acidic buffer, then added H^+ ions react with acetate ions to produce undissociated acetic acid molecules.



Since acetic acid is a weak acid, it dissociates to a very small amount, specially in presence of strong electrolyte sodium acetate. So the concentration of H^+ ions does not increase i.e its **pH remains unchanged.**

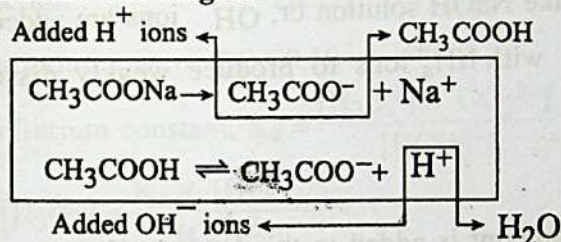


Fig- 4.26(A) : Mechanism of a acidic buffer solution

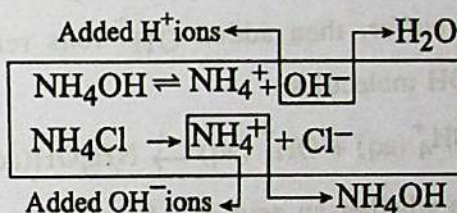
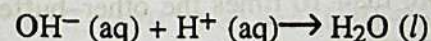


Fig- 4.26 (B) : Mechanism of basic buffer solution.

(B) Removal of added small amount of OH^- ions :

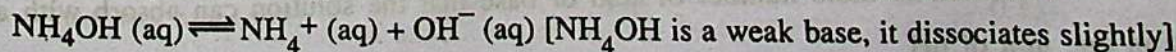
When a small amount of strong alkali like NaOH solution i.e. OH^- ions are added to this acidic buffer, then added OH^- ions react with the H^+ ions present in solution and produce H_2O molecules. Then the equilibrium of dissociation of the acetic acid is shifted towards right side to produce more H^+ ions. and thus to compensate for the reacting H^+ ions.

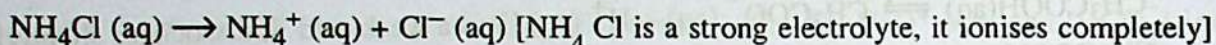


So we see that whether an acid or a base is added in small amount to an acidic buffer solution, due to interaction with the component ions, the concentration of H^+ ions or its pH does not change appreciably.

(2) Mechanism of Basic buffer solution :

To explain the mechanism of basic buffer solutions, let us take NH_4OH and NH_4Cl buffer as an example. The components of this buffer dissociate in solution as follows :

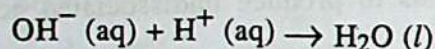




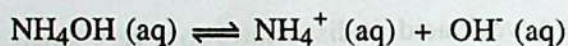
So in this buffer solution, three ions like NH_4^+ ion, OH^- ion and Cl^- ion are present.

(A) Removal of added small amount of H^+ ions :

When a small amount of strong acid like HCl acid or H^+ ions are added to this basic buffer, then added H^+ ions react with OH^- ions to produce water molecules.

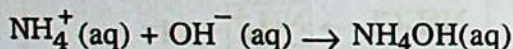


The OH^- ions neutralised by added H^+ ions are then compensated by the dissociation of weak NH_4OH .



(B) Removal of added small amount of OH^- ions :

When a small amount of strong alkali like NaOH solution or, OH^- ions are added to this basic buffer, then added OH^- ions react with NH_4^+ ions to produce weakly dissociating NH_4OH molecules.



So whether an acid or a base in small amount is added to this basic buffer solution then the concentration of H^+ ions or its pH value does not change appreciably.

Buffer Range :

The Buffer range is the pH range over which the buffer acts effectively and it is related to the relative component concentrations. The more the buffer component concentration ratio is from 1, the less effective the buffering action (that is, the lower the buffer capacity.) In practice, if the $[\text{A}^-]/[\text{HA}]$ or $[\text{salt}]/[\text{acid}]$ ratio is greater than 10 or less than 0.1 – that is, if one component concentration is more than 10 times the other – buffering action is poor. Recalling that $\log 10 = 1$ and $\log 0.1 = -1$, We find that buffers have a usable range within $\pm 1 \text{ pH}$ unit of the pK_a of the acid component. $\text{pH} = \text{pK}_a + \log [\text{salt}]/[\text{acid}] = \text{pK}_a + \log 10 = \text{pK}_a + 1$. Again $\text{pH} = \text{pK}_a + \log 0.1 = \text{pK}_a - 1$. So the wanted pH value of a buffer, there should be $\pm 1 \text{ pH}$ of difference from pK_a value of the acid used. Otherwise, the buffer action of that buffer will not be good effectively. Then it will be a 'poor buffer'.

Buffer Capacity :

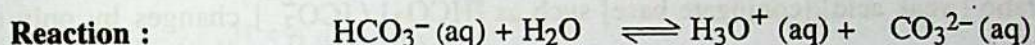
The Buffer range is the pH range over which the buffer acts effectively. Buffering ability of a buffer solution is expressed by the term **buffer capacity**. It is a measure of the amount of mole number of acid or base that the solution can absorb with a change in one unit of pH.

$$\text{Buffer Capacity} = \frac{\text{no. of mole of acid or base mixed in 1L buffer}}{\text{Total change in pH value}}$$

Buffer capacity is also a measure of how little the pH changes with the addition of a given amount of acid or base. Buffer capacity depends on how many moles of weak acid and conjugate base are present in the buffer solution. For equal volumes of solution, the more concentrated the solution, the greater is the buffer capacity.]

Worked Example-4.54 : What will be the change in pH of the alkaline buffer containing 0.10M Na_2CO_3 and 0.10M NaHCO_3 solutions, if 0.01 mol NaOH is added to the buffer? Here K_a of the acid (HCO_3^-) is 5.6×10^{-11} ?

Strategy : Calculate pH of the buffer before adding NaOH Solution : Bicarbonate ionizes as follows :



Equilibrium concn. (M) : $0.10 - x$ $(0.10 + x)$

$$\text{Equilibrium constant, } K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$\therefore [\text{H}_3\text{O}^+] = \frac{K_a \times [\text{HCO}_3^-]}{[\text{CO}_3^{2-}]}$$

As Na_2CO_3 is a strong electrolyte, the concentration of CO_3^{2-} will be equal to Na_2CO_3 such as 0.10 M. Again HCO_3^- is a weak electrolyte and it ionizes slightly and then it will increase concentration of CO_3^{2-} ion slightly.

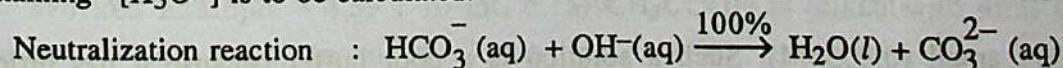
$$[\text{H}_3\text{O}^+] = \frac{K_a \times (0.10 - x)}{(0.10 + x)} = K_a \times \frac{0.10}{0.10} = K_a$$

$\therefore [\text{H}_3\text{O}^+]$ will be equal to 5.6×10^{-11} ; because $K_a = 5.6 \times 10^{-11}$. Here value of x is very small, so $(0.10 - x)$ and $(0.10 + x)$ each is taken as equal to initial concentration.

$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (5.6 \times 10^{-11}) = \boxed{10.25}$$

\therefore The buffer has pH value 10.25

Solution : On adding 0.01 mol (x mol) NaOH, neutralization reaction occurs and then remaining $[\text{H}_3\text{O}^+]$ is to be calculated.



