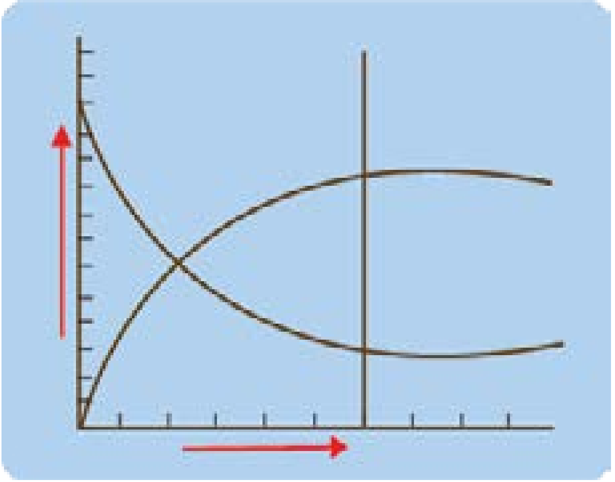
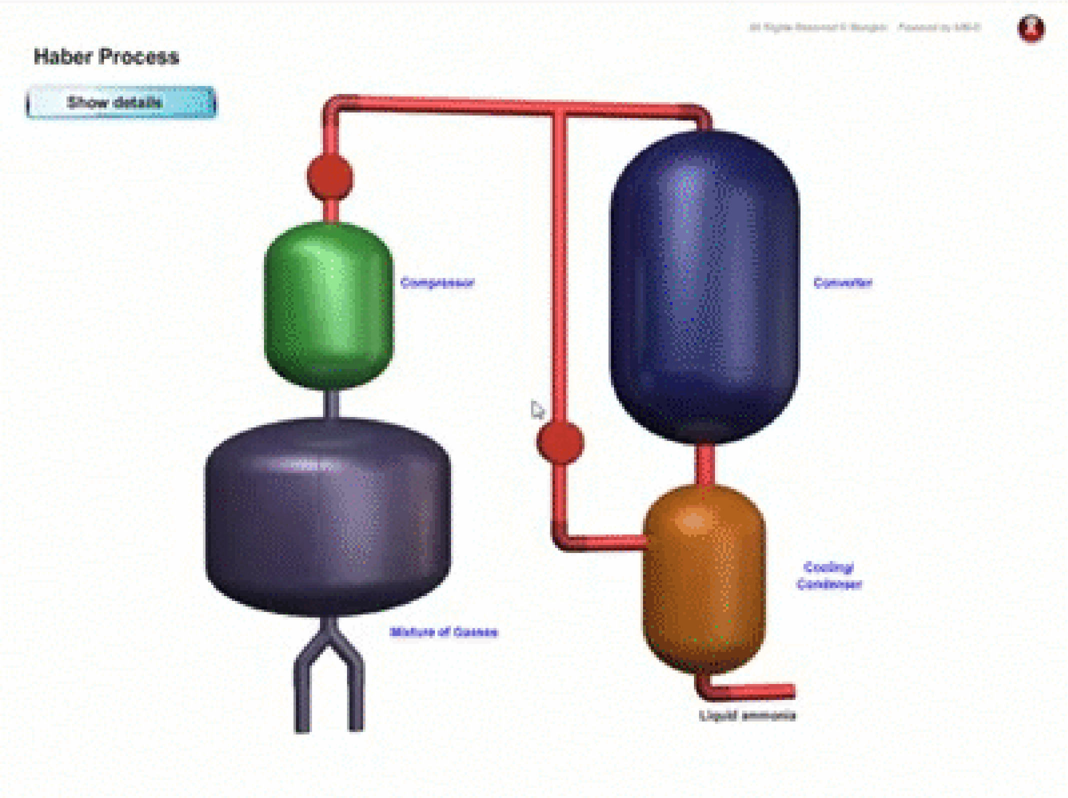
CHAPTER

8



CHEMICAL EQUILIBRIUM



Animation 8.1: Haber's Process
Source & Credit: makeagif

8.1.0 REVERSIBLE AND IRREVERSIBLE REACTIONS

A chemical reaction can take place in both directions, i.e. forward and reverse, but in some cases the tendency of reverse reaction is very small and is negligible. For example, sodium reacts with water to form sodium hydroxide and hydrogen gas.

$$2Na(s)+2H_2O(\ell) \rightarrow 2NaOH(aq)+H_2(g)$$

The tendency for hydrogen to react with sodium hydroxide to form sodium and water is negligible at normal temperature. This is an example of irreversible reaction.

Let us take another example of the reaction between two parts of hydrogen and one part of oxygen by means of an electric spark at normal temperature and pressure. The reaction occurs stoichiometrically according to the following chemical equation.

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$$

If hydrogen and oxygen are present in correct proportion, there will be no residual gases i.e. hydrogen and oxygen. If the product is heated to a temperature of 1500^{0}C, a noticeable quantity of H_2O decomposes, producing hydrogen and oxygen. It means that reverse reaction does occur, but only at higher temperature. It is very likely that the reverse reaction occurs at low temperature, but it is too small to be noticeable. The reaction between stoichiometric amounts of hydrogen and oxygen proceeds to completion in the presence of electric spark. Such reactions are called irreversible reactions and they take place in one direction only.

Now, consider a reaction between nitrogen and hydrogen at 450^{0}C under high pressure in the presence of iron as a catalyst.

$$N_2(g) + 3H_2(g) \xrightleftharpoons[\text{high pressure}]{\text{Fe/450}^{0}\text{C}} 2HN_3(g)$$

There action mixture, after some time, will contain all the three species i.e. nitrogen, hydrogen and ammonia. No matter, how long the reaction is allowed to continue, the percentage composition of species present remains constant. The conditions are favourable for the forward as well as for a reverse reaction to occur to a measurable extent. This type of reaction is described as a reversible reaction.

8.1.1 State of Chemical Equilibrium

If a reversible reaction is allowed to continue for a considerable long time, without changing the conditions, there is no further change in composition of the reaction mixture. The reaction is said to have attained a state of chemical equilibrium. Once this equilibrium has been established, it will last forever if undisturbed.

To illustrate an example of the attainment of equilibrium, let us consider a general reaction in which A reacts with B to produce C and D.

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

Suppose that all the substances are in gaseous state.

Let the initial concentrations of A and B be equal. As time goes on, concentrations of A and B decrease, at first quite rapidly but later slowly. Eventually, the concentrations of A and B level off and become constant.

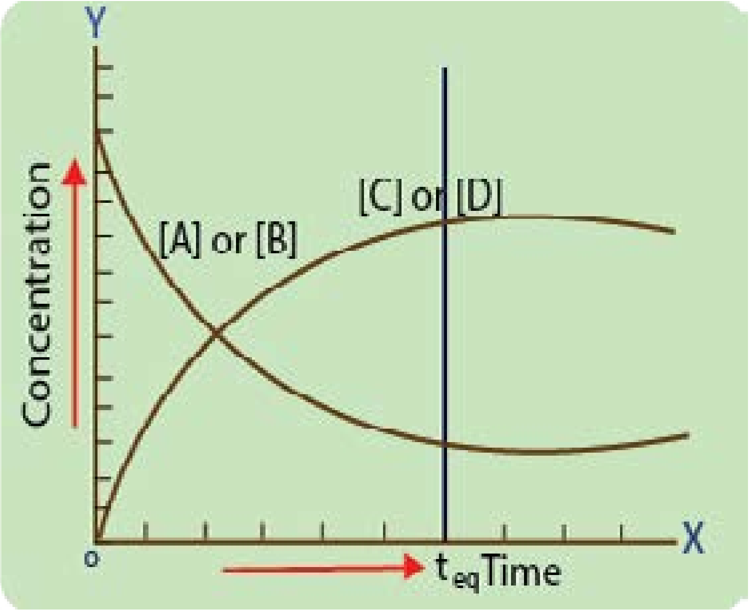


Fig (8.1) Reversible reaction and state of equilibrium

The graph is plotted between time and concentrations for reactants and products, Fig(8.1). The initial concentrations of C and D are zero. As the time passes the products C and D are formed. Their concentrations increase rapidly at first and then level off. At the time of equilibrium concentrations become constant. This is how the chemical equilibrium is attained and state of equilibrium is reached.

Now, let us consider the example of a reversible reaction between hydrogen gas and iodine vapours to form hydrogen iodide at 425^0 C. At equilibrium three components will be present in definite proportions in the reaction mixture Fig (8.2). The equilibrium is established when the rising curve of product HI and the falling curve of reactants $[H_2]$ and $[I_2]$ become parallel to time axis.

$$H_2(g) + I_2(g) \overset{425^0C}{\rightleftharpoons} 2HI(g)$$

The same equilibrium mixture is obtained irrespective whether the reaction starts by mixing hydrogen and iodine or by decomposition of hydrogen iodide. The situation suggests two possibilities of the state of reaction at equilibrium

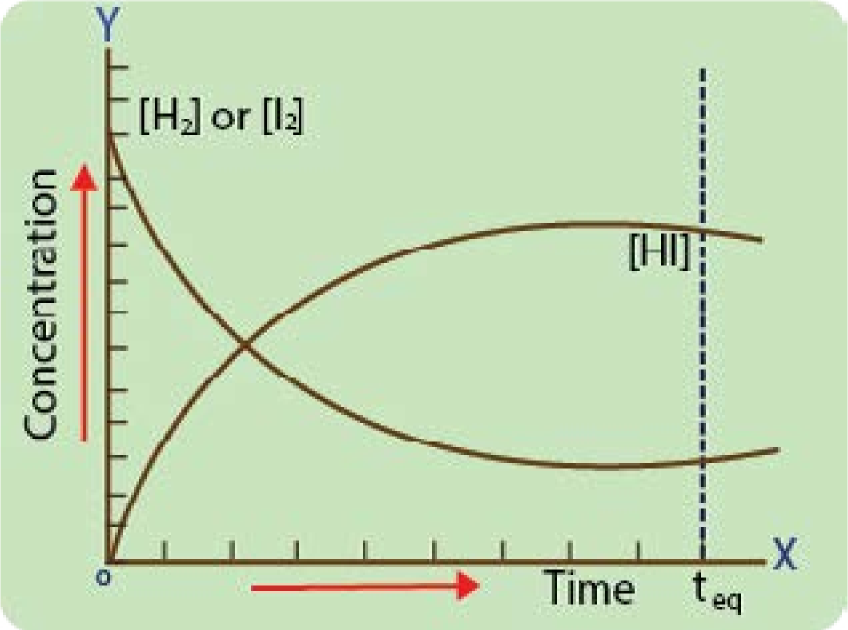
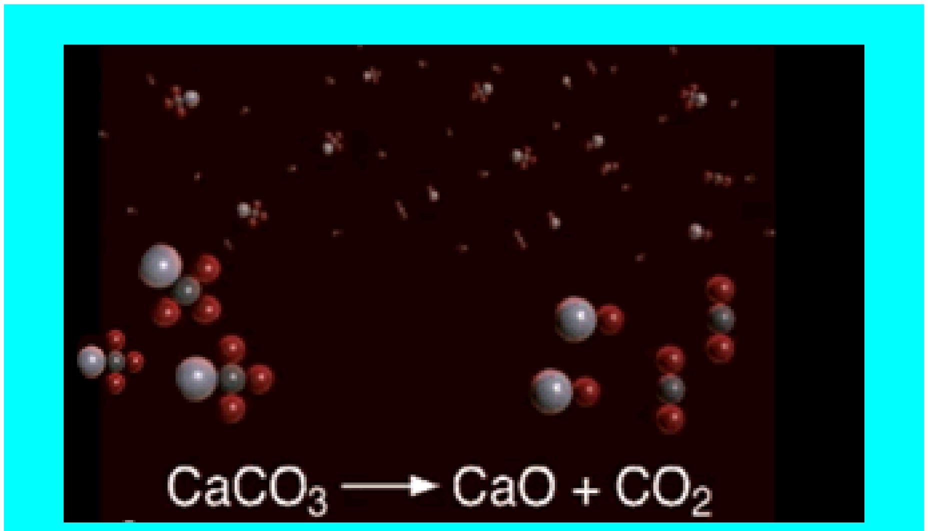


Fig (8.2) State of dynamic equilibrium

(i) All reactions cease at equilibrium so that the system becomes stationary.
(ii) The forward and reverse reactions are taking place simultaneously at exactly the same rate.

It is now universally accepted that the later conditions prevail in a reversible reaction at equilibrium stage of reaction. It is known as the state of dynamic equilibrium.



Animation 8.2: Chemical Equilibrium
Source & Credit : dynamicscience

8.1.2 Law of Mass Action

A state of dynamic equilibrium helps to determine the composition of reacting substances and the products at equilibrium. We use the relationship which was derived by C.M. Guldberg and R Waage in 1864. **It is known as the law of mass action. It states that the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants.**

The term active mass represents the concentration in mole dm^{-3} of the reactants and products for a dilute solution.

Now, consider a general reaction in which A and B are the reactants and C and D are the products. The reaction is represented by the following chemical equation.

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

The equilibrium concentrations of A, B, C and D are represented in square brackets like [A], [B], [C] and [D] respectively and they are expressed in moles dm^{-3}. According to the law of mass action, the rate of the forward reaction, is proportional to the product of molar concentrations of A and B.

$$\text{Rate of forward reaction } (R_f) \propto [A][B]$$

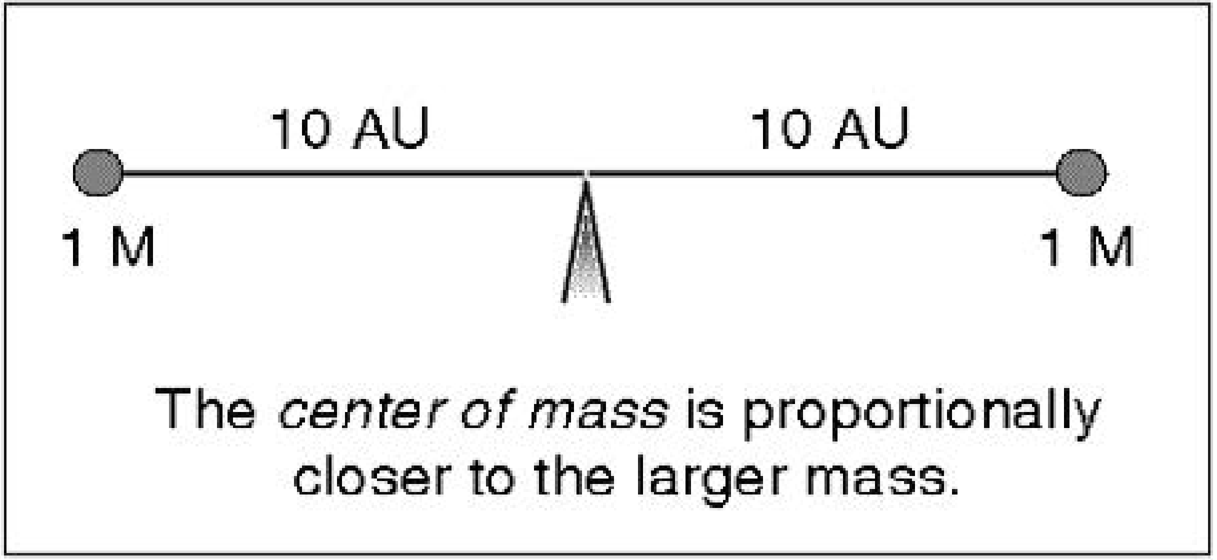
or $$R_f = k_f[A]\,[B]$$

k_f is the proportionality constant and is called rate constant for forward reaction and R_f is the rate of forward reaction. Similarly, the rate of reverse reaction (R_r) is given by

$$\text{Rate of reverse reaction } (R_r) \propto [C][D]$$

$$R_r = k_r[C]\,[D]$$

Where kr is the proportionality constant and is called the rate constant for backward reaction. Remember that C and D are the reactants for backward step.



