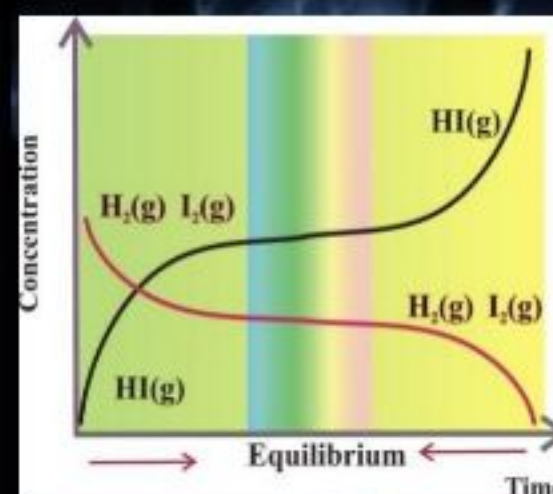


2. Chemical Equilibrium



Contents

2.1 The concept of equilibrium

- 2.1.1 Equilibrium in physical processes
- 2.1.2 Equilibrium in chemical processes
- 2.1.3 Law of chemical equilibrium and equilibrium constant
- 2.1.4 Equilibrium constant expression for a reaction in general terms
- 2.1.5 Extent of reaction
- 2.1.6 Different forms of writing equilibrium constant expression
- 2.1.7 Equilibrium constant in gaseous system
- 2.1.8 Heterogeneous equilibria
- 2.1.9 Equilibrium constant expressions for multi-step reactions
- 2.1.10 Predicting the direction of reaction and calculations based on equilibrium constant
- 2.1.11 Calculating equilibrium concentrations
- 2.1.12 Factors affecting the equilibrium

2.2 Ionic equilibrium in aqueous solutions

- 2.2.1 Acids, bases (and salts)
- 2.2.2 Conjugate acid – base pairs
- 2.2.3 Ionization of acids and bases
- 2.2.4 The ionization constant of water and its ionic product
- 2.2.5 The pH scale
- 2.2.6 Weak acids and ionization (dissociation) constant
- 2.2.7 Weak bases and base ionization constant
- 2.2.8 Relation between K_a and K_b
- 2.2.9 Hydrolysis of salts and the pH of their solutions
- 2.2.10 Aqueous solutions containing a common ion
- 2.2.11 Volumetric titrations

- 2.2.12 Di- and polybasic acids and di- and polyacidic bases
- 2.2.13 Acid-base indicators

2.3 Buffer solutions

2.4 Solubility equilibria

- 2.4.1 Ionic and covalent solutions
- 2.4.2 Solubility product (solubility product constant)
- 2.4.3 Solubility and solubility product calculations
- 2.4.4 Predicting the formation of a precipitate
- 2.4.5 Factors affecting solubility
- 2.4.6 pH effect
- 2.4.7 Application of solubility product in qualitative (cation) analysis

2.5 Equilibria in different phases

- 2.5.1 Evaporation of a liquid in a closed container
- 2.5.2 Measuring the equilibrium (saturated) vapour pressure
- 2.5.3 The variation of saturated vapour pressure with temperature
- 2.5.4 Boiling point
- 2.5.5 Enthalpy of vapourization
- 2.5.6 Phase diagrams of pure substances

2.6 Liquid - vapour equilibrium in binary liquid systems

- 2.6.1 Characteristics of ideal mixtures
- 2.6.2 Immiscible liquid – liquid systems

2.7 Partition/ Distribution coefficient

Introduction

In the previous units, we have analyzed key questions about chemical reactions: What happens, how fast and by what mechanism does it happen? It is very much needed to know that “to what extent does it happen?” The stoichiometry of the balanced chemical equation, and the kinetics of the reaction explain the answers to first two questions respectively, and in this unit we look for the answer to the question, how far does a reaction proceed toward completion before it reaches a state of **equilibrium** a state in which the concentrations of reactants and products no longer change. This state is reached when the concentrations of reactants and products remain constant over time. Equilibrium can be established for both physical processes and chemical reactions. The reaction may be fast or slow depending on the experimental conditions and the nature of the reactants. When the reactants in a closed vessel at a particular temperature react to give products, the concentrations of the reactants keep on decreasing, while those of products keep on increasing for some time after which there is no change in the concentrations of either the reactants or products. This stage of the system is the dynamic equilibrium and the rates of the forward and reverse reactions become equal. At this dynamic equilibrium stage it is recognized that there is no change in macroscopic properties such as pressure, colour of the solution, or concentration of the solution at a constant temperature. However, at the atomic level, atoms, ions, and/or molecules are in constant reaction. When a system is a gas partial pressures are used to represent the amounts of substances present in the equilibrium condition.

The extent of a reaction in equilibrium varies with the experimental conditions such as concentrations/pressures of reactants, temperature, etc. Some important aspects of equilibrium involving physical and chemical processes are dealt in this unit along with the equilibrium involving ions in aqueous solutions which is called ionic equilibrium. Finally, the equilibrium in gas-liquid systems will be discussed.

2.1 The concept of equilibrium

Consider a chemical reaction between reactants **A** and **B** to form products **C** and **D**. After allowing sufficient period of time for the reaction, upon analyses, when **A** and **B** are absent in the reaction mixture, the reaction is understood to be completed and only the presence of **C** and **D** will be detected. That reaction can be written as,



In this reaction, the reverse reaction to form back the reactants never occurs even when the reaction vessel is a closed one. Reactions which go to completion and never proceed in the reverse direction are called **irreversible reactions**.