Before reaction (mol) : 0.10 + 0.01 0.10

Change occurs (mol) : -0.01 - 0.01 + 0.01

After reaction (mol) : 0.09 0.0 0.11

If we assume that the solution's volume remains constant at 1.00L, then concentrations of the buffer components after neutralization are :

$$[\text{HCO}_3^-] = \frac{0.09 \text{ mol}}{1.00 \text{ L}} = 0.09 \text{ M}; [\text{CO}_3^{2-}] = \frac{0.11 \text{ mol}}{1.00 \text{ L}} = 0.11 \text{ M}$$

Substituting these concentrations into the expression for $[\text{H}_3\text{O}^+]$, we can then calculate the pH of the final buffer solution :

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{5.6 \times 10^{-11} \times (0.09)}{(0.11)} = 4.58 \times 10^{-11} \text{ M}$$

$$\therefore \text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (4.58 \times 10^{-11}) = \boxed{10.34}$$

Adding 0.01 mol of NaOH changes $[\text{H}_3\text{O}^+]$ by only a small amount, because the concentration ratio [weak acid]/[conjugate base] such as $[\text{HCO}_3^-] / [\text{CO}_3^{2-}]$ changes by only a small amount, from 1.0 to 9/11 (figure-4.25), which plays the main role for change in pH from 10.25 to 10.34.

Worked Example– 4.55 : Using Henderson Equation :

What ratio of $[\text{NH}_3]/[\text{NH}_4^+]$ is required for a buffer solution that has pH = 7.0? Why is a mixture of NH_3 and NH_4Cl a poor choice for a buffer having pH = 7.0?

Strategy : Calculate required $[\text{NH}_3]/[\text{NH}_4^+]$ ratio from Henderson equation

Solution : As K_b value of $\text{NH}_3 = 1.8 \times 10^{-5}$; then K_a value of NH_4^+ ion will be related as :

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$\therefore \text{p}K_a = -\log (5.6 \times 10^{-10}) = 9.25$$

$$\begin{aligned} \text{Again, } \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]} &= (\text{pH} - \text{p}K_a) \\ &= (7.0 - 9.25) = -2.25 \end{aligned}$$

$$\therefore [\text{NH}_3]/[\text{NH}_4^+] = \text{antilog} (-2.25) = 5.6 \times 10^{-3}$$

Poor buffer : For a typical value of $[\text{NH}_4^+]$, say 1.0 M, then NH_3 concentration would

have to be very small (0.0056M). Such a solution is a poor buffer because it has little capacity to absorb added acid. Also, because the $[\text{NH}_3]/[\text{NH}_4^+]$ ratio is far from 1.0, addition of a small amount of H_3O^+ or OH^- ions will result in a large change in the pH value.

MCQ-4.16 : $\text{A} (\text{H}_2\text{O}) \xrightarrow{\text{H}^+} \text{B} (\text{H}_3\text{O}^+)$; Here
 (i) structures of A, B, same
 (ii) Both central atoms have same orbital hybridisation (iii) At 25°C pure A has pH 7.
 Which will be correct?
 (a) i, ii (b) ii, iii (c) i, iii (d) i, ii and iii

Worked Example-4.56 : (a) Calculate pH of buffer solution containing equal volumes of 0.1M CH_3COOH and 0.1M CH_3COONa solutions. (b) What is molar concentration of H^+ ion of this solution? [$K_a = 1.0 \times 10^{-5}$]

Solution : (a) From Henderson equation, $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

From question, $K_a = 1.0 \times 10^{-5}$; $\therefore \text{p}K_a = -\log K_a = -\log 1.0 \times 10^{-5} = 5$

Here, $[\text{salt}] = 0.1$, and $[\text{acid}] = 0.1$, putting these values we get,

$$\text{pH} = 5 + \log \frac{0.1}{0.1} = 5 + \log 1 = (5 + 0) = 5$$

(b) Again, $[\text{H}^+] = 10^{-\text{pH}} = 10^{-5}$; \therefore Molar concentration of H^+ ion = 10^{-5} M.

Worked Example-4.57 : At 25°C , for acetic acid $\text{p}K_a = 4.76$. How can you prepare a buffer solution of pH 5.0 with this acid?

Solution : From Henderson equation, $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$\text{or, } \log \frac{[\text{salt}]}{[\text{acid}]} = \text{pH} - \text{p}K_a = (5.0 - 4.76) = 0.24$$

$$\text{or, } \frac{[\text{salt}]}{[\text{acid}]} = \text{antilog } 0.24 = 1.738 = \frac{1.738}{1.0}$$

So sodium acetate and acetic acid in mole proportion of 1.738 : 1.0 are to be mixed per litre solution.

Worked Example-4.58 : What is the pH of the buffer solution containing 0.1molL^{-1} CH_3COOH acid and 0.15molL^{-1} CH_3COONa solutions. Here $K_a = 1.77 \times 10^{-5}$.

Solution : From Henderson equation,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]},$$

$$\therefore \text{pH} = -\log K_a + \log \frac{[\text{CH}_3\text{COONa}]}{[\text{CH}_3\text{COOH}]}$$

$$\text{pH} = -\log (1.77 \times 10^{-5}) + \log \frac{0.15}{0.10}$$

$$\text{pH} = (4.7521 + 0.1761) = 4.9282; \therefore \text{pH} = 4.93$$

$$\text{Here, } K_a = 1.77 \times 10^{-5}$$

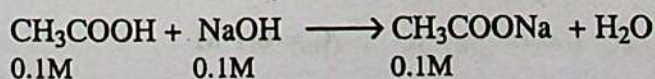
$$[\text{CH}_3\text{COOH}] = 0.10 \text{ M}$$

$$[\text{CH}_3\text{COONa}] = 0.15 \text{ M}$$

$$\text{pH} = ?$$

Worked Example - 4.59 : 10 mL 0.1M CH_3COOH is mixed with 4mL 0.1M NaOH solution. What is pH of the mixed solution? [$\text{p}K_a = 4.76$]

Solution : 4 mL 0.1M NaOH reacts with 4mL 0.1M CH_3COOH to produce 4 mL 0.1M CH_3COONa solution.



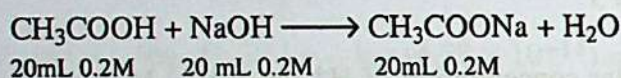
∴ In the mixture residual acetic acid = (10 – 4) mL = 6 mL. Here sodium acetate and acetic acid are in 4 : 6 mol concentration.

From Henderson equation :

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} = \left(4.76 + \log \frac{4}{6} \right) = 4.584$$

Worked Example – 4.60 : 20 mL 0.2M NaOH solution is mixed with 50 mL 0.2M CH₃COOH solution. What is pH of this mixed solution? Here $K_a = 1.8 \times 10^{-5}$.

Solution : NaOH solution reacts with CH₃COOH as follows :



∴ 20 mL 0.2M NaOH reacts with 20 mL 0.2M acid to form 20 mL 0.2M CH₃COONa salt which is diluted in total volume 70 mL. So at last (50 – 20) mL = 30 mL 0.2M equivalent CH₃COOH is present in total volume 70 mL mixture.

$$\therefore \text{ In 70 mL mixed solution, present mol. number of CH}_3\text{COONa} = \frac{0.2 \times 20}{1000} = 0.004$$

$$\text{In 70 mL mixed solution, present mol. number of CH}_3\text{COOH} = \frac{0.2 \times 30}{1000} = 0.006$$

$$\therefore \text{ For buffer solution, } \text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\therefore \text{ pH} = -\log (1.8 \times 10^{-5}) + \log \frac{0.004}{0.006}; \text{ or, } \text{pH} = (-\log 1.8 - \log 10^{-5} + \log 4 - \log 6)$$

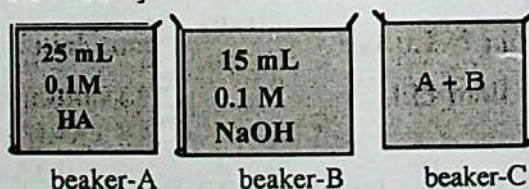
$$\text{or, } \text{pH} = (-0.255 - 5 + 0.602 - 0.778) = 4.56787; \therefore \text{pH} = 4.57$$

Worked Example–4.61 :

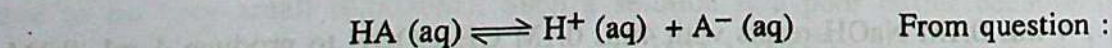
[R. B. 2017; Di. B. 2017; D. B. 2016]

(a) Calculate pH of solution in beaker-A; [$K_a = 1.8 \times 10^{-4}$]

(b) If a small amount of HCl acid is added in beaker-C of the given stem, whether pH value of that solution will change or not; explain.