Animation 8.3: Mass Action
Source & Credit : astronomynotes

At equilibrium,

$$R_f = R_r$$

or $$k_f[A]\,[B] = k_r[C]\,[D]$$

On rearranging, we get

$$\frac{k_f}{k_r} = \frac{[C][D]}{[A][B]}$$

Let $$\frac{k_f}{k_r} = K_c$$

So, $$K_c = \frac{[C][D]}{[A][B]}$$

The constant K_c is called the equilibrium constant of the reaction. K_c is the ratio of two rate constants.

Conventionally, while writing equilibrium constant, the products are written as numerator and reactants as denominator.

$$K_c = \frac{[\text{products}]}{[\text{reactants}]} \quad \text{or} \quad K_c = \frac{\text{rate constant for forward step}}{\text{rate constant for reverse step}}$$

For a more general reaction

$$aA + bB \underset{k_r}{\overset{k_f}{\rightleftharpoons}} cC + dD$$

Where a, b, c and d are the coefficients of balanced chemical equation. They are number of moles of A, B, C and D, respectively in the balanced equation.
The equilibrium constant is given by

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

Hence, the coefficients in the equation appear as exponents of the terms of concentrations in the equilibrium constant expression.

Units of Equilibrium Constants

Equilibrium constant is the ratio of the products of the concentrations of the products to the product of concentrations of the reactants. If the reaction has equal number of moles on the reactant and product sides, then equilibrium constant has no units. When the number of moles is unequal then it has units related to the concentration or pressure. But it is a usual practice that we don't write the units with K_p or K_c values.

Following are some important reversible reactions. Their units of K_c are expressed as

(i) $CH_3COOH(aq) + C_2H_5OH(aq) \rightleftharpoons CH_3COOC_2H_5(aq) + H_2O(\ell)$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]}{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]} = \text{no units}$$

(ii) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[\text{moles dm}^{-3}]^2}{[\text{moles dm}^{-3}][\text{moles dm}^{-3}]^3} = \text{moles}^{-2}\text{dm}^{+6}$$

In the expression of K_c, we have ignored the physical states for the sake of convenience.

Example 1:

The following reaction was allowed to reach the state of equilibrium.

$$2A(aq) + B(aq) \rightleftharpoons C(aq)$$

The initial amounts of the reactants present in one dm³ of solution were 0.50 mole of A and 0.60 mole of B. At equilibrium, the amounts were 0.20 moles of A and 0.45 mole of B and 0.15 mole of C. Calculate the equilibrium constant K_c.

Solution

Equation: $$2A(aq) + B(aq) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} C(aq)$$

K_c for the reaction is given by

$$K_c = \frac{[C]}{[A]^2[B]}$$

$$2A(aq) + B(aq) \rightleftharpoons C(aq)$$

Initial concentrations	0.50 mol	0.60 mol	0.00 mol
Equilibrium concentrations	0.20 mol	0.45 mol	0.15 mol

Since $$K_c = \frac{[C]}{[A]^2[B]}$$

Putting values of concentrations, which are present at equilibrium stage

So, $$K_c = \frac{(0.15)}{(0.20)x(0.20)x(0.45)}$$

$$K_c = \frac{1}{0.20x0.20x3} = \frac{1}{0.12} = \boxed{8.3} \text{ Answer}$$

The units have been ignored for the sake of convenience.

8.1.3 Equilibrium Constant Expressions for Some Important Reactions

i. Formation of Ester from an Organic Acid and Alcohol (aqueous phase reaction)

This is a well known reversible reaction in the solution state.

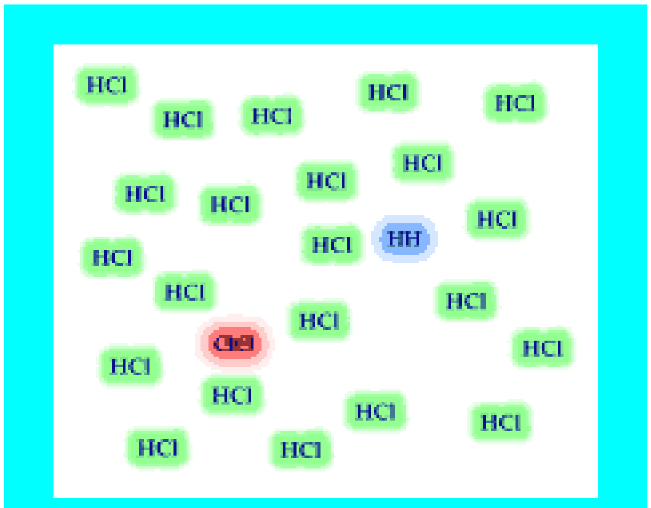
$$CH_3COOH(aq) + C_3H_2OH(aq) \xrightleftharpoons{H_3O^+} CH_3COOC_2H_5(aq) + H_2O(\ell)$$

acid alcohol ester water

Let us suppose that 'a' moles of CH_3COOH and 'b' moles of C_2H_5OH are initially taken in a vessel in the presence of small amount of a mineral acid as a catalyst.

The progress of the reaction can be studied by finding out the concentrations of acetic acid after regular intervals.

A very small portion of the reaction mixture is withdrawn and the concentration of acetic acid is determined by titrating it against a standard solution of sodium hydroxide. The concentration of acetic acid will decrease until the attainment of state of equilibrium, when it will become constant. At equilibrium stage, x moles of ester and 'x' moles of H_2O are produced. The number of moles of acid and alcohol left behind are 'a-x' moles and 'b-x' moles respectively. If the volume of reaction mixture at equilibrium stage is 'V' dm^3, then



Animation 8.4: Equilibrium Constant
Source & Credit : mainstreet

$$\begin{array}{llcllr}
CH_3COOH(aq) + & C_2H_5OH(aq) & \rightleftharpoons & CH_3COOC_2H_5(aq) + & H_2O(\ell) & \\
\text{'a' moles} & \text{'b' moles} & \rightleftharpoons & \text{'0' moles} & \text{'0' moles} & t=0sec \\
\text{(a-x) moles} & \text{(b-x) moles} & \rightleftharpoons & \text{'x' moles} & \text{'x' moles} & t=t_{eq}
\end{array}$$

When number of moles are divided by total volume of the reaction mixture, we get concentration of each species at equilibrium stage in moles dm^{-3}.

$$\left(\frac{a-x}{V}\right)\text{moles dm}^{-3} + \left(\frac{b-x}{V}\right)\text{moles dm}^{-3} \rightleftharpoons \left(\frac{x}{V}\right)\text{moles dm}^{-3} + \left(\frac{x}{V}\right)\text{moles dm}^{-3}$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

Since

Brackets [ ] denote the concentrations in moles dm^{-3}.

Putting concentrations at equilibrium

$$K_c = \frac{\frac{X}{V}\cdot\frac{X}{V}}{\frac{(a-x)}{V}\cdot\frac{(b-x)}{V}}$$

Simplifying the right hand side, we get

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

In this expression of K_c, the factor of volume is cancelled out. So, the change of volume at equilibrium stage does not affect the K_c value or equilibrium position of reaction.

ii. Dissociation of PCl_5 (gaseous phase reaction)

The dissociation of PCl_5 into PCl_3 and Cl_2, is a well known homogeneous gaseous phase reaction. This reaction has unequal number of moles of reactants and products.

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

Let 'a' moles of PCl_5 present initially are decomposed by 'x' moles. So, at equilibrium stage, 'a-x' moles of PCl_5 are left behind while 'x' moles of PCl_3 and 'x' moles of Cl_2 are produced. If the volume of equilibrium mixture is 'V' dm^3, then

$$\begin{array}{llllll} PCl_5(g) & \rightleftharpoons & PCl_3(g) & + & Cl_2(g) & \\ \text{'a'moles} & & \text{'O'moles} & & \text{'O'moles} & t = 0\text{sec} \\ (a - x)\text{ moles} & & \text{'x' moles} & & \text{'x' moles} & t = t_{eq} \end{array}$$

Dividing the number of moles by total volume of reactants and products at equilibrium.

$$\left(\frac{a-x}{V}\right)\text{moles dm}^{-3} \rightleftharpoons \left(\frac{x}{V}\right)\text{moles dm}^{-3} + \left(\frac{x}{V}\right)\text{moles dm}^{-3}$$

Since $$K_c = \frac{[PCl_3][Cl_2]}{PCl_5}$$

Putting the concentrations at equilibrium

$$K_c = \frac{\frac{X}{V}.\frac{X}{V}}{\frac{(a-x)}{V}}$$

Simplifying the right hand side, we get

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

The final expression is not independent of the factor of volume. So, the change of volume at equilibrium stage disturbs the equilibrium position of the reaction. We will discuss this reaction in Le-Chatelier's principle with reference to effect of volume change and its effect on change of equilibrium position.

iii. Decomposition of N_2O_4 (gaseous phase reaction)

Similarly, for decomposition of N_2O_4 (g). the expression of K_c involves the factor of volume.

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

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

'a' is the initial number of moles of N_2O_4 'x' is number of moles of N_2O_4 decomposed and 'V' is total volume of N_2O_4 , and NO_2 at equilibrium stage.

iv. Synthesis of NH_3 (gaseous phase reaction)

For the synthesis of ammonia,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

the expression of K_c is

$$K_c = \frac{4x^2V^2}{(a\text{-}x)(b\text{-}3x)^3}$$

Where 'a' and 'b' are the initial number of moles of N_2 and H_2 and 'x' is number of moles of N_2, decomposed at equilibrium stage. 'V' is the total volume of N_2, H_2 and NH_3 at equilibrium. The final expression involves V^2 in the numerator:

Hence, it depends upon the coefficients of balanced equation that whether the factor of volume will appear in numerator or denomenator.

8.1.4 Relationship Between Equilibrium Constants

The expressions of equilibrium constants depend upon the concentration units used. Mostly the concentrations are expressed in mole dm^{-3}. Let us consider the following reversible reaction.

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

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{or} \quad K_c = \frac{C_C{}^c D_D{}^d}{A_A{}^a B_B{}^b}$$

The square brackets represent the concentration of species in moles dm^{-3}. Anyhow, the capital C is also used for molar concentrations.

If the reactants A, B, and the products C, D of the reaction under consideration are ideal gases, then molar concentration of each gas is proportional to its partial pressure . When the concentrations are expressed in terms of partial pressures, the expression of K_p is,

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

Here P_A, P_B, P_C and P_D are partial pressures of A, B, C, D respectively at equilibrium position. As long as the number of moles of products and reactants, which are in the gaseous state, are equal, the values of K_C and K_P remain the same. Otherwise, the following relationship between K_P and K_C can be derived by using Dalton's law of partial pressures.

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

Where 'Δn' is the difference between number of moles of the gaseous products and the number of moles of gaseous reactants.

Δn = no. of moles of products - no. of moles of reactants

'R' is the general gas constant and 'T' is absolute temperature at which the reaction is being carried out

Where, $\Delta n = 0$, then all the equilibrium constants have the same values.

Example 2:

N_2 (g) and H_2 (g) combine to give NH_3 (g). The value of K_c in this reaction at 500 °C is 6.0×10^{-2}. Calculate the value of K_p for this reaction.

Solution:

The reaction for the synthesis of NH_3 is

$$N_2(g) + 3H_2(g) \quad □ \quad 2NH_3(g)$$

This reaction takes place with decrease in the number of moles. The relationship of K_p and K_c is

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

Now $K_p = 6.0 \times 10^{-2}$

Temperature $= 500 + 273 = 773$ K

Δn = no of moles of products - no of moles of reactants

$\Delta n = 2 - 4 = -2$

$R = 0.0821$ dm^3 atm K^{-1} mol^{-1}

Substituting these values in the expression

$K_p = 6.0 \times 10^{-2} (773 \times 0.0821)^{-2} \quad = 6.0 \times 10^{-2} (63.5)^{-2}$

$$K_p = \frac{6.0\text{x}10^{-2}}{(63.5)^2}$$

$$K_p = \boxed{1.5\text{x}10^{-5}} \quad \text{Answer}$$

In this case the value of K_p is smaller than K_c . Those reactions, which take place with the increase in the number of moles mostly have greater K_p than K_c.

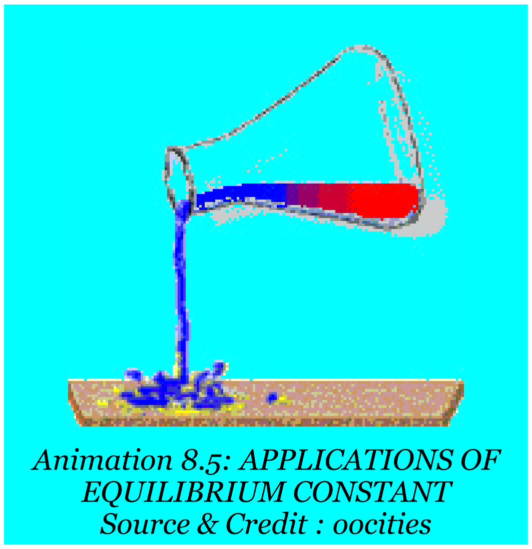
8.1.5 APPLICATIONS OF EQUILIBRIUM CONSTANT

The value of equilibrium constant is specific and remains constant at a particular temperature.

The study of equilibrium constant provides us the following informations:

(i) Direction of reaction (ii) Extent of reaction

(iii) Effect of various factors on equilibrium constant and equilibrium position.



Animation 8.5: APPLICATIONS OF EQUILIBRIUM CONSTANT
Source & Credit : oocities

(i) Direction of Reaction

we know that, $K_c = \dfrac{[\text{Products}]}{[\text{Reactants}]}$ for any reaction.