However, even after allowing sufficient period of time for reaction, when the presence of **A** and **B** are always detected along with **C** and **D**, then such reactions are understood to be never completed. i.e. Initially the reaction proceeds to form **C** and **D** until a certain period of time and with further increase in the reaction time, **C** and **D** molecules start to

produce back **A** and **B** and in such a way, the reaction mixture always contains **A**, **B**, **C** and **D** for any length of time until external factors like temperature, pressure, catalyst etc. are applied. Reactions which never proceed to completion in both forward and backward direction are called **equilibrium reactions** (*or reversible reactions*) and the system is said to be reached an **equilibrium state**. A mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**. And the chemical equation of such reactions are represented as,



To indicate that the reaction can proceed in both forward and reverse directions, we write the balanced equation with two arrows, \rightleftharpoons , one pointing from reactants to products and the other pointing from products to reactants.

These two cases of completion of reaction and reaching a reaction to an equilibrium state can be represented graphically as shown in the Figure 2.1 below.

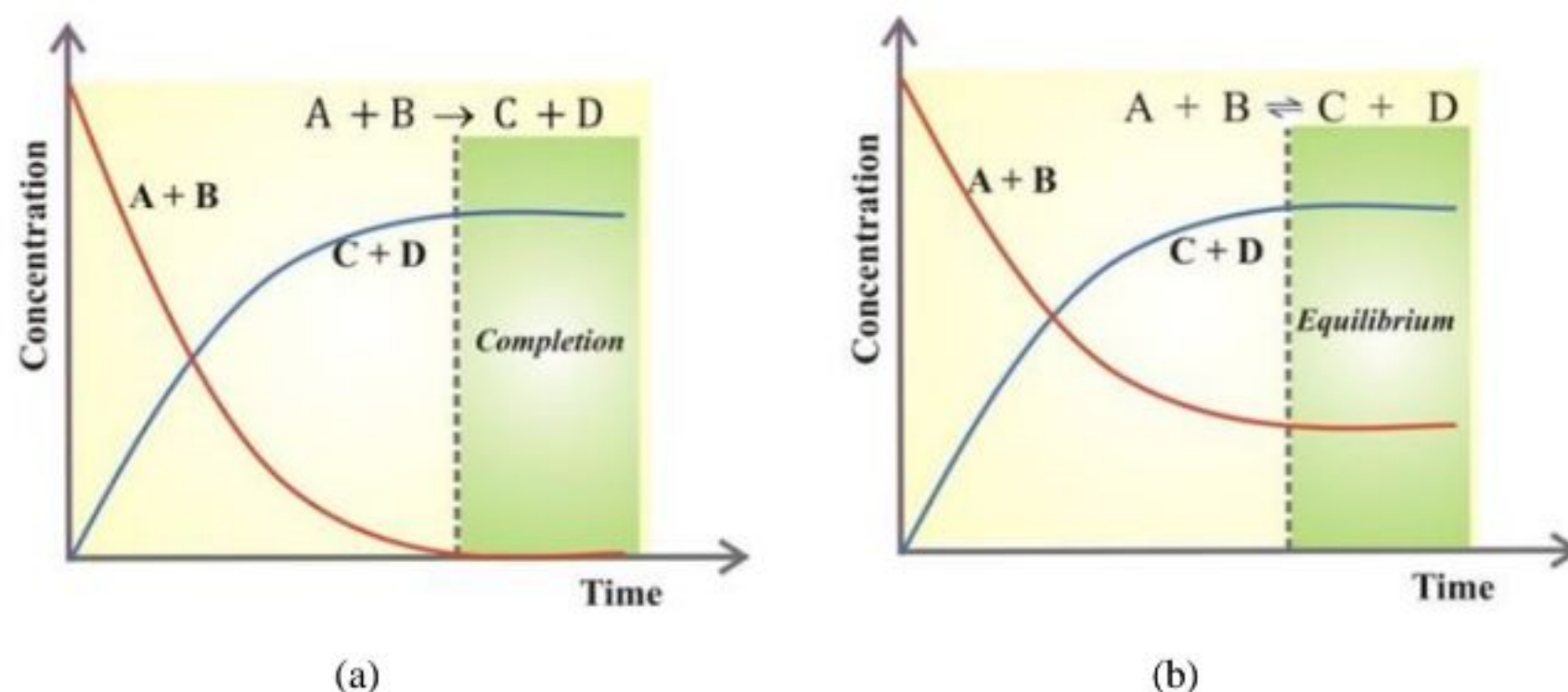


Figure 2.1 Change in concentrations of reactants and products over the time
(a) for an irreversible and (b) equilibrium reactions at a given temperature

At the start of a reversible reaction, first reaction proceeds in the forward direction to form products. Once the product concentration increases with time they begin to react back to form reactant molecules. Therefore, the chemical equilibrium may be defined as the state of a reversible reaction when the two opposing reactions occur at the **same rate** and the concentration of reactants and products do not change with time. The true equilibrium of a reaction can be attained from both sides proving that the chemical equilibrium is a dynamic process. This nature can be illustrated for the reaction (2) with the help of Figure 2.2. It has to be noted that the equilibrium concentrations of reactants are different from their initial concentrations.