Solution : (a) As per given stem, the solution in beaker-A is a weak acid solution. Because K_a of HA = 1.8×10^{-4} as per question. Weak acid ionises partly in solution. From Ostwald dilution law dissociation amount (α) is to calculate for calculation of pH of weak acid HA.



$$\text{At equilibrium :} \quad (1 - \alpha) C \quad \alpha C \quad \alpha C \quad K_a = 1.8 \times 10^{-4}$$

$$\text{Here, } K_a = \alpha^2 C. \quad C = 0.1 \text{ M}$$

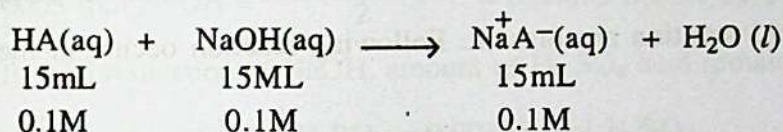
$$\therefore \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-4}}{0.1}} = 0.0424$$

From above equation, $[H^+] = \alpha C$

$$\text{or, } [H^+] = 0.0424 \times 0.1 \text{ M} = 0.00424 \text{ M}$$

$$\therefore \text{pH} = -\log [H^+] = -\log (0.00424) = 2.373$$

Solution : (b) : As per stem, the mixed solution (A + B) in beaker 'C' is an acidic buffer solution.



From above equation, 15 mL 0.1M NaOH solution reacts with 15mL 0.1M HA acid solution to produce 15mL 0.1M NaA salt solution. Beside this in mixed solution (25 + 15) mL = 40 mL, actually (25-15)mL = 10mL 0.1M HA equivalent acid is present together with equivalent 15 mL 0.1M NaA salt solution.

$$\therefore \text{In 40 mL mixed solution, mole number of HA} = \frac{10 \times 0.1}{1000} = 0.0010$$

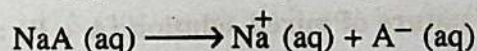
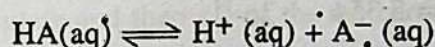
$$\text{and in 40 mL mixed solution, mole number of NaA} = \frac{15 \times 0.1}{1000} = 0.0015$$

$$\therefore \text{For buffer solution, } \text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

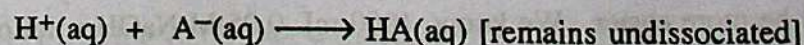
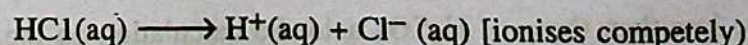
$$\therefore \text{pH} = -\log 1.8 \times 10^{-4} + \log \frac{0.0015}{0.0010}; \text{ or, } \text{pH} = -\log 1.8 - \log 10^{-4} + \log \frac{15}{10}$$

$$\text{pH} = (-0.255 + 4.0 + 0.176), \therefore \text{pH} = 3.921$$

From property of buffer solution, if small amount of HCl acid is added in this buffer solution, then pH value of it will not markedly change. The mechanism for keeping pH fixed is explained below. This buffer solution contains following ions in solution :



When a small amount of dil. HCl acid is added in this buffer solution, it ionises completely to produce H^+ ion and Cl^- ion. Later H^+ ion combines with negative ion A^- of the buffer solution to form weak electrolyte HA acid. In presence of strong HCl acid, weak HA acid remains undissociated. For this no change in molar concentration of H^+ ion in that buffer solution occurs; hence pH of the buffer solution remains unchanged.



Worked Example-4.62 :

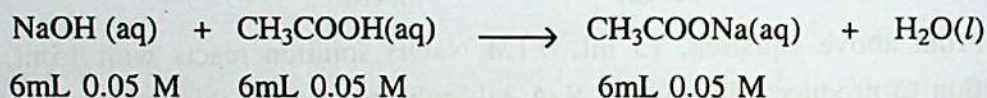
[B. B. 2017; Di. B. 2017; J. B. 2016]

- (a) Calculate pH of mixed solution (B + C) of the stem.
 (b) What will be the nature of mixed solution (A + B) of given stem; explain it.

H_2SO_4 20 mL 0.1 M	NaOH 6 mL 0.05 M	CH_3COOH 150 mL 0.05 M	$\leftarrow K_a = 1.85 \times 10^{-5}$
A	B	C	

Solution : (a) Calculation of pH of mixed solution (B + C) :

As per given stem, in 'B' container 6 mL 0.05 M NaOH solution and in 'C' container 150 mL 0.05 M CH_3COOH acid solution are present. Following reaction occurs in their mixed solutions :



From equation, 6mL 0.05M NaOH solution reacts with 6mL 0.05M CH_3COOH acid to form 6mL 0.05M CH_3COONa salt solution. Besides this, in mixed solution (150 + 6) mL or 156 mL actually (150 – 6) mL or 144 mL 0.05 M equivalent CH_3COOH acid is present together with 6mL 0.05M equivalent CH_3COONa salt solution.

$$\therefore \text{In 156 mL mixed solution, mole number of } \text{CH}_3\text{COOH} = \frac{144 \times 0.05}{1000} = 0.0072$$

$$\text{and in 156 mL mixed solution, mole number of } \text{CH}_3\text{COONa} = \frac{6 \times 0.05}{1000} = 0.0003$$

$$\therefore \text{For buffer solution, } \text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]} = -\log K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\therefore \text{pH} = -\log (1.85 \times 10^{-5}) + \log \frac{0.0003}{0.0072}$$

Given :

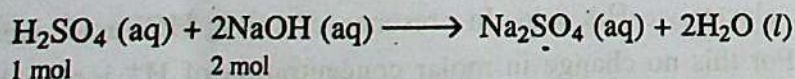
$$\text{or, pH} = -\log 1.85 - \log 10^{-5} + \log (0.04171)$$

$$K_a = 1.85 \times 10^{-5}$$

$$\text{or, pH} = (-0.267 + 5.0 - 1.379) = 3.354$$

Solution : (b) Determination of nature of mixed solution (A + B) :

As per given stem, solution 'A' is 20 mL 0.1M H_2SO_4 and solution 'B' is 6mL 0.05 M NaOH solution. Both the strong acid and alkali react as follows :



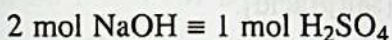
From question, in comparison to H_2SO_4 acid, both molar concentration and volume of NaOH solution are less than those of H_2SO_4 acid. So calculation on the basis of less amount of NaOH, will be more easier. We know, 1000 mL 0.05 M NaOH solution = 0.05 mol NaOH.

$$\therefore \text{From question, } 6\text{mL } 0.05 \text{ M NaOH} \equiv \frac{0.05 \times 6}{1000} = \boxed{0.0003 \text{ mol NaOH}}$$

$$\text{Again } 1000 \text{ mL } 0.1\text{M H}_2\text{SO}_4 \text{ acid solution} \equiv 0.1 \text{ mol H}_2\text{SO}_4$$

$$\therefore \text{From question, } 20\text{mL } 0.1\text{M H}_2\text{SO}_4 \text{ soln} \equiv \frac{0.1 \times 20}{1000} = \boxed{0.002 \text{ mol H}_2\text{SO}_4}$$

As per above neutralisation reaction :



$$\therefore 0.0003 \text{ mol NaOH} \equiv \frac{1 \times 0.0003 \text{ mol}}{2} = 0.00015 \text{ mol H}_2\text{SO}_4$$

\therefore After neutralisation of NaOH, amount of H_2SO_4 acid remained

$$= (0.002 - 0.00015) \text{ mol H}_2\text{SO}_4 = 0.00185 \text{ mol H}_2\text{SO}_4$$

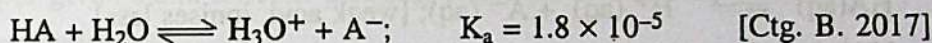
\therefore In mixed solution $(20 + 6) \text{ mL} = 26 \text{ mL}$ $0.00185 \text{ mol H}_2\text{SO}_4$ remained.