The direction of a chemical reaction at any particular time can be predicted by means of [products] / [reactants] ratio, calculated before the reaction attains equilibrium. The value of [product] / [reactants] ratio leads to one of the following three possibilities.

(a) The ratio is less than K_c. This implies that more of the product is required to attain the equilibrium, therefore, the reaction will proceed in the forward direction.

(b) The ratio is greater than K_c. It means that the reverse reaction will occur to attain the equilibrium.

(c) When the ratio is equal to K_c, then the reaction is at equilibrium.

Example 3:

Esterification reaction between ethanol and acetic acid was carried out by mixing definite amounts of ethanol and acetic acid alongwith some mineral acid as a catalyst. Samples were drawn out of the reaction mixturq to check the progress of the esterification reaction. In one of the samples drawn after time t, the concentrations of the species were found to be $[CH_3COOH] = 0.025$ mol dm^{-3}, $[C_2H_5OH] = 0.032$ mol dm^{-3}, $[CH_3COOC_2H_5] = 0.05$ mol dm^{-3}, and $[H_20] = 0.04$ mol dm^{-3}. Find out the direction of the reaction if K_c for the reaction at 25°C is 4.

Solution:

Esterification reaction is represented by the following stoichiometric equation.

$$CH_3COOH + C_2H_5OH \overset{H^+}{\rightleftharpoons} CH_3COOC_2H_5 + H_2O$$

All the substances are present in the same volume of solution, therefore K_C is given by

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

The various values of concentrations, at time t are substituted to get the ratio

$$K_c = \frac{0.05 \text{x} 0.04}{0.025 \text{x} 0.032} = \boxed{2.50} \text{ Answer}$$

The given value of K_c for this reaction is 4 and 2.5 is less than K_c. Therefore, the reaction will proceed in the forward direction to attain the equilibrium.

(ii) Extent of Reaction

(a) If the equilibrium constant is very large, this indicates that the reaction is almost complete.
(b) If the value of K_c is small, it reflects that the reaction does not proceed appreciably in the forward direction.
(c) If the value of K_c is very small, this shows a very little forward reaction.

Examples:

Equilibrium constant for the decomposition of ozone to oxygen is 10^{55} at 25°C.

i.e., $2O_3 \rightleftharpoons 3O_2, \quad K_c=10^{55} \quad \text{at } 25^{\circ}C$

It infers that at room temperature 0_3 is unstable and decomposes very rapidly to 0_2. This reaction is almost complete.

On the other hand the value of equilibrium constant for the decomposition of HF at 2000°C is 10^{-13}.

$$2HF(g) \rightleftharpoons H_2(g) + F_2(g) \quad K_c=10^{-13} \quad \text{at } 2000^{\circ}C$$

It indicates high stability and slow decomposition of HF, even at 2000°C.

(iii) The Effect of Conditions on the Position of Equilibrium

Equilibrium constant and position of equilibrium are two different entities. K_c is equilibrium constant and has constant value at a particular temperature whereas the ratio of products to reactants in equilibrium mixture is described as the position of equilibrium and it can change if the external conditions e.g. temperature, pressure and concentrations are altered. If K_c is large the position of equilibrium lies on the right and if it is small, the position of the equilibrium lies on the left, for a reversible reaction.

Chemists are interested in finding the best conditions to obtain maximum yield of the products in reversible reaction, by favourably shifting the position of equilibrium of a reaction. For this purpose, we have to discuss an important principle in this respect i.e.Le-Chatelier's principle.

8.1.6 The Le-Chatelier's Principle

Le-Chatelier studied the effects of concentration, pressure and temperature on equilibria.

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

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

Animation 8.6: The Le-Chatelier's Principle
Source & Credit : Anotherequilibriumsite

(a) Effect of Change in Concentration

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

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

The equilibrium constant expression for above reaction can be written as

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

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

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

(b) Effect of Change in Pressure or Volume

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

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

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

(c) Quantitative Effect of Volume on Equilibrium Position

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

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

$$K = \frac{4x\ \ V}{(a\text{-}2x)\ \ (b\text{-}x)}$$

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

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

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

PCl_5 dissolves to give PCl_3 and Cl_2

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

K_c for this reaction is as follows:

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

The dissociation of N_2O_4 gives NO_2 gas

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

The K_c for this reaction is as follows

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

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

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

(d) Effect of Change in Temperature

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

The equilibrium constant changes by the change of temperature, because the equilibrium position shifts without any substance being added or removed. Consider the following exothermic reaction in gas phase at equilibrium taking place at a known temperature.

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

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

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

$$KI(s) \rightleftharpoons KI(aq) \qquad \Delta H = 21.4\,kJ\,mol^{-1}$$

Let us have a saturated solution of KI in water at a given temperature. It has attained equilibrium at this temperature. A rise in temperature at equilibrium favours more dissolution of the salt.

Equilibrium is shifted to the forward direction. On the other hand, cooling will favour crystallization of salt. Hence the solubility of KI in water must increase with increase in temperature. For some salts the heat of solution is close to zero (heat is neither evolved or absorbed). The solubility of these salts in water is not affected by the change in temperature. Formation of aqueous solution of NaCl is an example of such a salt.

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

(e) Effect of Catalyst on Equilibrium Constant

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

Actually, a catalyst lowers the energy of activation of both forward and reverse steps by giving new path to the reaction.

8.2 APPLICATIONS OF CHEMICAL EQUILIBRIUM IN INDUSTRY

Concept of chemical equilibrium is widely applicable for preparation of certain materials on industrial scale. Let us discuss the manufacture of NH_3 and SO_3 gases on industrial scale.

8.2.1 Synthesis of Ammonia by Haber's Process

The process of ammonia synthesis was developed by German chemist F. Haber and first used in 1933. This process provides an excellent setting in which to apply equilibrium principle and see the compromises needed to make an industrial process economically worth while. The chemical equation is as follows.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H=-92.46kJ$$

When we look at the balanced chemical equation it is inferred, from Le-Chatelier's principle that one can have three ways to maximize the yield of ammonia.

(i) By continual withdrawl of ammonia after intervals, the equilibrium will shift to forward direction in accordance with Le-Chatelier's principle. To understand it look at the effect of change of concentration in Le-Chatelier's principle.

ii) In crease the pressure to decrease the volume of the reaction vessel. Four moles of the reactants combine to give two moles of the products. High pressure will shift the equilibrium position to right to give more and more ammonia.

(iii) Decreasing the temperature will shift it to the forward direction according to Le-Chatelier's principle.

Table (8.2) Effect of temperature on K_c for ammonia synthesis

T(K)	K_c
200	7.7x10^{15}
300	2.69x10^{8}
400	3.94x10^{1}
500	1.72x10^{2}
600	4.53x10^{0}
700	2.96x10^{-1}
800	3.96x10^{-2}

So high pressure, low temperature and continual removal of ammonia will give the maximum yield of ammonia. Table (8.2) shows the effect of the rise in temperature on the value of Kc and the Fig. (8.3) shows the optimum conditions to get maximum yield of ammonia. Fig (8.3) shows percent yield of ammonia vs. temperature (^{0}C) at five different operating pressures.

At very high pressure and low temperature (top left), the yield of NH_3 is high but the rate of formation is low. Industrial conditions denoted by circle are between 200 and 300 atmospheres at about 400^{0}C.

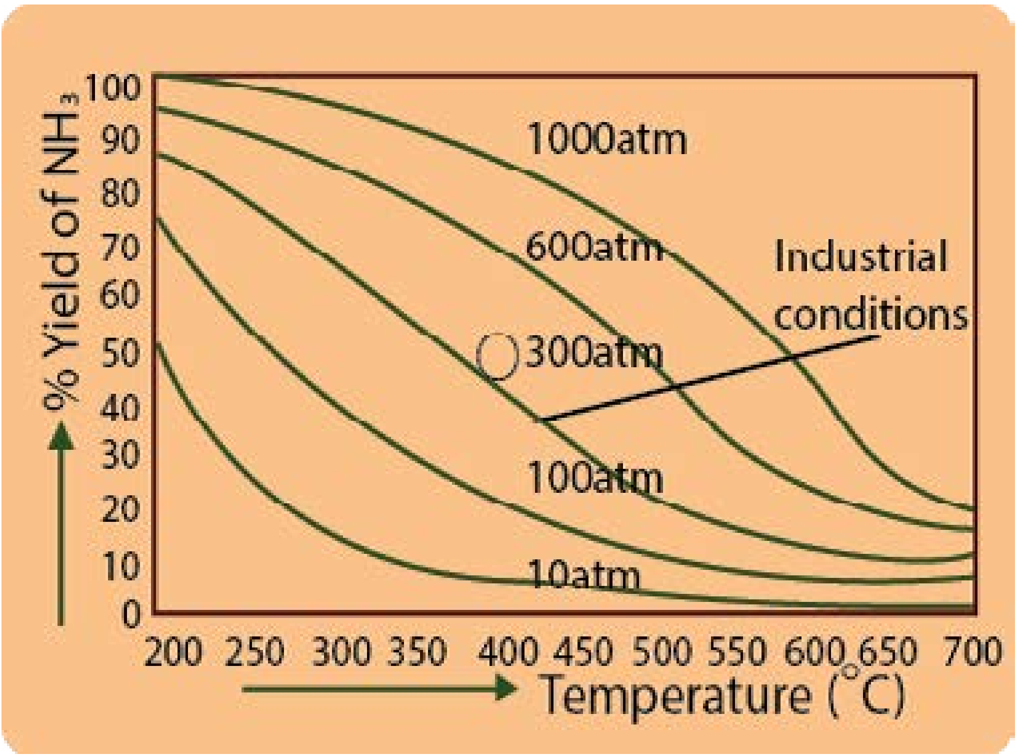
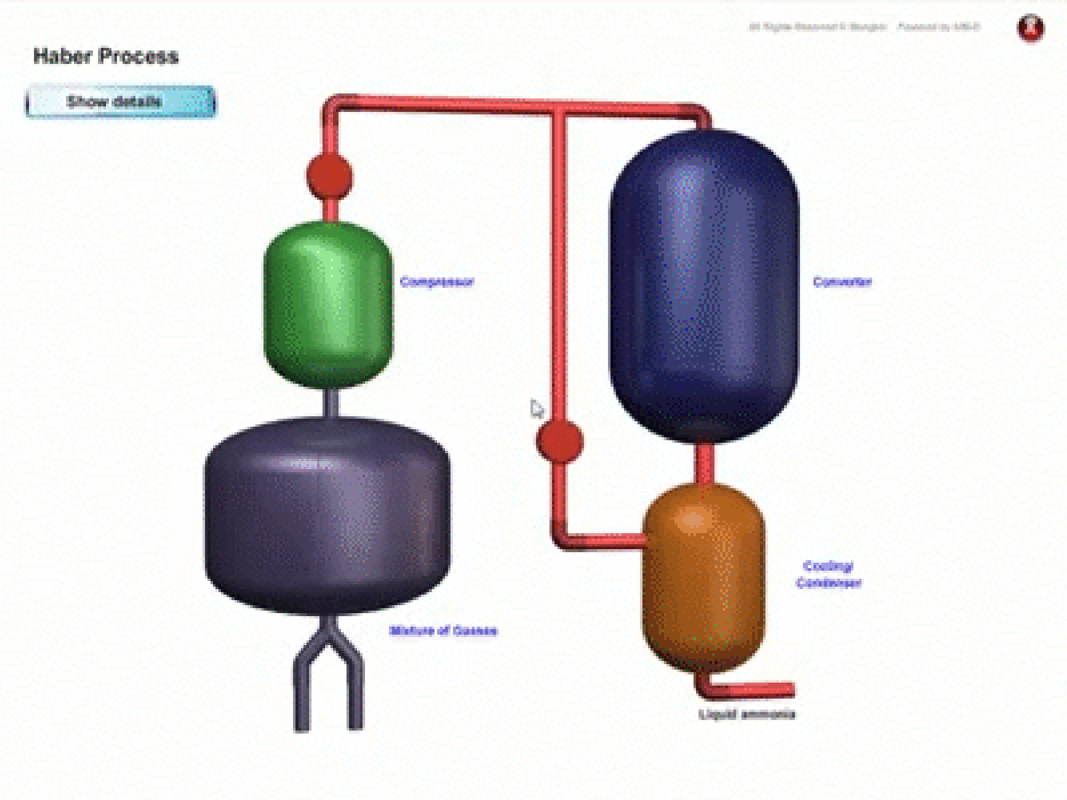


Fig (8.3). Graphical representation of temperature and pressure for NH_3 synthesis.

No doubt, the yield of NH_3 is favoured at low temperature, but the rate of its formation does not remain favourable. The rate becomes so slow and the process is rendered uneconomical. One needs a compromise to optimize the yield and the rate. The temperature is raised to a moderate level and a catalyst is employed to increase the rate. If one wants to achieve the same rate without a catalyst, then it requires much higher temperature, which lowers the yield. Hence the optimum conditions are the pressure of 200-300 atm and temperature around 673 K (400^0C). The catalyst is the pieces of iron crystals embedded in a fused mixture of MgO, Al_2O_3 and SiO_2.

The equilibrium mixture has 35% by volume of ammonia. The mixture is cooled by refrigeration coils until ammonia condenses (B.P = -33.4^0C) and is removed. Since, boiling points of nitrogen and hydrogen are very low, they remain in the gaseous state and are recycled by pumps back into the reaction chamber.

Nearly 13% of all nitrogen fixation on earth is accomplished industrially through Haber's process. This process synthesizes approximately 110 million tons of ammonia in the world. About 80% of this is used for the production of fertilizers and some is used in manufacture of explosives or the production of nylon and other polymers.



Animation 8.7: Haber's Process
Source & Credit : makeagif

8.2.2 Preparation of Sulphur Trioxide

In the contact process for manufacture of H_2SO_4, the conversion of SO_2 to SO_3 is achieved in a reversible reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -194 kJ/mol$$

The temperature and pressure are the most essential factors for controlling the rate of this reaction. The principles involved here are the same as those discussed previously for Haber's process. At low temperature, the equilibrium constant for formation of SO_3 is large but equilibrium is reached very slowly. As the temperature is raised the rate increases but the yield of SO_3 drops off according to Le-Chatelier's principle. High pressure tends to increase yield of SO_3. However, instead of using high pressure, the concentration of O_2 (air) is increased to increase the yield of SO_3. Table (8.3) helps to understand the effect of different conditions on the yield of SO_3. During the process pressure is kept at one atmosphere.