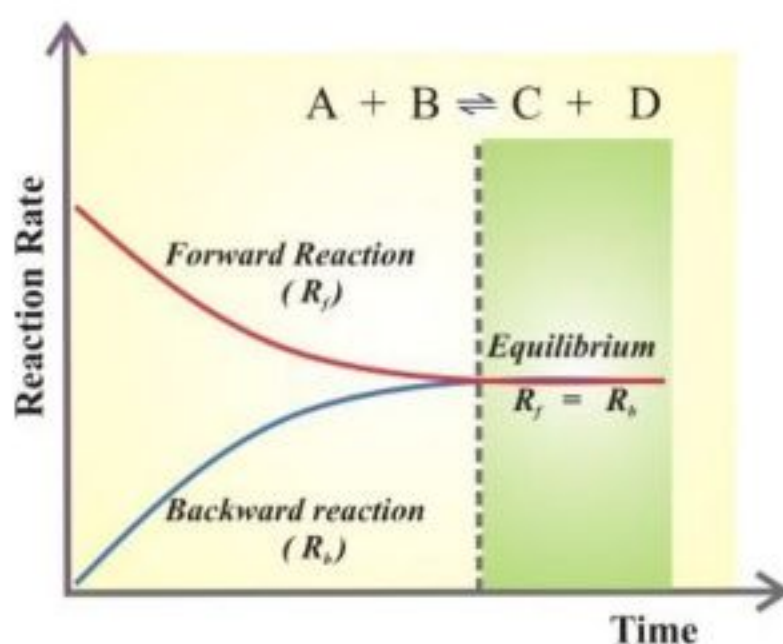


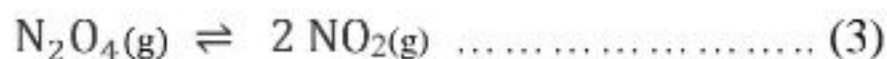
Figure 2.2 When the two rates become equal at a given temperature, an equilibrium state is attained with equalizing the rates of forward and backward reactions and there are no further changes in concentrations.

When a reversible reaction attains equilibrium it appears that the concentrations of individual reactants and that of the products remain constant with time. Actually, the reactant molecules are always reacting to form the product molecules. When the product molecules are able to react with themselves under the same experimental condition to form the same amount of reactants simultaneously (at the same time) in an equal rate of the forward reaction, then the process is a ceaseless phenomenon. Thus chemical equilibrium is **dynamic** when the forward and reverse reactions take place **endlessly and simultaneously with equal rates**. Therefore a chemical equilibrium is called a **dynamic equilibrium**. Hence, we can understand that;

- (i) When a chemical equilibrium is established in a closed container at constant temperature, the concentrations of various species like reactants and products remain unchanged.
- (ii) Equilibrium can be initiated from either side. The state of equilibrium of a reversible reaction can be arrived at whether we start from reactants or products.
- (iii) Equilibrium cannot be attained in an open container. Only in a closed container, a reaction can be considered to attain equilibrium since no part of reactants or products should escape out. In an open container, gaseous reactants or products may escape so that no possibility of attaining equilibrium exists. Equilibrium can be attained when all the reactants and products are in contact with each other.

The phenomenon discussed above can be understood by the following example. Consider a simple system that contains only one reactant and one product, the reversible dissociation of dinitrogen tetroxide ($\text{N}_2\text{O}_4(\text{g})$) to nitrogen dioxide ($\text{NO}_2(\text{g})$). $\text{NO}_2(\text{g})$ is responsible for the brown color we associate with smog. In a sealed vessel containing $\text{N}_2\text{O}_4(\text{g})$, the red-brown colour of $\text{NO}_2(\text{g})$ appears. Therefore the reaction can be followed

visually because the product ($\text{NO}_2(\text{g})$) is coloured, whereas the reactant ($\text{N}_2\text{O}_4(\text{g})$) is colourless.



This system can be used to understand the reversible nature of a reaction which attains equilibrium in three ways.

- When gaseous $\text{N}_2\text{O}_4(\text{g})$ is injected into an evacuated flask brown colour appears immediately, indicating the formation of $\text{NO}_2(\text{g})$ molecules. The colour intensifies with the time as the dissociation of $\text{N}_2\text{O}_4(\text{g})$ continues until eventually equilibrium is reached and remains at a constant intensity. At this point, the concentrations of both $\text{N}_2\text{O}_4(\text{g})$ and $\text{NO}_2(\text{g})$ remain constant.
- We can also bring about an equilibrium state by starting with pure $\text{NO}_2(\text{g})$. As some of the $\text{NO}_2(\text{g})$ molecules combine to form $\text{N}_2\text{O}_4(\text{g})$, the colour fades and remains at constant intensity once the equilibrium is attained.
- Another way to create this equilibrium state is to start with a mixture of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ and monitor the system until the color stops changing. The important thing to keep in mind is that at equilibrium, the conversions of $\text{N}_2\text{O}_4(\text{g})$ to $\text{NO}_2(\text{g})$ and $\text{NO}_2(\text{g})$ to $\text{N}_2\text{O}_4(\text{g})$ are still going on. We do not see a colour change because the two rates are equal, i.e. the removal of $\text{NO}_2(\text{g})$ molecules takes place as fast as the production of $\text{NO}_2(\text{g})$ molecules, and $\text{N}_2\text{O}_4(\text{g})$ molecules are formed as quickly as they dissociate. Figure 2.3 summarizes these three situations.