\therefore In mixed solution, molarity of H_2SO_4 , $M = \frac{\text{mole number of H}_2\text{SO}_4}{\text{volume of solution in litre}}$

$$\therefore \text{Molarity, } M = \frac{0.00185 \text{ mol}}{0.026\text{L}} = 0.071 \text{ molL}^{-1} \text{ (or M)}$$

\therefore Mixed solution (A + B) of given stem is acidic and has 0.071 M concentration.

Worked Example – 4.63 : Following the equation based stem; answer related questions:

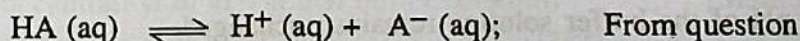


(a) As per stem, calculate pH of 0.1M HA acid solution.

(b) Prepare a buffer solution with that acid (HA) and explain the mechanism of buffer action.

Solution : (a) Calculation of pH of 0.1M HA solution :

Here HA is a weak acid; because K_a of HA acid is 1.8×10^{-5} given in question. Weak acid ionises a little in aqueous solution. So by using Ostwald's dilution law, HA dissociation amount (α) is to calculate and then pH of the acid solution will be calculated :



$$\text{At equilibrium : } (1 - \alpha)C \quad \alpha C \quad \alpha C \quad C = 0.1\text{M}$$

$$K_a = 1.8 \times 10^{-5}$$

Here for acid HA, $K_a = \alpha^2 C$

$$\therefore \alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}} = 0.0134$$

Again from above equation, $[\text{H}^+] = \alpha C$; or, $[\text{H}^+] = 0.0134 \times 0.1\text{M} = 0.00134\text{M}$

$$\therefore \text{pH} = -\log [\text{H}^+] = -\log (0.00134) = 2.873.$$

Solution : (b) Preparation of a buffer solution with HA :

As per given stem HA acid is a weak acid, because K_a of HA is 1.8×10^{-5} . So a buffer solution of a particular pH with this acid (HA) and its salt (NaA) with strong alkali NaOH solution in proper mole-ratio can be prepared as per Henderson's equation.

As per Henderson's equation, pH of an acidic buffer solution remains near to pK_a value of weak acid 'HA'. Only small value comes from relation $\log [\text{salt}]/[\text{acid}]$.

From given stem, $pK_a = -\log 1.8 \times 10^{-5} = 4.7447$. So a buffer solution of pH 5 will be prepared using Henderson's equation.

We know, $pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$;

or, $\log \frac{[\text{salt}]}{[\text{acid}]} = pH - pK_a = (5.0 - 4.7447) = 0.2553$

or, $\log \frac{[\text{NaA}]}{[\text{HA}]} = 0.2553$; or, $\frac{[\text{NaA}]}{[\text{HA}]} = \text{anti log } (0.2553)$

or, $\frac{[\text{NaA}]}{[\text{HA}]} = \frac{1.8}{1.0}$. So pH 5 buffer solution has prepared by mixing 1.0 molL^{-1} HA acid solution with 1.8 molL^{-1} NaA salt solution.

By using pH meter it is confirmed that the prepared buffer solution has pH 5.

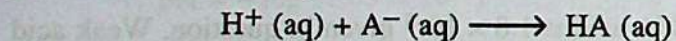
Explanation of Buffer Action :

In this prepared buffer solution, related weak acid and its salt ionise as follows :

$\text{HA(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{A}^-(\text{aq})$; [weak acid, ionises less]

$\text{NaA(aq)} \longrightarrow \text{Na}^+(\text{aq}) + \text{A}^-(\text{aq})$; [ionic salt, ionises more;]

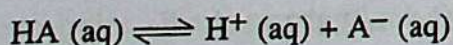
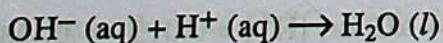
(i) Addition of small amount of acid or H^+ ion : In acid buffer solution if a small amount of acid like HCl or H^+ ion is added then H^+ ion reacts with negative ion A^- (here) to produce weak electrolyte HA molecule :



The product HA is a weak acid and it ionises in a very negligible amount in presence of strong electrolyte NaA salt solution. So added H^+ ions can not change pH value of the buffer solution i.e. pH of the buffer solution remains unchanged.

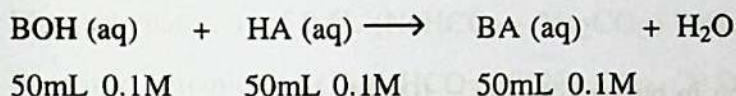
(ii) Addition of small amount of alkali or, OH^- ion :

When a small amount of alkali like NaOH or, OH^- ion is added in acidic buffer solution, then it reacts with H^+ ion of buffer solution to form H_2O molecule. Then equilibrium of HA (aq) weak acid slightly shifts towards right to supply more H^+ ions to cover the used up H^+ ions. Thus concentration of H^+ ion of the buffer remains same i. e. pH remains unchanged.



Worked Example-4.64 : In a beaker there is 50 mL 0.1M BOH alkali solution and in other beaker 0.1M 150 mL HA acid solution, K_a of HA = 1.8×10^{-5} . (a) What will be pH of the mixture of two solutions of two beakers? (b) What is pH of above BOH alkali solution?

Solution : (a) When both alkali (BOH) and acid (HA) solutions of two beakers are mixed, then 50 mL 0.1M BOH reacts with 50 mL 0.1M HA acid to produce 50mL 0.1M BA salt solution and water as follows :



So unreacted (150 – 50) mL or, 100 mL 0.1M HA acid remains in the mixture; and molar ratio of salt (NaA) and acid (HA) in the mixture will be 50 : 100 or, 1 : 2.