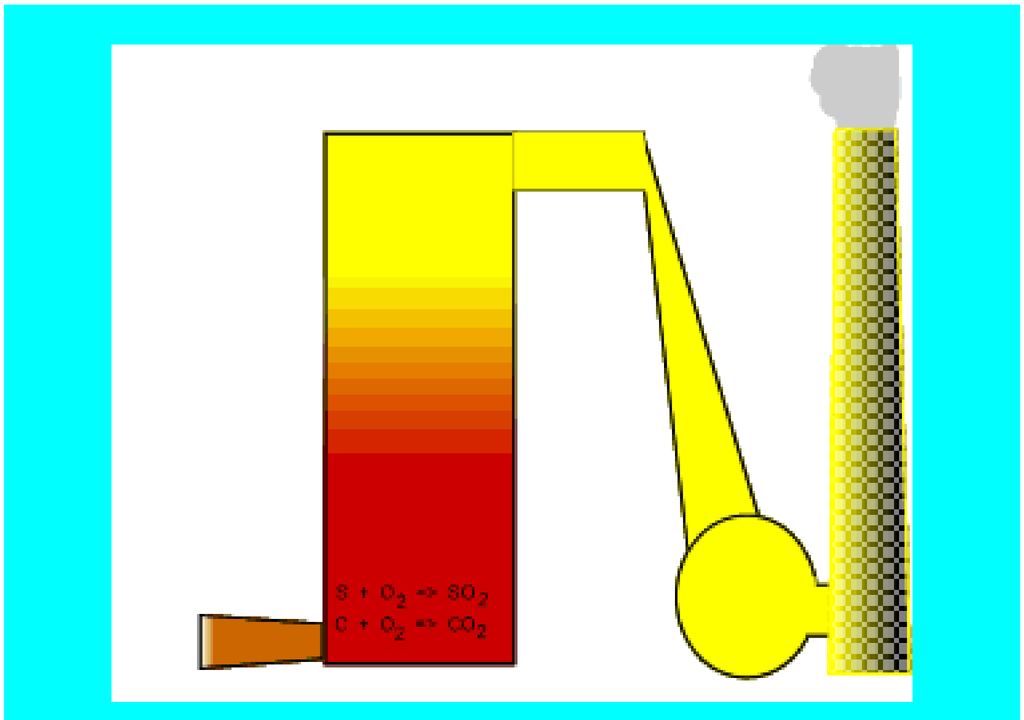
To have the best possible yield of SO_3 within a Table (8.3) Effect of temperature reasonable time, a mixture of SO_2 and O_2 (air) at 1 atm pressure is passed over a solid catalyst at 650^0C.

Table (8.3) Effect of temperature on the yield of SO_3

Temp. ^{0}C	K_c	Mole% of SO_3
200	5500	98
300	690	91
400	160	75
500	55	61
600	25	46
700	13	31

The equilibrium mixture is then recycled at lower temperature, 400 to 500^0C, to increase the yield of SO_3. The most effective catalysts are V_2O_5 and finely divided platinum. SO_3 is dissolved in H_2SO_4 to get oleum, which is diluted to get H_2SO_4.

H_2SO_4 is the king of chemicals. A country's industrial progress is measured by the amount of H_2SO_4 manufactured each year.



Animation 8.8: Preparation of Sulphur Trioxide
Source & Credit : dynamicscience

8.3.0 IONIC PRODUCT OF WATER

Pure water is a very poor conductor of electricity but its conductance is measurable. Water undergoes self ionization as follows and the reaction is reversible.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

or

$$H_2O \rightleftharpoons H^+ + OH^-$$

The equilibrium constant for this reaction can be written as follows.

$$K_c = \frac{[H^+][OH^-]}{H_2O} = 1.8 \text{ x } 10^{-16} \text{moles dm}^{-3}$$

The concentration of H_2O i.e.$[H_2O]$ in pure water may be calculated to be 1000gdm^3 divided by 18gmol^{-1} giving 55.5 moles dm^{-3}

Since, water is present in very large excess and very few of its molecules undergo ionization, so its concentration remains effectively constant. Constant concentration of water is taken on L.H.S. and multiplied with K_c to get another constant called K_w.

$$1.8 \text{ x } 10^{-16} \text{ x } 55.5 = 1.01\text{x}10^{-14} = [H^+][OH^-]$$

This 1.01x10^{-14} is called K_w of water of 25^{0}C

$$K_c[H_2O] = [H^+][OH^-]$$

So, $$K_w = [H^+][OH^-] = 10^{-14} \text{at } 25^oC.$$

K_w is called ionic product of water or dissociation constant of water. The value of K_w increases almost 75 times when temperature is increased from 0°C to 100°C. Anyhow, the increase in K is not regular. The effect of temperature on K. is shown in Table (8.4).

Table (8.4) K_w at various temperatures.

Temp. (^{0}C)	K_w
ne0	0.11x10^{-14}
10	0.30x10^{-14}
25	1.0x10^{-14}
40	3.00x10^{-14}
100	7.5x10^{-14}

When ever some quantity of acid or base is added in water, then K_w remains the same, but $[H^+]$ and $[OH^-]$are no more equal. Anyhow, in neutral water

$$[H^+] = [OH^-]$$

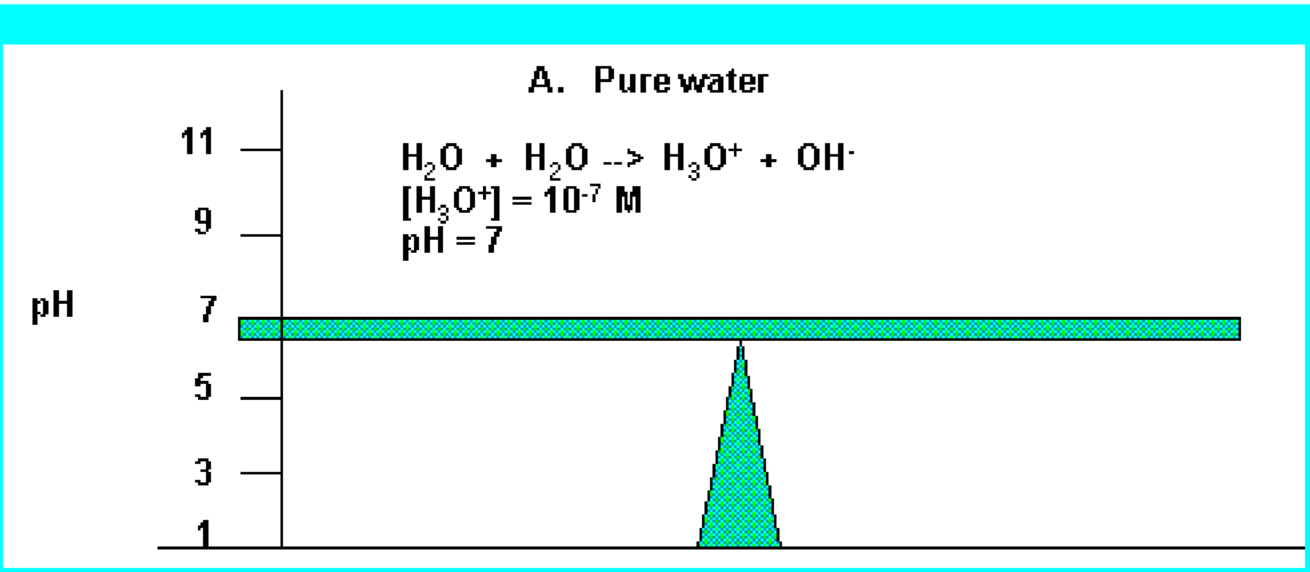
or $$[H^+][H^+] = 10^{-14}$$

$$[H^+]^2 = 10^{-14}$$

$$[H^+] = 10^{-7}\text{moles dm}^{-3}$$

and $$[OH^-] = 10^{-7}\text{moles dm}^{-3}$$

This means that out of 55.5 moles of pure water in one dm^3 of it, only 10^{-7} moles of it have dissociated into ions. This shows that water is a very weak electrolyte. At 40^0C, the $[H^+] = [OH^-]$ but the values are more than 10^{-7} moles dm^{-3} and pure water is again neutral at 40°C. Similarly, pure water is neutral at 100^0C. $[H^+]$ and $[OH^-]$ are greater than those at 40°C.



Animation 8.9: IONIC PRODUCT OF WATER
Source & Credit : employees.csbsju

In case of addition of small amount of an acid

$$[H^+] > [OH^-]$$

While in the case of addition of few drops of a base

$$[OH^-] > [H^+]$$

During both of these additions, the value of K_w will remain the same i.e. 10^{-14} at 25^0C.

pH and pOH

Actually, in all the aqueous solutions, the concentration of H^+ and OH^- are too low to be conveniently expressed and used in calculations. In 1909, Sorenson, a Danish biochemist, introduced the term pH and pOH. So, the scales of pH and pOH have been developed. pH and pOH are abbreviations of negative log of hydrogen ion concentration and negative log of hydroxide ion concentration, respectively.

$$pH = -\log[H^+]$$

and

$$pOH = -\log[OH^-]$$

For neutral water, $pH = -\log 10^{-7} \ \ = 7$

$$pOH = -\log 10^{-7} \ \ = 7$$

when

$$pH = 7, \rightarrow \text{ solution is neutral}$$
$$pH < 7, \rightarrow \text{ solution is acidic}$$
$$pH > 7, \rightarrow \text{ solution is basic}$$

If we take the negative log of K_w, then it is called pK_w.

$$pK_w = -\log K_w$$

$$= -\log 10^{-14}$$

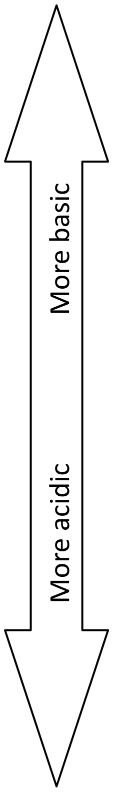
$$pK_w = 14\log 10$$ Since (log 10=1)

$$pK_w = 14x1 = 14(\text{at } 25^{\circ}C)$$

The value of pK_w is less than 14 at higher temperatures i.e. at 40^0Cand 100^0C.

The value of pH normally varies between 0 → 14 at 25°C. Solutions of negative pH and having values more than 14 are also known. Table (8.5) shows the relationship among $[H^+]$,$[OH^-]$, pH and pOH of various solutions.

Table (8.5) Relationship of $[H_30^+]$, $[OH^-]$, pH and pOH



	$[H_3O^+]$	pH	$[OH^-]$	pOH
Basic	$1x10^{-14}$	14.0	1x10	0.0
	$1x10^{-13}$	13.0	$1x10^{-1}$	1.0
	$1x10^{-12}$	12.0	$1x10^{-2}$	2.0
	$1x10^{-11}$	11.0	$1x10^{-3}$	3.0
	$1x10^{-10}$	10.0	$1x10^{-4}$	4.0
	$1x10^{-9}$	9.0	$1x10^{-5}$	5.0
	$1x10^{-8}$	8.0	$1x10^{-6}$	6.0
Neutral	$1x10^{-7}$	7.0	$1x10^{-7}$	7.0
Acidic	$1x10^{-6}$	6.0	$1x10^{-8}$	8.0
	$1x10^{-5}$	5.0	$1x10^{-9}$	9.0
	$1x10^{-4}$	4.0	$1x10^{-10}$	10.0
	$1x10^{-3}$	3.0	$1x10^{-11}$	11.0
	$1x10^{-2}$	2.0	$1x10^{-12}$	12.0
	$1x10^{-1}$	1.0	$1x10^{-13}$	13.0
	$1x10^{-0}$	0.0	$1x10^{-14}$	14.0

The pH values of some familiar aqueous solutions are shown inTable (8.6). This table can help you to understand the acidic or basic nature of commonly used solutions.

Table (8.6) Approximate pH and pOH of some common materials at 25°C

Material	pH	pOH	Material	pH	pOH
1.0 M HCl	0.1	13.9	bread	5.5	8.5
0.1 M HCl	1.1	12.9	potatoes	5.8	8.2
0.1 M CH_3COOH	2.9	11.10	rainwater	6.2	7.8
gastric juice	2.0	12.00	milk	6.5	7.5
lemons	2.3	11.7	saliva	6.5-6.9	7.5-7.1
vinegar	2.8	11.2	pure water	7.0	7.00
soft drinks	3.0	11.00	eggs	7.8	6.2
apples	3.1	10.9	0.1 M $NaHCO_3$	8.4	5.6
grapefruit	3.1	10.9	seawater	8.5	5.5
oranges	3.5	10.5	milkofmagnesia	10.5	3.5
tomatoes	4.2	9.8	0.1 M NH_3	11.1	2.9
cherries	3.6	10.4	0.05 M Na_2CO_3	11.6	2.4
bananas	4.6	9.4	0.1 M NaOH	13.0	1.00

8.4.0 IONIZATION CONSTANTS OF ACIDS (K_a)

Acids and bases when dissolved in water may or may not be completely dissociated. Many acids are weak electrolytes and they ionize to an extent which is much less than 100%. The value of K_a called the dissociation constant of acid, is the quantitative measure of the strength of the acid. Suppose we have an acid HA dissolved in water, in a reversible manner

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

K_c for the reversible reaction will be written as follows.

$$K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

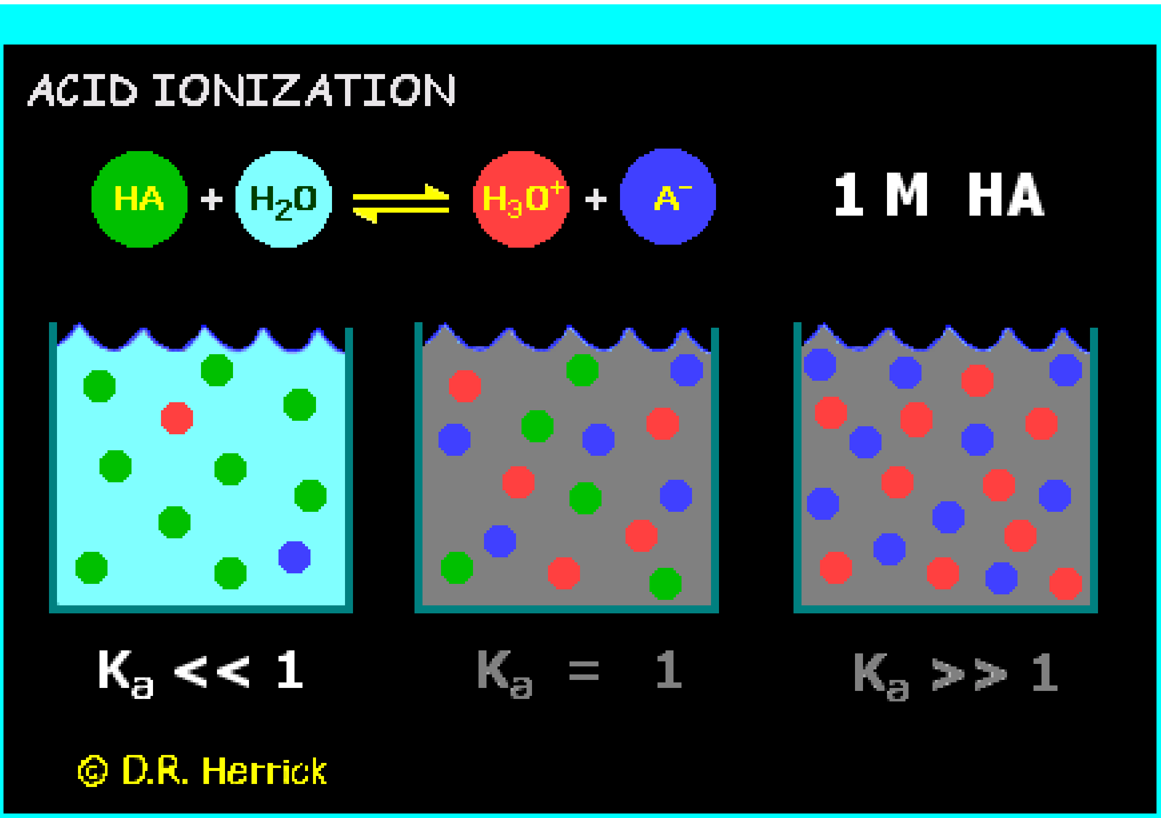
At the equilibrium stage, the concentration of water is almost the same as at the initial stages because it has been taken in large excess. A reasonable approximation, therefore, is to take the concentration of water to be effectively constant and take it on the left-hand side with K_c.

$$K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

Let $K_c[H_2O] = K_a$

K_a is another constant

Hence $K_a = \dfrac{[H_3O^+][A^-]}{[HA]}$



Animation 8.10: IONIZATION CONSTANTS OF ACIDS (K_a)
Source & Credit : eechem3

This equation can be used to calculate K_a for any acid solution if we know the pH or $[H^+]$ of that solution and the initial concentration of acid [HA] dissolved. This can also be used to calculate the equilibrium concentration of H_3O^+ and A^- produced if we know the initial concentration of acid HA and its K_a value.