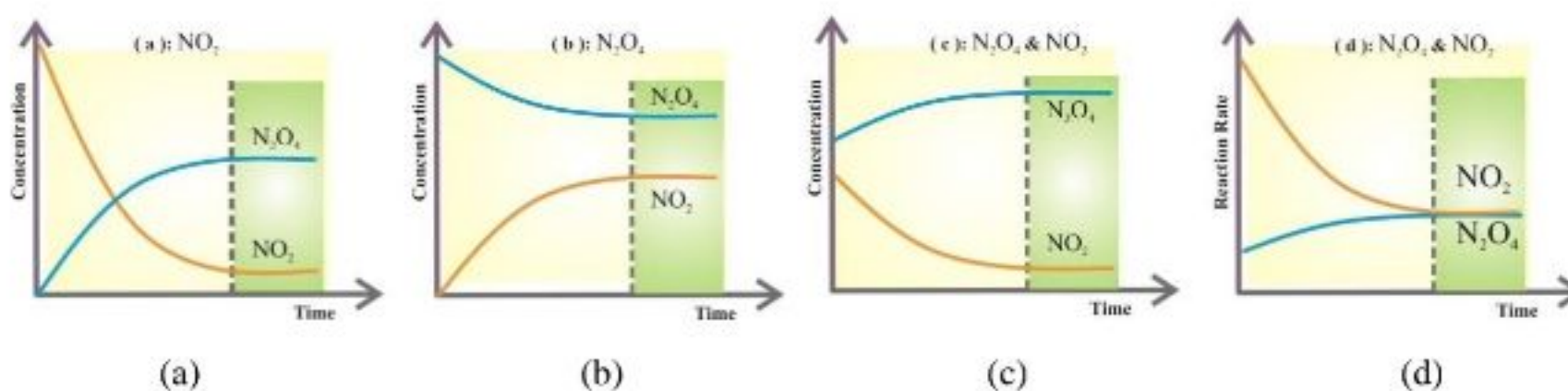


Figure 2.3 $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons \text{NO}_2(\text{g})$ equilibrium system: (a) Initially, the system contains gaseous $\text{NO}_2(\text{g})$ and no gaseous $\text{N}_2\text{O}_4(\text{g})$. The concentration of $\text{NO}_2(\text{g})$ decreases with time as the concentration of $\text{N}_2\text{O}_4(\text{g})$ increases. (b) Initially the system contains gaseous $\text{N}_2\text{O}_4(\text{g})$ and no gaseous $\text{NO}_2(\text{g})$. The concentration of $\text{N}_2\text{O}_4(\text{g})$ decreases with time as the concentration of $\text{NO}_2(\text{g})$ increases. (c) Initially a mixture of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ is present. Note that even though equilibrium is reached in all cases, the equilibrium concentrations of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are not the same. (d) Rates of forward and backward reactions in the mixture described in (c). Note also that even though the values of concentrations are not marked variation in concentrations are in parallel with the stoichiometry of the reaction.

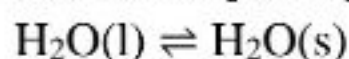
When there is a change in the state of occurrence of matter, then a physical transformation is said to have occurred. The equilibrium concepts are also applicable to physical state transformations of matter and some examples are discussed below.

2.1.1 Equilibrium in physical processes

The characteristics of a system at equilibrium are better understood if we examine some physical processes. The most familiar examples are **phase transformation processes**, e.g.: $\text{solid} \rightleftharpoons \text{liquid}$, $\text{liquid} \rightleftharpoons \text{gas}$, $\text{solid} \rightleftharpoons \text{gas}$ etc.

Solid-liquid equilibrium

Here, the solid and the liquid forms of a substance co-exist at characteristic temperature and pressure. At 1 atm and at the melting point of a substance, there is a solid-liquid equilibrium existing. For example, the solid-liquid equilibrium of water at 273 K (0 °C),



occurs at atmospheric pressure (1 atm, 101325 Pa). Here, both the liquid and ice exist together. We observe that the mass of ice and water do not change with time and the temperature remains constant. However, the equilibrium is not static. At the boundary between liquid and solid, molecules from the liquid water collide against ice and adhere to it and some molecules of ice escape into liquid phase. There is no change of mass of ice and water, as the rates of transfer of molecules from ice into water and of reverse transfer from water into ice are equal at atmospheric pressure and 273 K. It is obvious that ice and water are in equilibrium only at a particular temperature and pressure. *“For any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance”*. In this example, we can see that the system is in dynamic equilibrium and at the melting point of ice or freezing point of water, the rate of melting of ice equals to the rate of freezing of water so that the amount of ice and water remains constant. It has to be noted that with change in pressure, the temperature at which this equilibrium onsets changes.

Liquid-vapour equilibrium

Here, the solid and the vapour forms of a substance co-exist at a characteristic temperature and pressure in a closed system. At 1 atm and at the boiling point of a substance, there is a liquid- vapour equilibrium existing. For example, the liquid- vapour equilibrium of water at 373 K (100 °C),



occurs at atmospheric pressure. Here, both the liquid and vapour exist together. This can be demonstrated by a simple experiment by putting a watch glass containing certain amount of water in previously evacuated and dried box connected with a barometer (pressure-meter) at 100 °C. It will be observed that the mercury level in the right limb of

the manometer slowly increases and finally attains a constant value, that is, the pressure inside the box increases and reaches a constant value. Also the volume of water in the watch glass decreases. Initially there was no water vapour (or very less) inside the box. As water evaporated the pressure in the box increased due to addition of water molecules into the gaseous phase inside the box. The rate of evaporation is constant. However, the rate of increase in pressure decreases with time due to condensation of vapour into water. Finally it leads to an equilibrium condition when there is no net evaporation. This implies that the number of water molecules from the gaseous state into the liquid state also increases till the equilibrium is attained at which the rate of evaporation equals the rate of condensation.

At equilibrium the pressure exerted by the water molecules at a given temperature remains constant and is called the “*equilibrium vapour pressure*” of water (or just vapour pressure of water); vapour pressure of water increases with temperature.

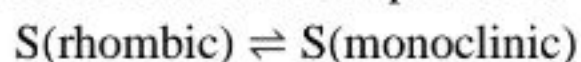
Here “*the vapour and the liquid forms of a substance exist simultaneously at 1 atm pressure and at a characteristic temperature called the boiling point*”. For example, at 1 atm pressure, 100 °C is the boiling point of water, and both liquid water and water vapour (steam) exist simultaneously, provided the vapour does not escape.

Solid - vapour equilibrium

If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After a certain time, the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimates to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as, $I_2(s) \rightleftharpoons I_2(g)$

Solid-solid equilibrium

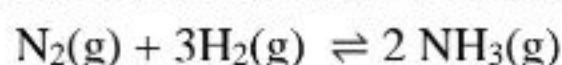
When a substance existing in a particular crystalline solid transforms to another crystalline form retaining its solid nature at a characteristic temperature called the transition temperature with both the solid forms coexisting at 1 atm pressure, it is said to be in solid-solid equilibrium. For example, solid sulphur exhibits equilibrium with rhombic to monoclinic forms at its transition temperature.