From Henderson's equation,

given, $K_a = 1.8 \times 10^{-5}$

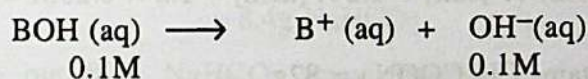
$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

For mixed soln, pH = ?

$$\text{or, } \text{pH} = -\log (1.8 \times 10^{-5}) + \log \frac{1}{2}; \text{ or, } \text{pH} = (4.745 - 0.301) = 4.444$$

\therefore pH of the mixed solutions is 4.44

Solution : (b) As per given stem, BOH is a strong alkali solution. So in aqueous solution 0.1M BOH ionises completely :



$$\therefore \text{pOH} = -\log [\text{OH}^-] = -\log 0.1 = 1.0; \text{pH of BOH} = (14 - \text{pOH}) = (14 - 1) = 13.$$

Worked Example-4.65 : (a) To prepare a 4.0 pH buffer solution how much mL of 0.1M sodium formate solution is to mix with 60mL 0.05 M formic acid solution? [$\text{p}K_a = 3.8$]

(b) What is molar concentration of H^+ in that buffer solution? [Madrasa B. 2017]

Solution : (a) From Henderson's equation, $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

Suppose, x mL 0.1M sodium formate (H-COONa) solution is needed.

$$\text{In } x \text{ mL } 0.1\text{M H-COONa soln mole number of HCOONa} = \frac{0.1 \times x \text{ mol}}{1000} = 0.0001x \text{ mol}$$

$$\text{In } 60. \text{ mL } 0.05\text{M H-COOH soln. mole number of H-COOH} = \frac{0.05 \times 60 \text{ mol}}{1000} = 0.003 \text{ mol}$$

From question, $\text{pH} = 4$ and $\text{p}K_a = 3.8$; putting these values in Henderson's equation :

$$4 = 3.8 + \log \frac{0.0001x}{0.003}; \text{ or, } \log \frac{0.0001x}{0.003} = (4 - 3.8) = 0.2 = \log 1.5849$$

$$\text{or, } 0.0001x = 0.003 \times 1.5849; \therefore x = \frac{0.003 \times 1.5849 \text{ mL}}{0.0001} = 47.55 \text{ mL (approx)}$$

\therefore Required sodium formate = 47.55 mL

Solution : (b) Calculation of molar concentration of H^+ ion in buffer solution :

From question, pH of buffer soln = 4.0

We know, $[\text{H}^+] = 10^{-\text{pH}} = 10^{-4}$

\therefore Molar concentration of H^+ ion in buffer solution = 10^{-4}M

Worked Example – 4.66 : How many gram of sodium ethanoate is to mix with 200 mL 0.25M ethanoic acid to make concentration of H_3O^+ ion $1.5 \times 10^{-5} \text{ g. ionL}^{-1}$

$$[\text{K}_a = 1.8 \times 10^{-5}]$$

Solution : From Henderson's equation : $\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$\text{or, } \log \frac{[\text{salt}]}{[\text{acid}]} = (\text{pH} - \text{pK}_a) = (-\log [\text{H}_3\text{O}^+] + \log \text{K}_a) = -\log (1.5 \times 10^{-5}) + \log (1.8 \times 10^{-5})$$

$$\text{or, } \log \frac{[\text{salt}]}{[\text{acid}]} = (4.8239 - 4.7447) = 0.0792$$

$$\text{or, } \frac{[\text{salt}]}{[\text{acid}]} = \log^{-1}(0.0792) = 1.2; \therefore [\text{salt}] = 1.2 \times [\text{acid}] = 1.2 \times 0.25\text{M} = 0.3\text{M}$$

\therefore 1M 1000 mL solution contains $\text{CH}_3\text{COONa} = 82\text{g}$

$$\therefore 0.30 \text{ M } 200 \text{ mL solution contains } \text{CH}_3\text{COONa} = \frac{82 \times 200 \times 0.30 \text{ g}}{1000} = 4.92\text{g}$$

\therefore 4.92g sodium ethanoate is to mix with the solution.

Worked Example – 4.67 : Each of two solutions, has $\text{pH} = 9$. Between them one is a buffer solution and other is NaOH solution. How can you differentiate these two solutions; explain.

Solution : From definition of a buffer solution, between the two solutions, the solution which pH value remains unchanged with addition of few drops of 0.1M HCl solution or 0.1M NaOH solution, will be a buffer solution. In other solution if a few drops of 0.1 M HCl or 0.1M NaOH solution is added then pH value of that solution will be decreased or increased respectively. Thus two solutions are differentiated.

Practical : Students' Work :**4.14 Name of the Expt. : To prepare carbonate buffer and to check its buffer action.**

Expt. No.— 13.

Date of Expt

Time : 1 Period

Principle : To prepare a carbonate buffer, as a weak acid sodium bicarbonate (NaHCO_3) and its conjugate base sodium carbonate (Na_2CO_3) solutions are used.

Plan : Preparation of 0.5L ($\text{NaHCO}_3 - \text{Na}_2\text{CO}_3$) buffer of pH = 10

Required Chemicals : (1) NaHCO_3 , (2) Na_2CO_3 . (3) Distilled Water
(4) dil. HCl, (5) dil. NaOH

Required Apparatus : (i) 500 mL measuring flask—2, (2) Funnel, (3) Wash bottle,
(4) Beaker (5) Chemical balance, (6) pH meter

Procedure : (1) Preparation of 0.20M NaHCO_3 solution in a 500 mL measuring flask :

$$1 \text{ mol NaHCO}_3 = (23+1+ 12 + 48) = 84 \text{ g NaHCO}_3$$

$$1000 \text{ mL 1M NaHCO}_3 = 84 \text{ g NaHCO}_3$$

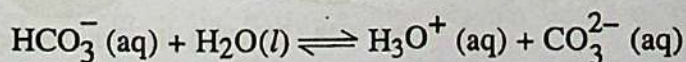
$$\therefore 500 \text{ mL 0.2M NaHCO}_3 = \frac{84 \times 500 \times 0.2}{1000 \times 1} \text{ g NaHCO}_3$$

$$= 8.4 \text{ g NaHCO}_3$$

(2) Weigh out 8.4g NaHCO_3 on a chemical balance and make solution in 500 mL measuring flask. It is 0.20 M NaHCO_3 soln.

(3) To calculate required amount of buffer component Na_2CO_3 :

From buffer-component concentrations ratio for buffer of pH 10, the amount of required $[\text{CO}_3^{2-}]$ can be calculated as follows :



$$\therefore K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

$$\therefore [\text{CO}_3^{2-}] = K_a \times \frac{[\text{HCO}_3^-]}{[\text{H}_3\text{O}^+]} \dots\dots\dots (1)$$

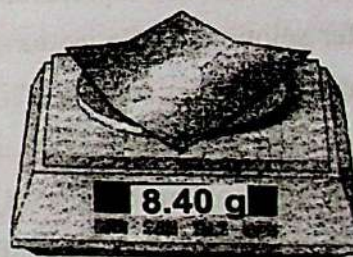


Fig- 4.27 Weighing NaHCO_3 in chemical balance.

MCQ-4.17 : What is the pH value of human blood? [D.B-2015]

(a) 6.4 (b) 7.4 (c) 8.3 (d) 9.4

Again, $\text{pH} = -\log [\text{H}_3\text{O}^+]$

$$\therefore [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-10} = 1.0 \times 10^{-10} \text{ M}; [\text{HCO}_3^-] = 0.20 \text{ M (prepared)}$$

$$[\text{K}_a \text{ of } \text{HCO}_3^-] = 5.6 \times 10^{-11} \text{ (From table)}$$

Substituting these values in equation (1), we get :

$$[\text{CO}_3^{2-}] = \frac{(5.6 \times 10^{-11}) \times (0.20)}{1.0 \times 10^{-10}} = 0.112 \text{ M}$$

\therefore Required mole of Na_2CO_3 for 500 mL buffer solution :

$$\begin{aligned} \text{Mole of } \text{Na}_2\text{CO}_3 &= \text{Volume of solution (L)} \times \text{Molarity of } \text{Na}_2\text{CO}_3 \\ &= \frac{0.5 \text{ L solution} \times 0.112}{1 \text{ L solution}} = 0.056 \text{ mol } \text{Na}_2\text{CO}_3 \end{aligned}$$

$$\begin{aligned} \text{Amount of } \text{Na}_2\text{CO}_3 \text{ in gram} &= \frac{106 \text{ g } \text{Na}_2\text{CO}_3 \times 0.056 \text{ mol } \text{Na}_2\text{CO}_3}{1 \text{ mol } \text{Na}_2\text{CO}_3} \\ &= 5.94 \text{ g } \text{Na}_2\text{CO}_3 \text{ (approx.)} \end{aligned}$$

(4) Now weigh out 5.94 g Na_2CO_3 on a chemical balance.