When $K_a < 10^{-3}$ acid is weak

$K_a = 1$ to 10^{-3} acid is moderately strong

$K_a > 1$ acid is strong

The values of K_a for some acids are given in the Table (8.7)

Table (8.7) Dissociation constants of some acids at 25^{0}C and their relative strength

Acid	Dissociation	K_a	Relative strength
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	very large(10^{+7})	Very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^-$	very large(10^{+3})	Very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Large(10^{+2})	Very strong
HSO^-_4	$HSO^-_4 \rightleftharpoons H^+ + SO_4^{2-}$	$1.3x10^{-4}$	Strong
HF	$HF \rightleftharpoons H^+ + F^-$	$6.7x10^{-5}$	Weak
CH_3COOH	$CH_3COOH \rightleftharpoons H^+ + CH_3COOH^-$	$1.85x10^{-5}$	Weak
H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$4.4x10^{-7}$	Weak
H_2S	$H_2S \rightleftharpoons H^+ + HS^-$	$1.0x10^{-7}$	Weak
NH_4^+	$NH_4 \rightleftharpoons H^+ + NH_3$	$5.7x10^{-10}$	Weak
HCO_3^-	$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$4.7x10^{-11}$	Weak
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	$1.8x10^{-16}$	Very weak

Percentage of Ionization of Acids

We can calculate the percentage ionization of weak acid and the formula is as follows:

$$\%\text{ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \text{ x } 100$$

The percentage ionization of weak acids depend upon the extent of dilution of their aqueous solutions. Table (8.8) shows the change in percentage ionization of acetic acid at different concentrations. Lesser the molarity, diluted the solution, greater the chances for electrolyte to be dissociated. When 0.1 mole of CH_3COOH is dissolved in 1000cm^3 of solution, then 1.33 molecules are dissociated out of 100, and 13.3 out of 1000. When the 0.001 moles are dispersed per dm^3 of solution then 12.6 molecules of CH_3COOH get dissociated out of 100. Remember that K_a remains the same at all dilutions at a constant temperature.

Table (8.8) Percentage ionization and ionization constants of acetic acid at 25^{0}C

Molarity	% Ionized	$[H_3O^+]$	$[CH_3COOH]$	K_a
0.10000	1.33	0.001330	0.098670	1.79×10^{-5}
0.0500	1.89	0.000945	0.049060	1.82×10^{-5}
0.0100	4.17	0.000417	0.009583	1.81×10^{-5}
0.0050	5.86	0.000293	0.004707	1.81×10^{-5}
0.0010	12.60	0.000126	0.000874	1.72×10^{-5}

Example 4:

What is the percentage ionization of acetic acid in a solution in which 0.1 moles of it has been dissolved per dm^3 of the solution.

Solution:

$$CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}O\text{-}H \rightleftharpoons CH_3\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- + H^+$$

$K_a = 1.85\times10^{-5}$

Initial conc. 0.10 moles 0 moles 0 moles $t = 0$ sec.

Change in concentration due to ionization

$(0.1{=}x)$ moles $\rightleftharpoons$ xmoles + xmoles t=equilibrium

Concentration at equilibrium

$(0.1-x) \approx 0.10 \rightleftharpoons$ xmoles + xmoles t=equilibrium

(0.1 - x) is approximately 0.1, because the value of x is very small as compared to 0.1. The reason is that CH_3COOH is a much weak electrolyte.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{x.x}{0.1}$$

Putting the value of K_a

$$1.85x10^{-5}=\frac{x^2}{0.1}$$

or $x^2=0.1x1.8x10^{-5}=1.8x10^{-6}$

Taking square root on both sides

x $= 0.1 \text{ x } 1.8 \text{ x } 10^{-5} = 1.8x10^{-6}$

In other words $[H^+] = 1.3 \text{ x } 10^{-3}$ mole dm^{-3} (amount of acid ionized)

$$\%ionization=\frac{\text{concentration of ionized acid}}{\text{original concentration}} \text{ x } 100$$

$$\%ionization=\frac{1.3x10^{-3}x100}{0.1}=\boxed{1.3} \text{ Answer}$$

Hence, out of 1000 molecules of acetic acid only 13 are dissociated into ions, when 0.1 molar solution is prepared. In other words when 6 g of CH_3COOH i.e 0.1 moles is dissolved in 1000 cm^3 of solution only 13 molecules ionize out of energy 1000 CH_3COOH molecules.

This is known as Ostwald's dilution law, that dilution increases the degree of dissociations.

8.5.0 IONIZATION CONSTANT OF BASES (K_b)

Unlike, strong bases weak Bronsted bases which are proton acceptors, usually consist of molecules or ions. They react with water, remove a proton from it, and generate OH^- ions. Take the examples of NH_3 and CO_3^{2-}.

$$NH_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^{1-}(aq) + OH^-(aq)$$

NH_3 and $C0_3^{2-}$ have acted as bases in above reactions. They have different abilities to accept protons from water molecules. We compare these abilities of bases by knowing the equilibrium constant K_b, which is called base ionization constant of a base.

Let the base is represented by B. Then

$$B(aq) + H_2O(\ell) \rightleftharpoons BH^+(aq) + OH^-(aq)$$

$$K_c = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

Since, the concentration of H_2O constant, being in large excess

So, $$K_c\ [H_2O] = \frac{[BH^+][OH^-]}{[B]}$$

Put $$K_c[H_2O] = K_b$$

Hence $$K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b value of a base is the quantitative measurement of strength of a base Smaller the K_b value, weaker the base. Table (8.9) gives the K_b values for some bases.

Table (8.9) K_b of some important bases

Base	Dissociation	K_b	Relative strength
$NaOH$	$NaOH \rightleftharpoons Na^+ + OH^-$	Very high	Very strong
KOH	$KOH \rightleftharpoons K^+ + OH^-$	Very high	Very strong
$Ca(OH)_2$	$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH$	High	Very strong
NH_4OH	$NH_4OH \rightleftharpoons NH_4^+ + OH^-$	1.81×10^{-5}	Weak
CH_3NH_2 (Mathyl amine)	$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$	4.38×10^{-4}	Weak
$C_6H_5NH_2$ (Aniline)	$C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$	4.7×10^{-10}	Very weak

pK_a and pK_b

Table (8.7) and (8.9), we conclude that the values of K_a and K_b for weak acids and bases are small numbers usually expressed in exponential form. It is convenient to convert them into whole numbers by taking their negative log. Thus we obtain pK_a and pK_b values of acids and bases.

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

Larger the pK_a, weaker is the acid and vice versa. Similarly, larger the pK_b, weaker is the base. If the difference of pK_a values of the two acids is one, then acid with smaller pK_a is ten times stronger than the other. If the difference is two, then one is hundred times stronger than the other.

8.6.0 LOWRY BRONSTED ACID AND BASE CONCEPT

According to this concept, acids are those species which donate the proton or have a tendency to donate and bases are those species which accept the proton or have a tendency to accept the proton.

Whenever, a weak acid or a weak base is dissolved in water, the conjugate acid base pair is produced. There is a close relationship between K_a of the acid, K_b of the conjugate base and K_w of water. Let us have an acid HA, and it gives protons to water in a reversible manner. H_3O^+ gives proton to A^- and is an acid, but A^- accepts H^+ from H_3O^+ and act as a conjugate base of HA.

$$\underset{\text{acid}}{HA} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\substack{\text{conjugate acid}\\ \text{of } H_2O}}{H_3O^+} + \underset{\substack{\text{conjugate base}\\ \text{of HA}}}{A^-}$$

Now,

$$K_c = \frac{[H_3O^+][A^-]}{[H_2O][HA]} \text{ or } K_a = \frac{[H^+][A^-]}{[HA]}$$

In case A^- is dissolved in water, the equation for hydrolysis of conjugate base A^- will be,

$$\underset{\text{base}}{A^-} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{acid}}{HA} + \underset{\text{base}}{OH^-}$$

So, its

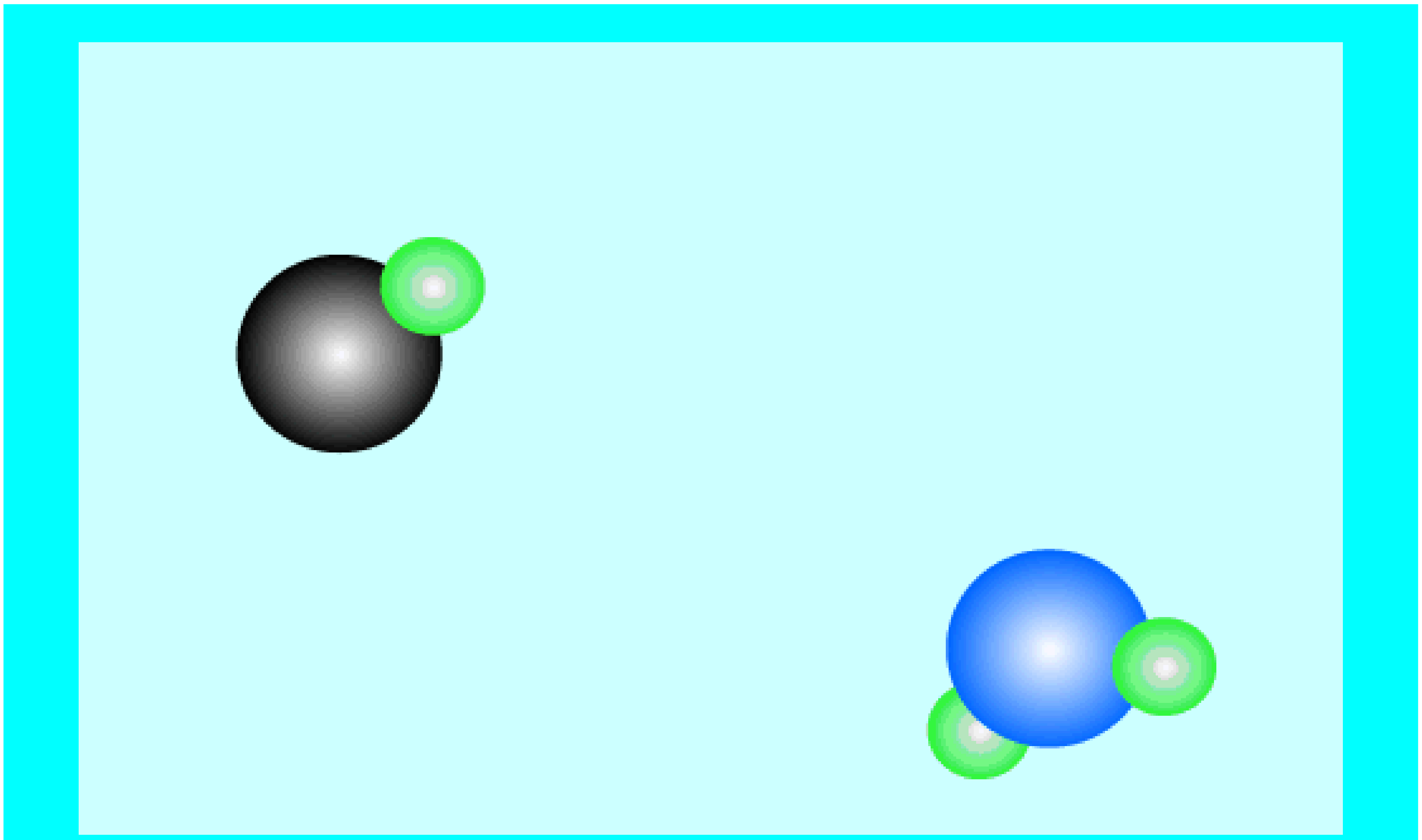
$$K_b = \frac{[HA][OH^-]}{[A^-]}$$

Let us multiply two expressions for K_a and K_b

$$K_a x K_b = \frac{[H^+][A^{1-}]}{[HA]} \text{ x } \frac{[OH^-][HA]}{[A^{1-}]}$$

Or $$K_a x K_b = [H^+][OH^-]$$

Or $$K_a x K_b = K_w$$



Animation 8.11: Lowry Bronsted
Source & Credit : dynamicscience

This equation is useful in the sense that if we know K_a of the acid, we can calculate K_b for the conjugate base and vice versa. The value of K_w is a constant at a given temperature. i.e 10^{-14} at 25c°

Let us take the log of above equation

$$\log(K_a x K_b) = \log(K_w)$$

or $$\log K_a + \log K_b = \log K_w$$

Multiply both sides by '-1'

$$-\log K_a - \log K_b = -\log K_w$$

Since $pK_a = -\log K_a$ and $pK_b = -\log K_b$

or $pK_a + pK_b = pK_w$

Since $pK_w = 14$, at 25^0C hence pK_a and pK_b of conjugate acid base pair has a very simple relation with each other.

$$pK_a + pK_b = 14 \text{ at } 25^oC$$

This equation proves the following facts.