2.1.2 Equilibrium in chemical processes

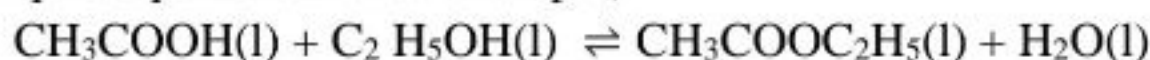
Homogeneous equilibrium

Chemical equilibrium exists in two types, homogeneous and heterogeneous. In a chemical reaction existing in equilibrium, if all the reactants and products are present in the same phase, a homogeneous equilibrium is said to have occurred. For example,



Here all the reactants and products exist in the gaseous state. This is an example of a gas-phase equilibrium.

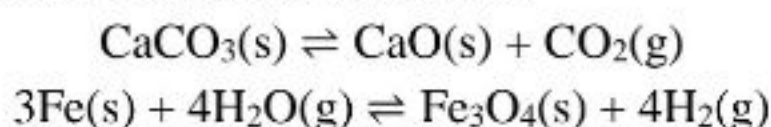
A chemical equilibrium in which all the reactants and products are in the liquid phase referred to as liquid equilibrium. For example,



Both gas phase and liquid phase equilibria are collectively called homogeneous equilibria.

Heterogeneous equilibrium

In a chemical equilibrium, if the reactant and product species are in different phases then heterogeneous equilibrium is said to have occurred.

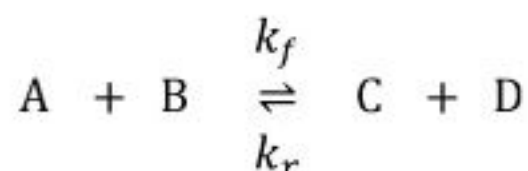


Here, when the reaction is carried out in a closed vessel, the equilibrium state is established.

2.1.3 Law of chemical equilibrium and equilibrium constant

It is important to know the relationship between the concentrations of reactants and products in an equilibrium mixture, how to determine equilibrium concentrations from initial concentrations and what factors can be exploited to alter the composition of an equilibrium mixture? Two Norwegian Chemists, Guldberg and Waage, studied experimentally a large number of equilibrium (reversible) reactions. In 1864, they postulated a generalization called the **law of mass action**. It states that: "the rate of a chemical reaction is proportional to the active masses of the reactants". By the term 'active mass', it is meant the molar concentration i.e., mol dm^{-3} . At a fixed temperature the rate of a reaction is determined by the number of collisions between the reactant molecules present in a unit volume and hence its concentration, which is generally referred to as the active mass.

Consider a reaction,



According to the law of mass action;

Rate of forward reaction: $R_f = k_f [\text{A}] [\text{B}]$

Rate of backward reaction: $R_r = k_r [\text{C}] [\text{D}]$

$[\text{A}]$, $[\text{B}]$, $[\text{C}]$ and $[\text{D}]$ are the molar concentrations of A,B,C and D at equilibrium, respectively.

k_f and k_r are the rate constants of forward and backward reactions, respectively.

At equilibrium,

$$R_f = R_r$$

Therefore we can write,

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

And

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

At any specific temperature $\frac{k_f}{k_r}$ is a constant since both k_f and k_r are constants. The ratio $\frac{k_f}{k_r}$ is called **equilibrium constant** and is represented by the symbol K_c . The subscript 'c' indicates that the value is in terms of concentration of reactants and products. The equation (I) may be written as

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

i.e. for a reversible reaction in equilibrium at constant temperature, a certain ratio of reactant and product concentrations has a constant value, K_c (the equilibrium constant).

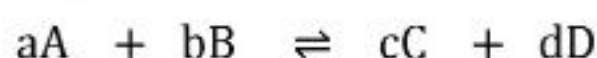
2.1.4 Equilibrium law and equilibrium constant expression for a reaction

For example in the study of analysis of experimental data by changing the initial concentrations of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ in a $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$ system at 25°C some interesting pattern is seen: Analysis of the equilibrium concentration data shows that although the ratio $[\text{NO}_2(\text{g})]/[\text{N}_2\text{O}_4(\text{g})]$ gives random values, the ratio $[\text{NO}_2(\text{g})]^2/[\text{N}_2\text{O}_4(\text{g})]$ gives a nearly constant value. i.e.

$$K_c = \frac{[\text{NO}_2(\text{g})]^2}{[\text{N}_2\text{O}_4(\text{g})]}$$

is a constant at a given temperature.

Likewise, similar kind of results was observed for the $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ reaction giving the ratio $[\text{HI}]^2/[\text{H}_2][\text{I}_2]$ as a constant. With this type of findings in many equilibrium systems at given temperature, we can derive a generalized form for the equilibrium expression of a reaction:



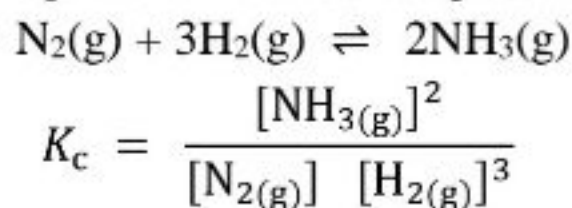
where a, b, c, and d are the stoichiometric coefficients for the reacting species A, B, C, and D,

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

where K_c is the equilibrium constant. The general definition of the equilibrium constant may thus be stated as:

The product of the equilibrium concentrations of the products divided by the product of the equilibrium concentrations of the reactants, with each concentration term raised to a power equal to the coefficient of the substance in the balanced equation.

For example, consider the equilibrium constant expression for the reaction,



If we write the chemical equation in the reverse direction, the new equilibrium constant expression is the reciprocal of the original expression and the new equilibrium constant ' is the reciprocal of the original equilibrium constant . (The prime distinguishes K_c' from K_c). i.e.