(5) Add 5.94 g Na_2CO_3 through a funnel into the second 500 mL measuring flask. Now add 500 mL 0.20M NaHCO_3 solution through funnel to dissolve Na_2CO_3 into this second measuring flask. Thus 500 mL $\text{NaHCO}_3 - \text{Na}_2\text{CO}_3$ buffer of pH 10 is prepared.

Checking pH of the prepared buffer solution : The electrode or probe of the pH meter is immersed in 200 mL of prepared buffer taken in a beaker. The pH meter records the pH of the buffer solution 10. So we have prepared the desired buffer correctly.

Checking buffer action : (i) Now add 2 mL 0.1M NaOH in 200 mL buffer taken in the beaker and mix well. This time pH meter shows pH of the buffer very near to 10. Similarly 200 mL buffer solution is taken in second beaker and 2 mL 0.1 M HCl is mixed. This time also pH meter shows the pH of the buffer very near to 10. Thus it proves the buffer action of the prepared desired buffer.

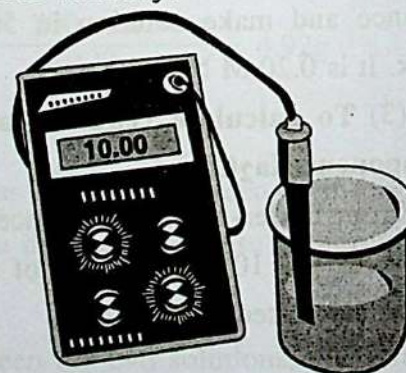


Fig 4.28 : Checking pH of the prepared buffer with pH meter.

4.15 pH of Human Blood

Human blood and other liquid parts of the body are composed of chemicals in such a way that every liquid system of a human body can act as a buffer with proper buffer capacity. As a result, the different aminoacids ($\text{H}_2\text{NCHR-COOH}$) can take part in definite

biochemical reactions properly. Among the different liquid systems of a body, blood is a good buffer, its pH is 7.4 under normal condition. In blood, bicarbonate-carbonic acid buffer system works effectively. So blood is a mild alkaline system. The pH of blood can vary from 7.8 to 7.0 from normal pH 7.4 by increasing or decreasing by ± 0.4 pH unit. If it goes outside this range by 0.5 or more than ± 0.5 unit of pH, then life becomes critical. When the change in pH value of blood remains within ± 0.1 pH unit, then blood can carry oxygen properly.

★ (i) When human blood pH is more than 7.45; then it is called **alkalosis state of blood** in medical term. More alkalosis state causes even to death of a patient.

★ (ii) When human blood pH is lower than 7.0; then it is called **acidosis state of blood** in medical term. More **acidosis state** causes nervous gradually weak and then to a state of deep unconsciousness called 'coma' state of patient.

pH control of a human blood : The following buffer systems involve in the control of pH of the blood in a human body directly or indirectly. For example.

(i) Bicarbonate buffer in blood.

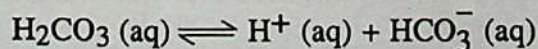
(ii) Inter-cellular phosphate buffer.

(iii) Protein buffer in human body.

MCQ-4.18 : What is the pH value of 0.05 M H_2SO_4 ? [C.B. 2015]
(a) 1.0 (b) 1.5 (c) 2.0 (d) 2.5

Here phosphate buffer system ($\text{Na}_2\text{HPO}_4 - \text{NaH}_2\text{PO}_4$; $\text{pK}_a = 6.8$) is being an inter-cellular buffer, it can not play any important role in blood plasma liquid due to its low concentration. Again protein buffer system is composed of plasma-protein and haemoglobin protein. Protein-buffer capacity depends on the value of pK_a of the different aminoacids. Haemoglobin protein contains sufficient basic amino acid histidine (35%) and hence its pK_a value is about 7. Haemoglobin protein, as a good buffer, can control about 2% of the bicarbonate-carbonic acid buffer of the blood.

(1) **Bicarbonate buffer system of blood** : In blood serum the effective buffer system is the sodium bicarbonate-carbonic acid ($\text{NaHCO}_3 - \text{H}_2\text{CO}_3$, $\text{pK}_a = 6.1$). It is the most important buffer system of the extra-cellular plasma liquid of blood. Here decomposition of carbonic acid (H_2CO_3) occurs as follows :



$$K_a = \frac{[\text{H}^+] \times [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}; [K_a = 7.9 \times 10^{-7}]$$

MCQ-4.19 : What is the pH value of 0.01 M NaOH solution? [D.B. 2015]
(a) 1 (b) 2 (c) 12 (d) 13

$$\therefore [\text{H}^+] = \frac{K_a \times [\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]}; pK_a = 6.1$$

$$\text{or, pH} = pK_a + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad \therefore \text{pH} = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Here the concentration of bicarbonate (HCO_3^-) is about 24 m mol/L in the plasma liquid of the blood, and the concentration of carbonic acid (H_2CO_3) or that of solution of CO_2 , it is equal to the product of the partial pressure (40 mmHg) of CO_2 gas and its solubility product constant. Here solubility product constant of CO_2 = 0.03.

$$\therefore \text{Concentration of } \text{H}_2\text{CO}_3 \text{ in plasma liquid} = 40 \times 0.03 \text{ m mol/L} = 1.2 \text{ m mol/L}$$

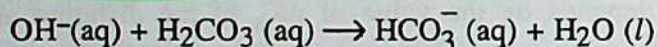
Putting the values in above equation, we get :

$$\text{pH} = 6.1 + \log \frac{24}{1.2} = (6.1 + \log 20) = 6.1 + 1.3 = 7.4$$

When excess hydrogen ions are absorbed in blood due to intaking more acidic food like lemon juice, then following reaction occurs in blood liquid to neutralize the absorbed H^+ ions:

$$\text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq}) \rightarrow \text{H}_2\text{CO}_3 (\text{aq}).$$

Later unstable carbonic acid (H_2CO_3) decomposes to H_2O and CO_2 gas which comes out through the lung during the expiration. On the otherhand, when the concentration of OH^- ions increases in the blood, following neutralization occurs :



Many medicines are injected in patient's body for treatment of different diseases. These injections are prepared in such a way that they can easily reach equilibrium with the blood and do not change its pH.

Worked Example– 4.68 : The ratio of acid and its salt present in blood serum is 0.05 and pH 7.4. Due to a special chemical mechanism the pH value of blood remains unchanged after intaking acidic or sour fruits like lemon juice or basic different substance like antacid.

(a) as per above stem, calculate K_a value of the weak acid of blood serum.

(b) explain the mechanism of keeping constant pH value in blood as per given stem.

Solution : (a) Calculation of K_a of the acid in blood :

As per given stem, the weak acid present in blood serum is carbonic acid (H_2CO_3) and its salt sodium bicarbonate ($NaHCO_3$). From question, ratio of acid and its salt or, ratio H_2CO_3 and $NaHCO_3$ concentrations = 0.05 and $pH = 7.4$. From Henderson's equation.

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} ; \text{ now putting values we get,}$$

$$\text{or, } 7.4 = -\log K_a + \log \frac{1}{0.05};$$

$$\text{or, } \log K_a = -7.4 + \log 20 = (-7.4 + 1.3) = -6.1$$

$$\text{or, antilog } K_a = \text{antilog } (-6.1) = 0.000000794$$

$$\text{or, } K_a = 7.94 \times 10^{-7}$$

Solution : (b) Mechanism of keeping constant value of pH of blood serum

Follow, article-4.15 (1) Bicarbonate buffer system of blood.