(a) Conjugate base of a very weak acid is relatively very strong base.
(b) Conjugate acid of a very strong base is relatively very weak acid.

So $K_a \propto \dfrac{1}{K_b}$

We can calculate the pK_b of CH_3COO^-, if we know pK_a of CH_3COOH. Similarly, if we know pK_b of NH_3, we can calculate pK_a of NH_4^+ .

8.7 COMMON ION EFFECT

The suppression of ionization of a weak electrolyte by adding a common ion from outside is called common ion effect.

We are familiar with purification of sodium chloride by passing hydrogen chloride gas through saturated brine. Sodium chloride is fully ionized in the solution. Equilibrium constant expression for this process can be written as follows:

$$NaCl(s) \rightleftharpoons Na^+(aq) + Cl^-(aq)$$

$$K_c = \frac{[Na^+][Cl^-]}{[NaCl]}$$

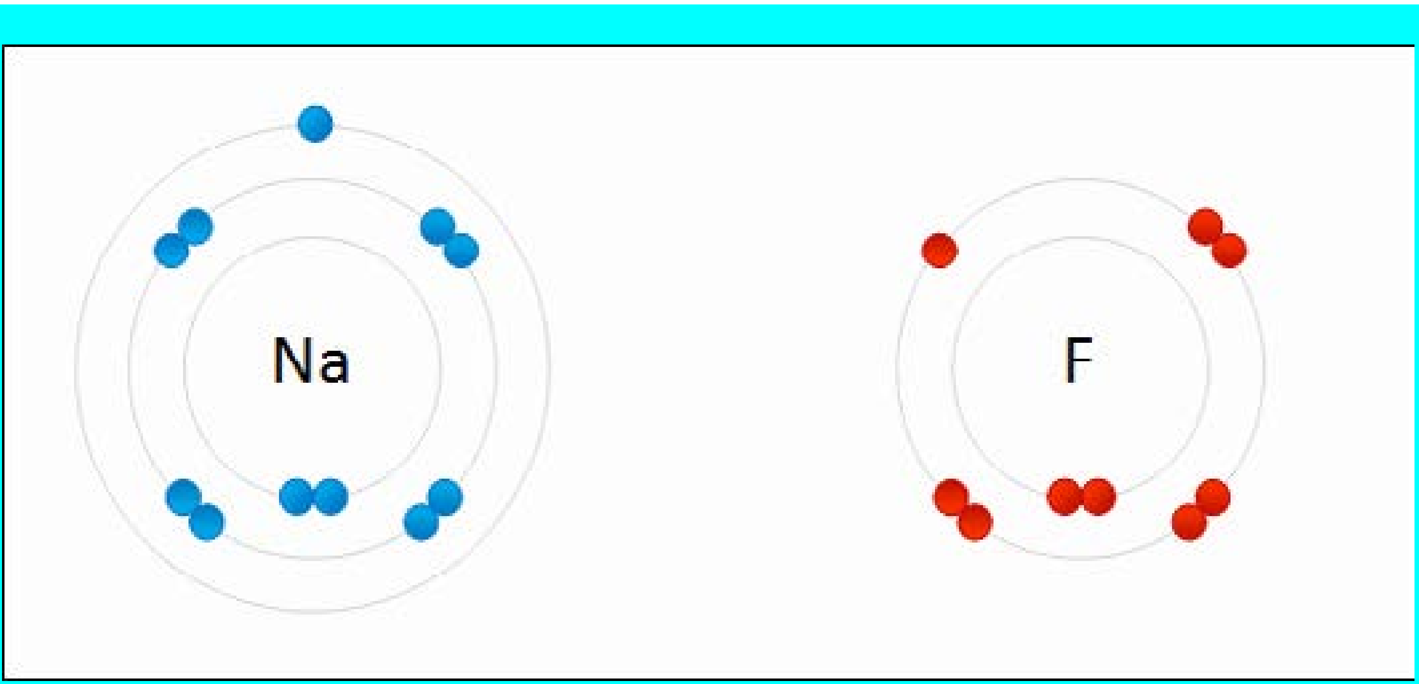
HCl also ionizes in solution

$$HCl \square \quad H^+(aq) + Cl^-(aq)$$

On passing HCl gas, concentration of Cl^- ions is increased, therefore NaCl crystallizes out of the solution to maintain the constant value of the equilibrium constant.

This type of effect is called the common ion effect. The addition of a common ion to the solution of a less soluble electrolyte suppresses its ionization and the concentration of unionized species increases, which may come out as a precipitate.

$$Na^+(aq) + Cl^-(aq) \square \quad NaCl(s)$$



Animation 8.12: COMMON ION
Source & Credit : boundless

More Examples of Common Ion Effect

(i) The solubility of a less soluble salts $KClO_3$ in water is suppressed by the addition of a more soluble salt KCl by common ion effect. K^+ is a common ion. The ionization of $KClO_3$ is suppressed and it settles down as precipitate.

$$KClO_3(s) \rightleftharpoons K^+(aq) + ClO^-_3(aq)$$

$$KCl \rightleftharpoons K^+(aq) + Cl^-(aq)$$

(ii) Similarly, the dissociation of a weak acid H_2S in water can be suppressed by the addition of stronger acid HCl. H^+ is a common ion. H_2S becomes less dissociated in acidic solution. In this way low concentration of S^{-2} ion is developed.

$$H_2S \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$$

This low concentration of S^{-2} ions helps to do the precipitation of radicals of second group basic radicals during salt analysis.

$$HCl(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

(iii) An addition of NH_4Cl in NH_4OH solution suppresses the concentration of OH^- (aq) due to the presence of a large excess of NH_4^+ from NH_4Cl. Actually, NH_4Cl is a strong electrolyte. The combination of these two substances is used as a group reagent in third group basic radicals

$$NH_4Cl(aq) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)$$

$$NH_4OH(aq) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

(iv) Common ion effect finds extensive applications in the qualitative analysis and the preparation of buffers.

8.8.0 BUFFER SOLUTIONS

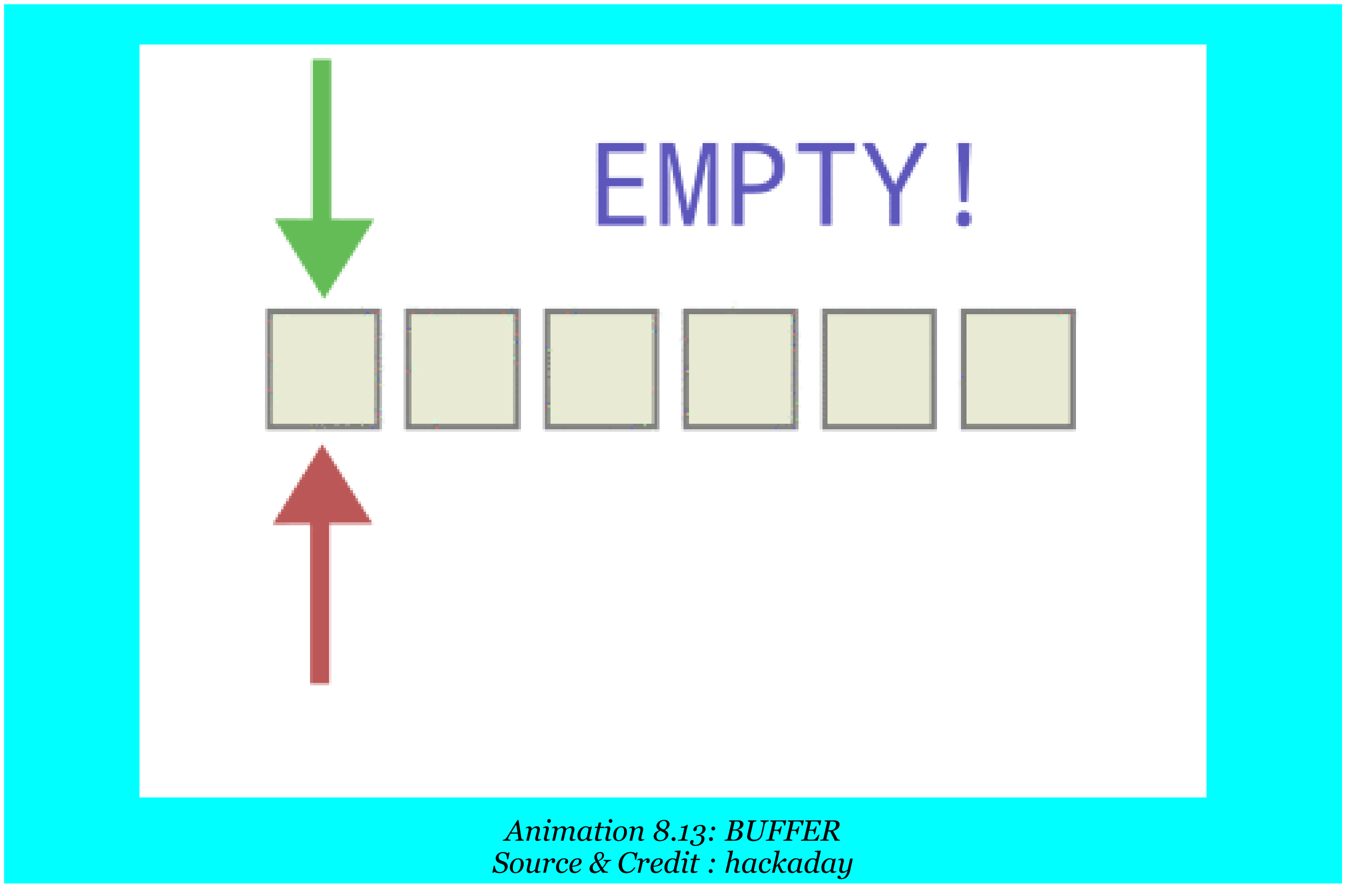
Those solutions, which resist the change in their pH when a small amount of an acid or a base is added to them, are called buffer solutions. They have a specific constant value of pH and their pH values do not change on dilution and on keeping for a long time. Buffer solutions are mostly prepared by mixing two substances.

(i) By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic buffers with pH less than 7. Mixture of acetic acid and sodium acetate is one of the best examples of such a buffer.

(ii) By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic buffers with pH more than 7. Mixture of NH_4OH and NH_4Cl is one of the best examples of such a basic buffer.

(a) Why Do We Need Buffer Solution?

It is a common experience that the pH of the human blood is maintained at pH 7.35, if it goes to 7.00 or 8.00, a person may die.



Animation 8.13: BUFFER
Source & Credit : hackaday

Sometimes one wants to study a reaction under conditions that would suffer any associated change in the pH of the reaction mixture. So, by suitable choice of the solutes, a chemist can ensure that a solution will not experience more than a very small change in pH, even if a small amount of a strong acid or a strong base is added. Buffers are important in many areas of chemistry and allied sciences like molecular biology, microbiology, cell biology, soil sciences, nutrition and the clinical analysis.

Buffer is not a new concept at this stage of our discussion, it is just the application of common ion effect.

(b) How Do the Buffers Act?

Let us take the example of an acidic buffer consisting of CH_3COOH and CH_3COONa. Common ion effect helps us to understand how the buffer will work. CH_3COOH, being a weak electrolyte undergoes very little dissociation. When CH_3COONa, which is a strong electrolyte, is added to CH_3COOH solution, then the dissociation of CH_3COOH is suppressed, due to common ion effect of CH_3COO^- .

$$CH_3COOH(aq)+H_2O(\ell) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

$$CH_3COONa(aq) \rightleftharpoons CH_3COO^-(aq) + Na^+(aq)$$

If one goes on adding CH_3COONa in CH_3COOH solution, then the added concentrations of CH_3COO^- decrease the dissociation of CH_3COOH and the pH of solution increases. The table (8.10) tells us how the pH value of a mixture of two compounds is maintained. Greater the concentration of acetic acid as compared to CH_3COONa, lesser is the pH of solution.

Table (8.10) Effect of addition of acetate ions on the pH of acetic acid solution

$[CH_3COOH]$ (mole dm^{-3})	$[CH_3COO^-]$ (mole dm^{-3})	% Dissociation	pH
0.10	0.00	1.3	2.89
0.10	0.05	0.036	4.44
0.10	0.10	0.018	4.74
0.10	0.15	0.012	4.92

Actually a buffer mentioned above is a large reservoir of CH_3COOH and CH_3COO^- components. When an acid or H_3O^+ ions are added to this buffer, they will react with CH_3COO^- to give back acetic acid and hence the pH of the solution will almost remain unchanged. The reason is that CH_3COOH being a week acid will prefer to remain undissociated. Similarly, the puffer solution consisting of NH_4Cl and NH_4OH, can resist the change of pH and pOH, when acid or base is added from outside. When a base or OH^- ions are added in it, they will react with H_3O^+ to give back H_2O and the pH of the solution again will remain almost unchanged.

Calculating the pH of a Buffer

Let us try to learn, how a buffer of definite pH can be prepared. Consider a weak acid HA and its salt NaA with a strong base say NaOH. The reversible reactions for dissociation of HA are as follows:

$$HA \rightleftharpoons H^+ + A^-$$

$$NaA \rightleftharpoons Na^+ + A^-$$

The dissociation constant of a weak acid HA is given by:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Rearranging the equation,

$$[H^+] = \frac{K_a[HA]}{[A^-]}$$

The concentration of A in the reaction mixture is predominantly being supplied by NaA which is a stronger electrolyte than HA, and the ionization of HA is being suppressed by common ion effect (A^- is the common ion in this buffer solution). Taking log of this equation.

$$\log[H^+] = \log\frac{K_a[HA]}{[A^-]}$$

$$\log[H^+] = \log(K_a) + \log\frac{[HA]}{[A^-]}$$

Multiplying with (-1) on both sides

$$-\log[H^+] = -\log(K_a) - \log\frac{[HA]}{[A^-]}$$

Since - $-\log[H^+] = pH$ and $-\log(K_a) = pK_a$

So, $$pH = pK_a - \log\frac{[HA]}{[A^-]}$$

$[A^-]$ refers to the concentration of the salt. Actually, maximum possible concentrate of A^- is given by NaA, being a strong electrolyte

$$pH = pK_a - \log\frac{[acid]}{[salt]}$$

Interchanging the numerator and denominator the sign of log changes

or $$pH = pK_a + \log\frac{[salt]}{[acid]}$$

This relationship is called Henderson's equation. This equation shows that two factors evidently govern the pH of a buffer solution. First is the pK_a of the acid used and second is the ratio of the concentrations of the salt and the acid. The best buffer is prepared by taking equal concentration of salt and acid.