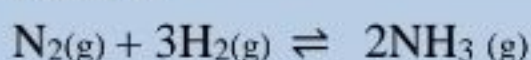
$$K_c' = \frac{[\text{N}_2(\text{g})] [\text{H}_2(\text{g})]^3}{[\text{NH}_3(\text{g})]^2} = \frac{1}{K_c}$$

Because the equilibrium constants K_c and K_c' have different numerical values, it is important to specify the form of the balanced chemical equation when quoting the value of an equilibrium constant. Further, it has to be noted that the physical states of the species appearing in the equilibrium constant expressions must be indicated for each as shown above.

Example 2.1

The following concentrations were measured for an equilibrium mixture of $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 500 K: $[\text{N}_2] = 3.0 \times 10^{-2} \text{ mol dm}^{-3}$, $[\text{H}_2] = 4.0 \times 10^{-2} \text{ mol dm}^{-3}$ and $[\text{NH}_3] = 2 \times 10^{-3} \text{ mol dm}^{-3}$. Calculate the equilibrium constants for both forward and reverse reactions at 500 K.

Answer



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

$$K_c = \frac{(2 \times 10^{-3})^2 (\text{mol dm}^{-3})^2}{(3 \times 10^{-2})(4 \times 10^{-2})^3 (\text{mol dm}^{-3})^4} = 2.083 \text{ mol}^{-2} \text{ dm}^6$$

$$K_c' = \frac{[\text{N}_2(\text{g})] [\text{H}_2(\text{g})]^3}{[\text{NH}_3(\text{g})]^2} = \frac{(3 \times 10^{-2})(4 \times 10^{-2})^3 (\text{mol dm}^{-3})^4}{(2 \times 10^{-3})^2 (\text{mol dm}^{-3})^2}$$

$$= 0.48 \text{ mol}^2 \text{ dm}^{-6}$$

or

$$K_c' = \frac{1}{K_c} = \frac{1}{2.083 \text{ mol}^{-2} \text{ dm}^6} = 0.48 \text{ mol}^2 \text{ dm}^{-6}$$

Note: See the change in magnitude as well as the units when the equilibrium constant is defined in two opposite directions in the reaction. The equilibrium constant for a reaction written in reverse is the inverse of the equilibrium constant for the reaction as written originally.

2.1.5 Extent of reaction

If K (either K_c or K_p which pertains to the gas phase reactions) is much greater than 1 (that is, $K \gg 1$), the equilibrium will lie to the right and favours the products. That is concentration of products is higher than that of reactants. Conversely, if the equilibrium constant is much smaller than 1 (that is, $K \ll 1$), the equilibrium will lie to the left and favours the reactants, i.e. concentration of reactants is higher than that of products. Many reactions have equilibrium constants between 1000 and 0.001 ($10^3 \geq K \geq 10^{-3}$), indicating they are neither very large nor very small. At equilibrium, these systems tend to contain significant amounts of both products and reactants, indicating that there is not a strong tendency to form either products from reactants or reactants from products.

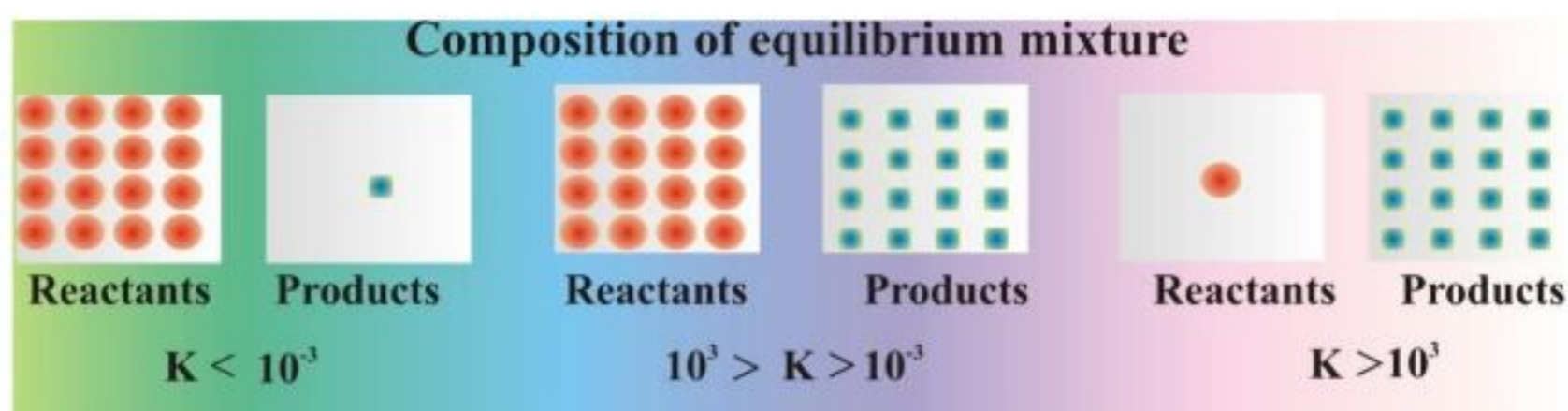


Figure 2.4 Representation of the extent and equilibrium position of a reaction with respect to the magnitude of equilibrium constant, K

Figure 2.4 summarizes the relationship between the magnitude of K and the relative concentrations of reactants and products at equilibrium for a general reaction, written as *reactants* \rightleftharpoons *products*. Because there is a direct relationship between the kinetics of a reaction and the equilibrium concentrations of products and reactants when $k_f \gg k_r$, K is a large number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f \ll k_r$, K is a very small number, and the reaction produces almost no products as written. Systems with $k_f \approx k_r$ have significant concentrations of both reactants and products at equilibrium. i.e.