Students' Work- 4.14 : Buffer Solution Based :

Problem-4.50 : (a) Use the Henderson-Hasselbach equation to calculate the pH of a buffer solution prepared by mixing equal volumes of 0.20M $NaHCO_3$ and 0.10M Na_2CO_3 solutions. [$K_{a1} = 7.9 \times 10^{-7}$; $K_{a2} = 5.6 \times 10^{-11}$] [Ans. pH = 9.95]

(b) 0.1M CH_3COOH solution is mixed with 0.1M CH_3COONa solution. What will be the pH of that buffer solution? [$K_a = 1.8 \times 10^{-5}$] [Ans. pH = 4.74]

(c) 20 mL 0.2M $NaOH$ solution is mixed with 25 mL 0.2M acetic acid solution. What is pH of the buffer produced? [$K_a = 1.0 \times 10^{-5}$] [Ans. pH = 5.60]

Problem-4.51 : (a) How would you prepare a $NaHCO_3$ - Na_2CO_3 buffer solution that has pH = 10.40? [$K_a = 4.7 \times 10^{-11}$] [Ans. Na_2CO_3 : $NaHCO_3$ = 1.18:1.0]

(b) How many mL of 0.1 M sodium formate is to be added to 60 mL 0.05 M formic acid solution to prepare a buffer solution of pH 4.0? [pK_a of $HCOOH$ is 3.8]

Note : For term $[\text{salt}] / [\text{acid}]$ in the related equation x mL 0.1M $HCOONa$ mole number = $0.1 \times x \text{ (mol)} / 1000 = 0.0001 \text{ mol}$ and 60 mL 0.05 M $HCOOH$ mole number = $0.05 \times 60 \text{ (mol)} / 1000 = 0.003 \text{ mol}$. [Ans. 47.55 mL]

(c) In what molar ratio of ethanoic acid and sodium ethanoate are to be mixed to prepare a buffer of pH 5? [$pK_a = 4.8$] [Ans. acid : Salt = 1: 16, or, 0.63:1]

[Note : $pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}$. or, $(5.0 - 4.8) = \log \frac{[\text{salt}]}{[\text{acid}]}$]

or, $0.2 = [\text{salt}]/[\text{acid}]$, $\text{antilog}(0.2) = [\text{salt}]/[\text{acid}]$

(d) Calculate pH of the buffer solution containing 0.1 molL^{-1} ethanoic acid and 0.15 molL^{-1} sodium ethanoate solutions. [$K_a = 1.77 \times 10^{-5}$] [Ans. 4.93]

(e) Calculate pH of the buffer solution containing 0.10 molL^{-1} ethanoic acid and 0.20 molL^{-1} sodium ethanoate solution. [$K_a = 1.8 \times 10^{-5}$] [Ans. 5.05]

(f) Calculate pH of the buffer solution containing 0.2M ethanoic acid and 0.3M sodium ethanoate. [Here $K_a = 1.80 \times 10^{-5}$] [Ans : 4.92]

(g) In a basic buffer solution $0.015 \text{ molL}^{-1} \text{NH}_4\text{OH}$ and $0.025 \text{ molL}^{-1} \text{NH}_4\text{Cl}$ solutions are present. Calculate pH of it. K_b of $\text{NH}_4\text{OH} = 1.77 \times 10^{-5}$. [Ans. 9.03]

(h) Calculate the ratio of sodium acetate and acetic acid required to prepare a buffer of pH 4.6. [Here $\text{pK}_a = 4.75$] [Ans. salt : acid = 0.708 : 1.0]

(i) What will be pH of a mixture of $15 \text{ mL } 0.1\text{M}$ CH_3COOH acid and $6\text{mL } 0.15 \text{ M}$ NaOH solutions? [$\text{pK}_a = 4.76$] [Ans. 4.58]

(j) A buffer solution of pH 4.95 is prepared by mixing 1.0M CH_3COOH and CH_3COONa solution. Calculate the concentration of CH_3COONa solution.

[Here $\text{pK}_a = 4.7447$] [Ans. 1.604M]

(k) A buffer solution of pH 4.23 is prepared by mixing $1.0\text{L } 1\text{M}$ CH_3COOH with 0.305L CH_3COONa solution. What is molar concentration of CH_3COONa ? [Ans. 1.0M]
here $\text{pK}_a = 4.7447$

(l) Calculate pH of the buffer solution prepared by mixing $50 \text{ mL } 0.175\text{M}$ methanoic acid with $50 \text{ mL } 0.09\text{M}$ NaOH solution. [Here $K_a = 1.8 \times 10^{-4}$] [Ans. 3.77]

(m) To prepare a buffer solution of pH 5 in what proportion of ethanoic acid and sodium ethanoate solutions are to be mixed? [$K_a = 1.8 \times 10^{-5}$] [Ans. acid : salt = 0.555 : 1.0]

4.16.1 Importance of pH in Agriculture

The control of pH of soil is very important for the production of crops in the agricultural field. The plants and trees can take their food from soil only if the pH of the soil remains within a definite range, otherwise not. The range of optimum pH depends on the plants and trees, but it is never below 3 pH (acidic soil) or higher than 9.5 (basic soil). For example, due to acid rain, pH value of the soil falls and plants and trees die there and the area becomes

barren and somewhat desert. For the acidic soil, basic compounds like lime (CaO), dolomite (CaCO_3 , MgCO_3) powder are to be mixed with soil to increase the pH value of the soil. In the more acidic soil of Lalmonirhat of our country, lime and, or dolomite powder are mixed with the agricultural land where maize, wheat are grown successfully. Again for the more basic soil, having pH value more than 9.5, the fertility of the agricultural land is destroyed due to death of the essential micro organism of the soil. Micro organism can grow more in soil when its pH value lies between 6.6 to 7.3, It supplies nutrients like N, S and P.

So to decrease the pH value of the more basic soil different nitrate fertilizers like KNO_3 , NH_4NO_3 and Phosphate fertilizer like T S P or monocalcium phosphate monohydrate $[\text{Ca}(\text{H}_2\text{PO}_4)_2]$, $(\text{NH}_4)_2\text{HPO}_4$ and super phosphate powder are mixed with the soil.

Super phosphate is a mixture of mono calcium phosphate monohydrate $[\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}]$ and gypsum $2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O})$ powder.

4.16.2 Importance of pH in Chemical Industries

In different chemical industries, the control of pH values plays an important role for quality and stability of the products and to increase the percentage of yield. It is most essential to maintain definite pH of the reaction mixture to produce individual products such as different medicines in the pharmaceutical industries; to produce alcohols by fermentation; to produce bakery foods, sweet substances like chocolate. Besides these, the chemists have to maintain a definite pH to the related different chemical industries such as during the tanning of skins and hides, in the preparation of biological cultures, to control the soil chemistry of the agricultural lands etc.

The pH value of the sugar-cane juice is to maintain properly to manufacture cane-sugar in sugar mills. If it is not done, yield will be less due to the acidic hydrolysis of sucrose into invert-sugar, an equi-molecular mixture of glucose (or aldo-hexose) and fructose (or keto-hexose). So, to stop inversion process of sucrose to invert-sugar, sugar chemist has to control pH range in sugar mills.

In dyeing industries, acidic dye and alkaline dye are used for different kinds of fabrics such as cotton fabrics, silk-fabrics and artificial polymer fabrics. Each type of dyeing chemical can combine with fibers of the fabric in a particular p^H range to act as fast colour.

Again if p^H is not controlled, then more acidic dye will destroy the fibres of the cloth and thus duration of life of the colour cloth is shorten.