So, pH is controlled by pK_a of the acid. For example, for acetic acid sodium acetate buffer, if

$$[CH_3COOH] = [CH_3COONa]$$

then $$pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$pH = pK_a + \log(1)$$

so $$pH = pK_a + 0 = pK_a$$

$$pH = 4.74.$$

It means that the pH of this buffer is just equal to the pK of the acid. Similarly for formic acid sodium formate buffer, if

$$[HCOOH] = [HCOONa]$$

then $$pH = pK_a + 0 = pK_a$$

so $$pH = 3.78.$$

To prepare a buffer of definite pH, we need a suitable acid for that purpose. We can also manage the buffer of our own required pH by suitably selecting the concentration ratio of the salt and the acid. If [CH_3COOH] is 0.1 mole dm and that of [CH_3COONa] is 1.0 mole dm^{-3} then

$$\text{pH}= 4.74 + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH}= 4.74 + \log \frac{1.0}{0.1} = 4.74 + \log 10$$

Since $\log 10 = 1$

$$\text{pH} = 4.74 + 1 = 5.74$$

$$\text{pH} = 5.74$$

Similarly, if [CH_3COOH] is 1.0 mole dm^{-3} and [CH_3COONa] is 0.1 moles dm^{-3} , then

$$\text{pH}= 4.74 + \log \frac{0.1}{1}$$

$$\text{pH}= 4.74 + \log \frac{1}{10} \qquad =4.74+\log 10^{-1}$$

$$\text{pH} = 4.74 - 1 = 3.74$$

or $\text{pH} = 3.74$

Anyhow, the above mentioned combination can be used to prepare buffers from 3.74 to 5.74. The buffer beyond this range will not be good buffers and will have small buffer capacities.

Just like acidic buffers, the basic buffer have their own Henderson equation. For this purpose, let us use the mixture of NH_4OH and NH_4Cl. NH_4OH is a solution of NH_3 in water and it can be represented as follows:

$$NA_3(aq) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

$$K_b= \frac{[NH_4^+][OH^{-1}]}{[NH_3]}$$

Taking the log, multiplying with negative sign and rearranging, we get

$$\text{pOH} = \text{pK}_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

Using this relationship, we can prepare a basic buffer of the required pOH or pH by suitably selecting a base and adj usting the ratio of [salt] / [base].

Example :

Calculate the pH of a buffer solution in which 0.11 molar CH_3COONa and 0.09 molar acetic acid solutions are present. K_a for CH_3COOH is 1.85×10^{-5}

Solution:

0.11M CH_3COONa solution means that 0.11 moles are dissolved in 1 dm^3 of solution.

$$[CH_3COONa] = 0.11\text{M}$$

$$[CH_3COOH] = 0.09\text{M}$$

$$K_a \text{ of } CH_3COOH = 1.85\text{x}10^{-5}$$

$$\text{pK} = -\log(1.8\text{x}10^{-5}) = 4.74$$

$$\text{pH} = \text{pK}_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pH} = \text{pK}_a + \log\frac{0.11}{0.09}$$

$$\text{pH} = 4.74 + 0.087 = \boxed{4.83} \text{ Answer}$$

Since, the concentration of CH_3COONa is more than that of CH_3COOH, so pH of buffer is greater than 4.74. In other words, the solution has developed the properties of a base, because CH_3COONa has Na^+ ion which is from a strong base.

8.8.1 Buffer Capacity

The buffer capacity of a solution is the capability of a buffer to resist the change of pH. It can be measured quantitatively that how much extra acid or base, the solution can absorb before the buffer is essentially destroyed. Buffer capacity of a buffer solution is determined by the sizes of actual molarities of its components. So,a chemist must decide before making the buffer solution, what outer limits of change in its pH can be tolerated.

Let us do some calculations to check the effectiveness of a buffer system. Consider, that we have a buffer having 0.11 molar CH_3COONa and 0.09 molar acetic acid. Its pH will be 4.83. Let us add 0.01 moles of NaOH in one dm^3 of the buffer solution (remember that addition of 0.01 moles NaOH per dm^3 of solution will change the pH from 7.00 to 12.00 in pure water).

Since NaOH is a strong base and it is 100% dissociated, it generates 0.01 moles OH^-. Out of 0.09 mole of CH_3COOH, 0.01 mole will react with OH^- and 0.08 moles of CH_3COOH is left behind in one dm^3 of solution. This neutralization of course makes the identical change in the amount of CH_3COONa and its concentration will increase from 0.11 mole to 0.12 mole.

Henderson equation is, $\text{pH} = \text{pK}_a + \log\frac{[\text{salt}]}{[\text{acid}]}$

Putting the new concentrations of salt and acid after addition of NaOH.

$$\text{pH} = 4.74 + \log\frac{0.12}{0.08}$$

$$\text{pH} = 4.74 + \log(1.5)$$

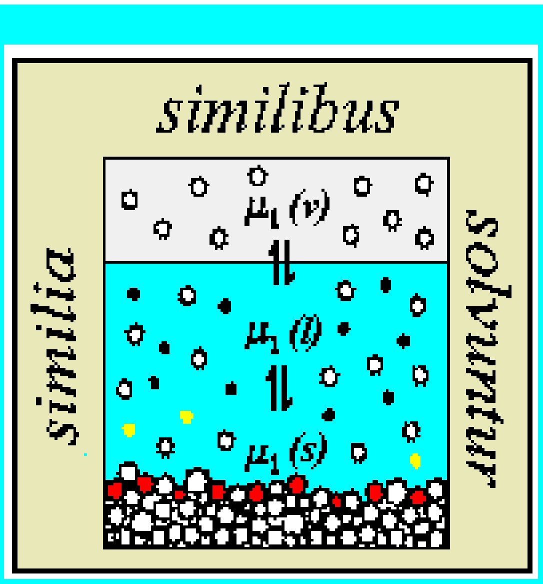
$$\text{pH} = 4.74 + 0.176$$

$$\text{pH} = \boxed{4.92}\ \text{Answer}$$

It means that there is a very small change in pH from 4.83 to 4.92, that is only a difference of 0.1. So we reach the conclusion that a buffer does not hold the pH exactly constant. But it does a very good job in limiting the change in pH to a very small amount.

8.9.0 EQUILIBRIA OF SLIGHTLY SOLUBLE IONIC COMPOUNDS (SOLUBILITY PRODUCT)

When a soluble ionic compound is dissolved in water, like NaCl, it dissociates completely into ions. But for slightly soluble salts the dissociation is not complete at equilibrium stage. For example, when $PbCl_2$ is shaken with water the solution contains Pb^{2+}, Cl^- and undissociated $PbCl_2$. It means that equilibrium exists between solid solute, $PbCl_2$ and the dissolved ions, Pb^{2+} and Cl^-.



Animation 8.14: SOLUBILITY
Source & Credit : iupac

$$PbCl_2(s) \rightleftharpoons PbCl_2(aq) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

According to law of mass action $K_c = \frac{[Pb^{2+}_{(aq)}][Cl^-_{(aq)}]^2}{[PbCl_2]}$

Lead sulphate is a well known sparingly soluble compound and it dissociates to a very small extent like $PbCl_2$.

$$PbSO_4(s) \rightleftharpoons PbSO_4(aq) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$$

Law of mass action applied to the dissociation of $PbSO_4$ gives equilibrium constant K_c

$$K_c = \frac{[Pb^{2+}][SO_4^{2-}]}{[PbSO_4]}$$

Being a sparingly soluble salt the concentration of lead sulphate ($PbSO_4$) almost remains constant. Bring $[PbSO_4]$ on L.H.S. with K_c

$$K_c[PbSO_4] = [Pb^{2+}][SO_4^{2-}]$$

if $$K_c[PbSO_4] = K_{sp}$$

then $$K_{sp}=[Pb^{2+}(aq)][SO_4^{2-}(aq)]= 1.6\text{x}10^{-8} \text{ at } 25^{\circ}C$$

K_{sp} is called the solubility product of $PbSO_4$. It is the product of molar solubilities of two ions at equilibrium stage.

Similarly,for $PbCl_2$ $$K_{sp}=[Pb^{2+}(aq)][Cl^{-}(aq)]^2$$

K_{sp} is usually a very small quantity at room temperature. The value of K_{sp} is temperature dependent. For a general, sparingly soluble substance, A_xB_y.

$$A_xB_y \rightleftharpoons xA^{+y}+yB^{-x}$$

$$K_{sp}=[A^{+y}]^x+[B^{-x}]^y$$

So, the solubility product is the product of the concentrations of ions raised to an exponent equal to the co-efficient of the balanced equation. The value of K_{sp} is a measure of how far to the right dissolution proceeds at equilibrium i.e. saturation. The following Table (8.10) shows us the K_{sp} values of slightly soluble ionic compounds.

Smaller the value of K_{sp}, lesser the capability to be dissociated.

Table (8.10) K_{sp} values for some ionic compounds (compounds are arranged alphabetically).

Salt	Ion Product	K_{sp}	Salt	Ion Product	K_{sp}
$AgBr$	$[Ag^+][Br^-]$	$5.0x10^{-13}$	CuS	$[Cu^{2+}][S^{2-}]$	$8x10^{-34}$
Ag_2CO_3	$[Ag^+]^2[CO_3{}^{2-}]$	$8.1x10^{-12}$	FeS	$[Fe^{2+}][S^{2-}]$	$6.3x10^{-18}$
$AgCl$	$[Ag^+][Cl^-]$	$1.8x10^{-10}$	Fe_2S_3	$[Fe^{3+}][S^{2-}]^3$	$1.4x10^{-85}$
Agl	$[Ag^+][I^-]$	$8.3x10^{-17}$	$Fe(OH)_3$	$[Fe^{3+}][OH^-]^3$	$1.6x10^{-39}$
Ag_2S	$[Ag^+]^2[S^{2-}]$	$8x10^{-48}$	HgS	$[Hg^{2+}][S^{2-}]$	$2x10^{-50}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	$3x10^{-34}$	$MgCO_3$	$[Mg^{2+}][CO_3{}^{2-}]$	$3.5x10^{-8}$
$BaCO_3$	$[Ba^{2+}][CO_3{}^{2-}]$	$2x10^{-9}$	$Mg(OH)_2$	$[Mg^{2+}][OH^-]^2$	$6.3x10^{-10}$
$BaSO_4$	$[Ba^{2+}][SO_4{}^{2-}]$	$1.1x10^{-10}$	MnS	$[Mn^{2+}][S^{2-}]$	$3x10^{-11}$
CdS	$[Cd^{2+}][S^{2-}]$	$8.0x10^{-27}$	$PbCl_2$	$[Pb^{2+}][Cl^-]^2$	$1.6x10^{-5}$
$CaCO_3$	$[Ca^{2+}][CO_3{}^{2-}]$	$3.3x10^{-9}$	$PbCrO_4$	$[Pb^{2+}][CrO_4{}^{2-}]$	$2.3x10^{-13}$
CaF_2	$[Ca^{2+}][F^-]^2$	$3.2x10^{-11}$	$PbSO_4$	$[Pb^{2+}][SO_4{}^{2-}]$	$1.6x10^{-8}$
$Ca(OH)_2$	$[Ca^{2+}][OH^-]^2$	$6.5x10^{-6}$	PbS	$[Pb^{2+}][S^{2-}]$	$8.0x10^{-28}$

8.9.1 Applications of solubility product

(a) Determination of K_{sp}, from solubility

From the solubility of the compounds, we can calculate K_{sp} of the salt. The solubility for most of the compounds are given in terms of the grams of the solute per 100 g of water. Since the quantity of solute is very very small, so 100 g of water solution is considered to be 100 ml of solution. The reason is that the density of water is very close to unity. Hence, we get the concentration in moles dm^{-3}. The number of moles of solute dm^{-3} of the solution is calculated by dividing the mass of solute by its molar mass. Then by using the balanced equation, we find the molarity of each ion and then find K_{sp}.

Example 6 :

The solubility of PbF_2 at 25^0C is 0.64 gdm^{-3}. Calculate K_{sp} of PbF_2.

Solution:

First of all convert the concentration from g dm 1 to moles dm 3;

$$\text{Mass of } PbF_2 \text{ dessolved } dm^{-3} = 0.64g$$

$$\text{Molecular mass of } PbF_2 = 245.2g\ mol^{-1}$$

Number of moles of $PbF_2 = \dfrac{0.64gdm^{-3}}{245.2gmol^{-1}} = 2.6x10^{-3}$

The balanced equation for dissociation of PbF_2 is,

$$PbF_2(s) \rightleftharpoons Pb^{2+}(aq) + 2F^{1-}(aq)$$

$2.6x10^{-3}M$ 0 + 0 t = 0 sec

"zero" moles $2.6x10^{-3}$moles + $2x2.6x10^{-3}$moles t=equilibrium

The expression of K_{sp} is

$$K_{sp} = [Pb^{2+}][F^-]^2$$

Putting values of concentration

$$K_{sp} = 2.6x10^{-3}x(2x2.6x10^{-3})^2 = \boxed{7.0x10^{-8}}\text{Answer}$$

(b) Determination of Solubility from K_{sp}

For this purpose we need the formula of the compound and K_{sp} value. Then the unknown molar solubility S is calculated and the concentration of the ions are determined. Table (8 .11) shows the relationship between the K_{sp} values and the solubility of some sparingly soluble compounds.

Table (8.11) Relationship between K_{sp} and the solubility of some compounds.

Formula	No. of ions	$\frac{\text{Cation}}{\text{Anion}}$	K_{sp}	Solubility gdm^{-3}
$MgCO_3$	2	1 / 1	$3.61\text{x}10^{-8}$	$1.9\text{x}10^{-4}$
$PbSO_4$	2	1 / 1	$1.69\text{x}10^{-8}$	$1.3\text{x}10^{-4}$
$BaCrO_4$	2	1 / 1	$1.96\text{x}10^{-10}$	$1.4\text{x}10^{-5}$
$Ca(OH)_2$	3	1 / 2	$6.5\text{x}10^{-6}$	$1.175\text{x}10^{-2}$
BaF_2	3	1 / 2	$1.35\text{x}10^{-5}$	$7.2\text{x}10^{-3}$
CaF_2	3	1 / 2	$3.2\text{x}10^{-11}$	$2.0\text{x}10^{-4}$
Ag_2CrO_4	3	2 / 1	$2.6\text{x}10^{-12}$	$8.7\text{x}10^{-5}$

Example 7 :

$Ca(OH)_2$ is a sparingly soluble compound. Its solubility product is $6.5\text{x}10^{-6}$ Calculate the solubility of $Ca(OH)_2$.