- If, $K_c > 10^3$, products predominate over reactants. If it is very large, the reaction proceeds nearly to completion.
- If, $K_c < 10^3$, reactants predominate over products. If it is very small, the reaction proceeds hardly at all.
- If, $10^3 \geq K_c \geq 10^{-3}$, appreciable concentrations of both reactants and products are present.

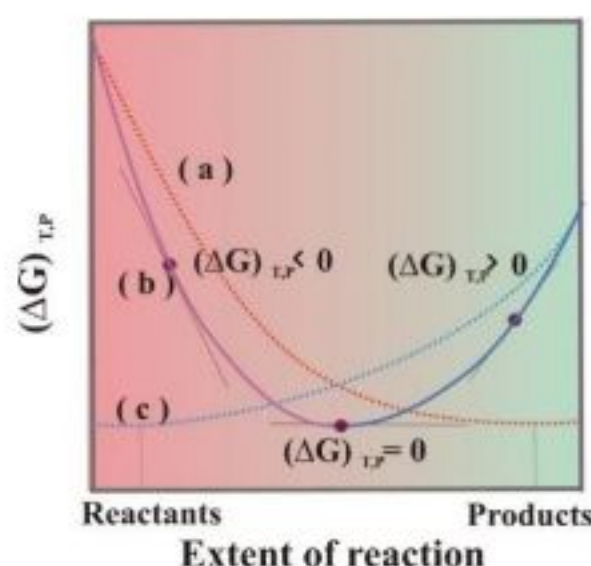


Figure 2.5 Representation of a spontaneous reaction towards minimum Gibbs function at equilibrium at given temperature and pressure. As the reaction proceeds the slope of the Gibbs function changes. Equilibrium point corresponds to the zero slope.

In addition to the simple description used in Figure 2.4 to understand the position of equilibrium, this equilibrium concept can further be understood by the knowledge of thermochemistry described in unit 05 to explain the spontaneity of reactions. In Figure 2.5, curve (a) shows that the position of equilibrium lies close to products indicating that the reaction goes to completion where Gibbs energy difference $(\Delta G)_{T,P} < 0$. The curve (b) represents the state of equilibrium consisting of significant amounts of both reactants and products in the mixture where $(\Delta G)_{T,P} = 0$. In curve (c) we can see that the position of equilibrium lies close to the reactants where $(\Delta G)_{T,P} > 0$, or the reaction is non-spontaneous.

Note: Here $(\Delta G)_{T,P}$ means the value of free energy change per change in number of moles $((\Delta G)_{T,P}/\Delta n)$. However, for a given reaction the use of $(\Delta G)_{T,P} = \Delta H - T \Delta S$ gives the standard free energy change of the complete reaction (i.e. ΔG_r°). In general, ΔG_r of a given reaction at a given temperature is given by; $\Delta G_r = \Delta G_r^\circ + RT \ln Q$, and we know that at equilibrium, $\Delta G_r = 0$ indicating that any reaction has its own (characteristic) ΔG_r° value. In other words, for a reaction at a given temperature, $\Delta G_r^\circ \neq 0$, or $\Delta G_r^\circ = -RT \ln K$. (This is just for the clarification and the equation here is not tested in G.C.E (A/L) examination)

The description of Figure 2.5 can also be represented by the following three diagrams in Figure 2.6 for understanding better about the Gibbs energy changes in a spontaneous chemical reaction, a reaction that goes to completion and a reaction that never proceeds to products.