Besides these, p^H control plays very important and essential roles in production of pen-ink, in concentration of sulphide ores by oil-froth floatation process in metallurgy, in CETP (combined effluent treatment plants) for the purification of harmful wastes of different industries.

4.16.3 Importance of p^H in Toiletries

Now-a-days toiletries mean toilet soap, shampoo, face wash and tooth paste. These substances are used to wash skin of the body, hair and skull of the head and teeth, gum, inner part of the mouth regularly. Skin plays a role to control the body temperature. Besides this, skin protects our body from the attack of fungus, virus and bacteria and other germs that can create skin diseases.

To protect the body skin from the attack of these harmful micro-organism, acidic protective layer is essential on the body skin. For this cause, naturally, skin produces on its epidermis an oily polish acid-mantle called **sebum** secreted by the sebaceous gland lying below the skin. Then p^H of the skin remains at a range of 4.0 to 5.5 generally. But the soft skin of the baby of 2–1 month maintains a more p^H range such as 7–8. This acidic mantle of epidermis maintains moisture on skin, creates softness, elasticity in skin. So when this acid-mantle is destroyed by any cause, then it causes total harm to the skin protection. For example, detergents and soap, used for cloth and utensils washing, contain more strong alkali, their aqueous solutions produce p^H value 11–13. So this soap with high p^H value causes harm to the epidermis of the hands of the frequent users. Then their skin becomes dry, uneven and rough. So the p^H value must be maintained strictly within the proper range of each of the toiletries during their production. For example,

- (i) To save skin from bacteria, the p^H of the skin must be maintained at range of 4.0– 5.5. In this case, intaking of anti-oxidants like vitamin A, C, E and green tea plays an important role.
- (ii) To maintain p^H 7 – 8 in soaps which are used during bathing.
- (iii) To maintain p^H 5–7 in shampoo which are used for washing hair and skull.

(iv) To maintain pH 6–8 in face-wash producing.

(v) To maintain pH 8 in toothpaste producing.

4.16.4 Importance of pH in Taking Medicine

We know that different physiological chemical reactions are controlled by enzymes in the cells of the each organ of a human body and each fluid in each organ maintains a definite pH value. For example.

(1) Tear of eye, pH = 4.8 – 7.5,

(2) Saliva, pH = 6.35 – 6.68,

(3) Mother milk, pH = 6.6 – 6.9,

(4) Human urine, pH = 4.8 – 7.5,

(5) Human blood, pH = 7.4;

(6) After vocal cavity, leading to stomach, most antibacterial acidic stomach fluid has pH $\approx 1.4 - 2.0$. As a result, stomach enzyme, pepsin becomes active. After that, at the beginning of the small intestine at duodenum, bile secreted from liver creates an alkaline medium with pH (7.4 – 8).

MCQ-4.20 : What is used to reduce pH value of soil? [Syl. B- 2015]

- (a) CaCO_3 (b) $(\text{NH}_4)_2\text{CO}_3$
(c) $(\text{NH}_4)_2\text{HPO}_4$ (d) CaO

We become ill, when any change occurs in physiological system based on pH value for any abnormal condition. Then we take medicine, a chemical substance, as tablet or injection for curing our ill body to healthy one. Here, medicine swallowed by mouth and medicinal drop added in eyes, in each case, medicine is absorbed intercellularly and then mixes in blood stream which carries the medicine to the affected organ to heal in proper pH medium.

According to the physician advice, medicine must be taken in proper dose. Then that medicine can be absorbed by the organ of the body in definite and active pH range to act properly at the affected part of the organ or on bacteria. The absorption of medicinal chemical substance can occur in each of the entrance of the human body through the cellular membrane. **The absorption process of molecules of drug or medicine depends on three factors :- (i) molecular solubility, (ii) degree of ionization and (iii) pH value.**

Each and every medicine or drug is more or less water soluble and the degree of dissociation is also different. Molecules of each drug remain in solution as dissociated ions and undissociated molecules both.

\therefore Medicine or drug taken = undissociated molecules + dissociated ions

Here undissociated molecules of drug or medicine are absorbed more effectively. For example,

(1) Acidic medicine such as **aspirin** and **paracetamol** used as antipyretic and pain-killer are **absorbed in stomach wall properly in acidic medium**. Because in acidic gastric medium (pH 1.4 – 2.0), those medicines ionize less, but remain as undissociated molecules more.

(2) Again **chloroquin** used as antipyretic is mild alkaline and it **ionizes less in alkaline medium of small intestine** (pH 7.5 – 8.0) and remains as undissociated molecules more. So in each case the undissociated molecules of medicine are absorbed more effectively as proper dose. depending on the value of pH range.

So, medicines can act properly in ill-health in definite range of pH of the body fluid where related medicines are absorbed as undissociated molecules.

4.17 Selection of Proper pH Cosmetics after Testing

The common and notable cosmetics of everyday use are the followings :

(1) toilet soap, (2) toothpaste, (3) cold cream/snow, (4) talcum powder etc.

Among these cosmetics, toothpaste is used to wash teeth and vocal cavity of the mouth to make free from bad odour and germs, if away. Other cosmetics such as toilet soap, cold cream, snow and talcum powder are used to take care of the skin throughout the year, cold or hot seasons.

The skins of grown up men and women maintain an acid-mantle with pH range 4 – 5.5 but the skin of baby maintains a pH range near about 7. So the cosmetics, those are used by the adults, can not be applied to baby skin. If those are used, baby skin will be injured and harsh. Again acidic medium exists in the vocal cavity. We use antiseptic mouth-wash, if tooth, gum is inflamed due to germ attack and bad odour comes out from mouth. The mouth wash bottle remains labelled with a mark pH 5.5; which is very near to pH 6.35 – 6.68 of the saliva of the mouth. But after taking food, within one hour, the pH of the saliva comes down to 3 due to hydrolysis of food particles and oxidation of sugar to carboxylic acid. So toothpaste contains mild basic substances with pH 8 to neutralize partly of the more acidic medium present in the mouth cavity. Now let us test different cosmetics available in the market practically in the chemistry laboratory to determine their pH values and then select those properly useable cosmetics for ourselves.

Student's Laboratory Work :**Determination of pH of Common Cosmetics****Expt. No.- 1**

Name of Expt.: Determination of pH of different branded soaps and their use ability

Date ..

Time : 2 period

- A. Aim :** To know if the different branded toilet soaps contain pH properly.
- B. Required substances :** 1. Different branded soaps such as Lux, Tibet, Nirma.
(2) Indicators strip or solution. (3) pH meter
- C. Required Apparatus :** (1) Beaker, (2) glass rod, (3) wash bottle,
(4) pH meter or universal indicator.

Table 4.5 : Different pH colour of the Universal Indicator

pH	3.4	5.6	7	8, 9, 10	11, 12	12	13, 14
Universal Indicator:	Red	Orange	Yellow	Green	Blue-green	Blue	Violet

D. Procedure :

1. Prepare soap solution of each of the branded soap in water taken in separate beakers.
2. Now dip electrode of pH meter into each of the soap solution and then record pH value shown on the screen of the pH meter, in the following data-table.

Or, add universal indicator strip or 2-3 drops of indicator into the each soap solution and then record the colour change with corresponding pH value.

- E. Result comparison and conclusion :** Now compare the pH value of soap approved and that of the experimental brand soap. Finally give comment on each branded soap with its pH value, if it is suitable, to use for adult or baby.

F. Experimental Data :

Sample of branded soap	pH of brand soap	Approved pH value	Sample's pH more/less	Comment on Expt. Result
1. Brand-1	7	7-8	1. pH is less	1. Suitable for dry skin
2. Brand-2	8.1		2. pH is more	2. Brand 2, 3 are suitable for oily skin as they contain more alkali
3. Brand-3	8.2		3. pH is more	