Solution:

Let the solubility is represented by S in terms of moles dm^{-3}.
The balanced equation is

$$Ca(OH)_2 \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

$Ca(OH)_2 \rightleftharpoons \quad 0 \quad + \quad 0$ Initial stage

$Ca(OH)_2 \rightleftharpoons \quad S \quad + \quad 2S$ Equilibrium stage

The $K_{sp}=6.5x10^{-6}$

The concentration of OH^- is double than the concentration of Ca^{2+}, so

$$K_{sp} = [Ca^{2+}][OH^-]^2 = S \text{ x } (2S)^2$$

$$4S^3 = 6.5 \text{ x } 10^{-6}$$

So, $$S = \left(\frac{6.5x10^{-6}}{4}\right)^{1/3} = (1.625x10^{-6})^{1/3}$$

$$S = (1.625)^{1/3} \text{ x}10^{-2}$$

$$S = 1.175 \text{ x}10^{-2}$$

Hence, at equilibrium stage 1.175 x 10^{-2} moles dm^{-3} of Ca^{2+} and 2x1.175 x 10^{-2} = 2.75 x 10^{-2} moles dm^{-3} OH^- are present in the solution. In this way, we have calculated the individual concentrations of Ca^{2+} and OH^- ion from the solubility product of $Ca(OH)_2$.

Effect of Common Ion on Solubility

The presence of a common ion decreases the solubility of a slightly soluble ionic compound. In order to explain it, consider a saturated solution of $PbCrO_4$, which is a sparingly soluble ionic salt.

$$PbCrO_4(aq) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$$

Now add Na_2CrO_4 which is a soluble salt. CrO_4^{2-} is the common ion. It combines with Pb^{2+} to form more insoluble $PbCrO_4$. So equilibrium is shifted to the left to keep K_{sp} constant.

KEY POINTS

1. There versible chemical reactions can achieve a state in which the forward and the reverse processes are occurring at the same rate. This state is called state of chemical equilibrium. The concentrations of reactants and products are called equilibrium concentrations and the mixture is called equilibrium mixture.
2. Law of mass action provides the relationship among the concentrations of reactants and products of a system at equilibrium stage.The ratio of concentrations of the products to the concentrations of reactants is called equilibrium constant. The equilibrium constants are expressed as K_c, K_p, K_n and K_x.
3. The value of equilibrium constant can predict the direction and extent of a chemical reaction.
4. The effect of change of concentration, temperature, pressure or catalyst in a reaction can be s adied witii the help of Le-Chatelier's principle. Increasing concentrations of reactants or decreasing concentrations of products or heating of the endothermic reactions shifts the reaction to the forward direction. The change of temperature disturbs the equilibrium position and the equilibrium constant of reaction. A catalyst decreases the time to reach the equilibrium and does not alter the equilibrium position and equilibrium constant under the given conditions.
5. Water is a very weak electrolyte and ionizes to a slight degree. The extent of this a autoionization is expressed by ionic product of water called K_w, having a value 10^{-14} at 25^0C. The addition of an acid or a base changes the $[H^+]$ and $[OH^-]$, but the ionic product remains the same at 25^0C.
6. The concentration of H^+ is expressed in terms of pH and that of $[OH^-]$ in terms of pOH. Neutral water has a pH = 7 and pOH= 7.The value of pK_w is 14 at 25^0C.
7. According to Lowry-Bronsted concept of an acid and a base the conjugate base of a strong acid is always weak. So $pK_a + pK_b = pK_w$ Where pK_a and pK_b are the parameters to measure the strengths of acids and bases.
8. Those solutions which resist the change of pH are called buffer solutions. Buffer solutions of pH below 7 are prepared by mixing a weak acid and salt of it with a strong base while basic buffers can be prepared by combining a weak base and salt of it with a strong acid. Hendersen's equation guides us quantitatively to have the buffer solutions of good buffer capacity and to select the pair of compounds for this purpose.
9. The solubility of sparingly soluble substances are calculated from the solubility product data. This data provides us the information about the selective precipitation and fractional precipitation.
10. Common ion effect operates best in buffer solutions, and purification of certain substances. It is one of the best applications of Le-Chatelier's principle.

EXERCISE

Q1. Multiple choice questions

i) For which system does the equilibrium constant, K_c has units of (concentration)’?

(a) $N_2+3H_2 \rightleftharpoons 2NH_3$

(b) $H_2+I_2 \rightleftharpoons 2HI$

(c) $2NO_2 \rightleftharpoons N_2O_4$

(d) $2HF \rightleftharpoons H_2+F_2$

ii) Which statement about the following equilibrium is correct

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -188.3 kJ\ mol^{-1}$$

(a) The value of K_p falls with a rise in temperature

(b) The value of K_p falls with increasing pressure

(c) Adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide

(d) The value of K_p is equal to K_c.

iii) The pH of 10^{-3} mol dm^{-3} of an aqueous solution of H_2SO_4 is

(a) 3.0 (b) 2.7 (c) 2.0 (d) 1.5

iv) The solubility product of AgCl is 2.0×10^{-10} mol^2 dm^{-6}. The maximum concentration of Ag^+ ions in the solution is

(a) 2.0×10^{-10} mol dm^{-3} (b) 1.41×10^{-5} mol dm^{-3}

(c) 1.0×10^{-10} mol dm^{-3} (d) 4.0×10^{-20} mol dm^{-3}

v) An excess of aqueous silver nitrate is added to aqueous barium chloride and precipitate is removed by filtration. What are the main ions in the filtrate?

(a) Ag^+ and NO_3^- only (b) Ag^+ and Ba^{2+} and NO_3^-

(c) Ba^{2+} and NO_3^- only (d) Ba^{2+} and NO_3^- and Cl^-

Q2. Fill in the blanks

i) Law of mass action states that the__________ at which a reaction proceeds, is directly proportional to the product of the active masses of the __________.

ii) In an exothermic reversible reaction,_______ temperature will shift the equilibrium towards the forward direction.

iii) The equilibrium constant for the reaction $2O_3 \rightleftharpoons 3O_2$ is 10^{55} at 25^0C, it tells that ozone is__________ at room temperature.

iv) In a gas phase reaction, if the number of moles of reactants are equal to the number of moles of the products, K_c of the reaction is__________ to the K_p.

v) Buffer solution is prepared by mixing together a weak base and its salt with or a weak acid and its salt with__________.

Q3. Label the sentences as True or False.

i) When a reversible reaction attains equilibrium both reactants and products are present in a reaction mixture.

ii) The K_c of the reaction

$$A + B \rightleftharpoons C + D$$

is given by

$$K_c = \frac{[C][D]}{[A][B]}$$

therefore it is assumed that

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

iii) A catalyst is a substance which increases the speed of the reaction and consequently increases the yield of the product.

iv) Ionic product K_w of pure water at 25^0C is 10^{-14} mol^2 dm^{-6} and is represented by an expression $K_w = [H^+][OH^-] = 10^{-14}$ mol^2 dm^{-6}

v) AgCl is a sparingly soluble ionic solid in water. Its solution produces excess of Ag^+ and Cl^- ions.

Q4 (a) Explain the term s" reversible reaction" and "state of equilibrium".

(b) Define and explain the Law of mass action and derive the expression for the equilibrium constant(K_c).

(c) Write equilibrium constant expression for the following reactions

(i) $Sn^{+2}(aq)+2Fe^{3+}(aq) \rightleftharpoons Sn^{4+}(aq)+2Fe^{2+}(aq)$

(ii) $Ag^{+}(aq)+Fe^{2+}(aq) \rightleftharpoons Fe^{3+}(aq)+Ag(s)$

(iii) $N_2(g)+O_2(g) \rightleftharpoons 2NO(g)$

(iv) $4NH_3(g)+5O_2(g) \rightleftharpoons 4NO(g)+6H_2O(g)$

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

Q5 (a) Reversible reactions attain the position of equilibrium which is dynamic in nature and not static. Explain it.

(b) Why do the rates of forward reactions slow down when a reversible reaction approaches the equilibrium stage?

Q6 When a graph is plotted between time on x-axis and the concentrations of reactants and products on y-axis for a reversible reaction, the curves become parallel to time axis at a certain stage.

(a) At what stage the curves become parallel ?

(b) Before the curves become parallel, the steepness of curves falls! Give reasons.

(c) The rate of decrease of concentrations of any of the reactants and rate of increase of concentrations of any of the products may or may not be equal, for various types of reactions, before the equilibrium time. Explain it.

Q7 (a) Write down the relationship of different types of equilibrium constants i.e. K_c and K_p for the following general reaction.

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

(b) Decide the comparative magnitudes of K_c and K_p for the following reversible reactions.

i) Ammonia synthesis ii) Dissociation of PCl_5

Q8 (a) Write down K_c for the following reversible reactions. Suppose that the volume of reaction mixture in all the cases is 'V' dm^3 at equilibrium stage.

i) $CH_3COOH + CH_3CH_2OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

ii) $H_2 + I_2 \rightleftharpoons 2HI$

iii) $2HI \rightleftharpoons H_2 + I_2$

iv) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

v) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

(b) How do you explain that some of the reactions mentioned above are affected by change of volume at equilibrium stage.

Q9 Explain the following two applications of equilibrium constant. Give examples

i) Direction of reaction ii) Extent of reaction

Q10 Explain the following with reasons.

(a) The change of volume disturbs the equilibrium position for some of the gaseous phase reactions but not the equilibrium constant.

(b) The change of temperature disturbs both the equilibrium position and the equilibrium constant of a reaction.

(c) The solubility of glucose in water is increased by increasing the temperature.

Q11 (a) What is an ionic product of water? How does this value vary with the change in temperature? Is it true that its value increase 75 times when the temperature of water is increased form 0^0C to 100 ^{0}C.

(b) What is the justification for the increase of ionic product with temperature?

(c) How would you prove that at 25^0C, $1dm^3$ of water contains 10^{-7} moles of H_3O^+ and10^{-7} moles of OH

Q12 (a)Define pH and pOH. How are they related with pK_w.

(b) What happens to the acidic and basic properties of aqueous solutions when pH varies from zero to 14?

(c) Is it true that the sum of pK_a and pK_b is always equal to 14 at all temperatures for any acid? If not why?

Q13 (a) What is Lowry Bronsted idea of acids and bases? Explain conjugate acid and bases.

(b) Acetic acid dissolves in water and gives proton to water, but when dissolved in H_2SO_4, it accepts protons. Discuss the role of acetic acid in both cases.

Q14 In the equilibrium

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad \Delta H = +90 kJ\ mol^{-1}$$

What is the effect on

(a) the position of equilibrium (b) equilibrium constant? if

i) temperature is increased ii) volume of the container is decreased

iii) catalyst is added iv) chlorine is added

Explain your answer.

Q15. Synthesis of ammonia by Haber's process is an exothermic reaction.

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ÄH= -92.46 kJ

(a) What should be the possible effect of change of temperature at equilibrium stage?
(b) How does the change of pressure or volume shifts the equilibrium position of this reaction?
(c) What is the role of the catalyst in this reaction?
(d) What happens to equilibrium position of this reaction if NH_3 is removed from the reaction vessel from time to time?

Q16 Sulphuric acid is the king of chemicals. It is produced by the burning of SO_2 to SO_3 through an exothermic reversible process.
(a) Write the balanced reversible reaction.
(b) What is the effect of pressure change on this reaction?
(c) Reaction is exothermic but still the temperature of 400-500^{0}C is required to increase the yield of SO_3. Give reasons.

Q17 (a) What are buffer solutions? Why do we need them in daily life?
(b) How does the mixture of sodium acetate and acetic acid give us the acidic buffer?
(c) Explain that a mixture of NH_4OH and NH_4Cl gives us the basic buffer.
(d) How do you justify that the greater quantity of CH_3COONa in acetic acid decreases the dissociating power of acetic acid and so the pH increases.
(e) Explain the term buffer capacity.

Q18 (a) What is the solubility product? Derive the solubility product expression for sparingly soluble compounds, AgCl, Ag_2CrO_4 and $PbCl_2$.
(b) How do you determine the solubility product of a substance when its solubility is provided in grams/100 g of water?
(c) How do you calculate the solubility of a substance from the value of solubility product?

Q19 K_c value for the following reaction is 0.016 at 520^{0}C

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

Equilibrium mixture contains [HI] = 0.08 M, [H_2] = 0.01M, [I_2] = 0.01M. To this mixture more HI is added so that its new concentration is 0.096M. What will be the concentration of [HI], [H_2] and [I_2] when equilibrium is re-established.

(Ans: 0.0926 mole, 0.01168 mole, 0.01168 mole)

Q20 The equilibrium constant for the reaction between acetic acid and ethyl alcohol is 4.0. A mixture of 3moles of acetic acid and one mole of C_2H_5OH is allowed to come to equilibrium. Calculate the amount of ethyl acetate at equilibrium stage in number of moles and grams. Also calculate the masses of reactants left behind.

(Ans: 79.5g,126g,4.6g)

Q21 Study the equilibrium

$$H_2O(g)+CO(g) \rightleftharpoons H_2(g)+CO_2(g)$$

(a) Write an expression of K_p

(b) When 1.00 mole of steam and 1.00 mole of carbon monoxide are allowed to reach equilibrium, 33.3 % of the equilibrium mixture is hydrogen. Calculate the value of K_p. State the units of K_p.

(Ans: 4, K, has no unit)

Q22 Calculate the pH of

(a) 10^{-4} mole dm^{-3} of HCl (Ans: 4)

(b) 10^{-4} mole dm^{-3} of $Ba(OH)_2$ (Ans: 10.3)

(c) 1.0 mole dm^{-3} of H_2X, which is only 50% dissociated. (Ans: zero)

(d) 1.0 mole dm^{-3} of NH_4OH which is 1% dissociated. (Ans: 12)

Q23

(a) Benzoic acid, C_6H_5COOH, is a weak mono-basic acid (K_a= 6.4 x 10^{-5} mol dm^{-3}). What is the pH of a solution containing 7.2 g of sodium benzoate in one dm^3 of 0.02 mole dm^{-3} benzoic acid.

(Ans: 4.59)

(b) A buffer solution has been prepared by mixing 0.2 M CH_3COONa and 0.5 M CH_3COOH in 1 dm^3 of solution. Calculate the pH of solution. pK_a of acid = 4.74 at 25⁰C. How the values of pH will change by adding 0.1 mole of NaOH and 0.1 mole of HCl separately.

(Ans: 4.34, 4.62, 3.96)

Q24 The solubility of CaF, in water at 25°C is found to be 2.05 x 10 1 mol dm f. What is the value of K_{sp} at this temperature.

(Ans: 3.446 x 10^{-11})

Q25 The solubility product of Ag_2CrO_4 is 2.6 x 10^{-2} at 25⁰C. Calculate the solubility of the compound.

(Ans: 0.1866 mol dm^{-3})