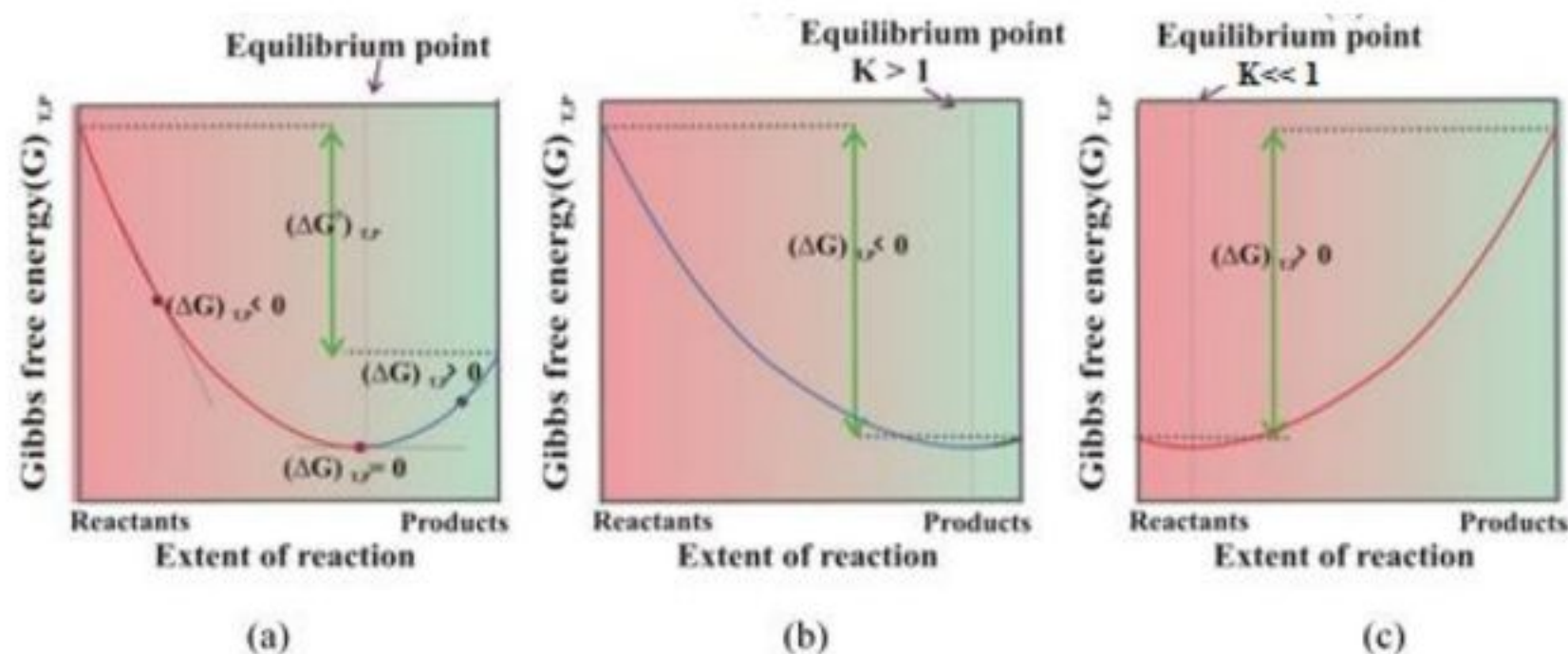


Figure 2.6 Details of Figure 2.5 (a) Variation of Gibbs free energy with composition for a reaction with spontaneous tendency. (b) A reaction which goes to a completion in which the equilibrium point lies very close to products ($K > 1$) and (c) A reaction which never reaches completion or a reaction which has no tendency to form products in which the equilibrium point lies very close to reactants ($K \ll 1$).

From the Figure 2.6 we can note that;

The equilibrium position, or how close to products or reactants the reaction will go is defined by the magnitude and sign of ΔG_r^\ominus .

$\Delta G_r^\ominus < 0$: products are favoured.

$\Delta G_r^\ominus \approx 0$: neither reactants nor products are favoured and the system is at equilibrium.

$\Delta G_r^\ominus > 0$: reactants are favoured.

2.1.6 Different forms of writing equilibrium constant expression

Writing an equation in different but chemically equivalent forms also causes both the equilibrium constant expression and the magnitude of the equilibrium constant to be different. For example, when the equation for the reaction $2\text{NO}_2(\text{g}) \rightleftharpoons \text{N}_2\text{O}_4(\text{g})$ with the equilibrium constant K is written as $\text{NO}_2 \rightleftharpoons \frac{1}{2} \text{N}_2\text{O}_4$, the equilibrium constant K'' ; can be written as follows.

$$K = \frac{[\text{N}_2\text{O}_4(\text{g})]}{[\text{NO}_2(\text{g})]^2}$$

$$K'' = \frac{[\text{N}_2\text{O}_4(\text{g})]^{1/2}}{[\text{NO}_2(\text{g})]}$$

We can see that the K'' and K has the relation, $K'' = (K)^{1/2}$ and according to the law of mass action, each concentration term in the equilibrium constant expression is raised to a power equal to its stoichiometric coefficient. Thus if you double a chemical equation throughout, the corresponding equilibrium constant will be the square of the original

value; if you triple the equation, the equilibrium constant will be the cube of the original value, and so on.

In general, if all the coefficients in a balanced chemical equation are subsequently multiplied by n , then the new equilibrium constant is the original equilibrium constant is raised to the n^{th} power.

Example 2.2

At 800 K, equilibrium constant K for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is 0.25. What is the equilibrium constant K'' for the reaction $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$ at 800 K?

Answer

We can write

$$K = \frac{[\text{NH}_{3(\text{g})}]^2}{[\text{N}_{2(\text{g})}] [\text{H}_{2(\text{g})}]^3}$$

$$K'' = \frac{[\text{NH}_{3(\text{g})}]}{[\text{N}_{2(\text{g})}]^{1/2} [\text{H}_{2(\text{g})}]^{3/2}} = K^{1/2} = (0.25)^{\frac{1}{2}} = 0.50$$

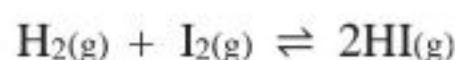
2.1.7 Equilibrium constant in gaseous systems

So far we have expressed equilibrium constant of the reactions in terms of molar concentration of the reactants and products, and used symbol, K_c for it. For reactions involving gases, however, it is usually more convenient to express the equilibrium constant in terms of partial pressures.

As we know, at constant temperature the pressure P of a gas is directly related to the concentration in mol dm^{-3} of the gas; that is, $P = (n/V) RT$ or $P = CRT$. Thus, for the equilibrium, $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, we can write,

$$K_p = \frac{(P_{\text{NO}_{2(\text{g})}})^2}{(P_{\text{N}_2\text{O}_{4(\text{g})}})}$$

Where $P_{\text{NO}_{2(\text{g})}}$ and $P_{\text{N}_2\text{O}_{4(\text{g})}}$ are the equilibrium partial pressures (in Pa) of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$, respectively. The subscript in K_p indicates that equilibrium concentrations are expressed in terms of pressure. In general, K_c is not always equal to K_p , since the partial pressures of reactants and products are not equal to their concentrations expressed in mol dm^{-3} . At a constant temperature, a simple relationship between K_p and K_c can be derived as follows. First, let us consider the following equilibrium in the gas phase:



We can write,

$$K_c = \frac{[\text{HI}_{(\text{g})}]^2}{[\text{I}_{2(\text{g})}] [\text{H}_{2(\text{g})}]}$$

$$K_p = \frac{(P_{\text{HI}_{(\text{g})}})^2}{(P_{\text{H}_{2(\text{g})}}) (P_{\text{I}_{2(\text{g})}})}$$

Applying $P = CRT$ relation, we can write,

$P_{\text{HI}_{(\text{g})}} = [\text{HI}_{(\text{g})}] RT$, $P_{\text{H}_{2(\text{g})}} = [\text{H}_{2(\text{g})}] RT$ and $P_{\text{I}_{2(\text{g})}} = [\text{I}_{2(\text{g})}] RT$ and substituting these in

$$K_p = \frac{(P_{\text{HI}_{(\text{g})}})^2}{(P_{\text{H}_{2(\text{g})}}) (P_{\text{I}_{2(\text{g})}})} = \frac{[\text{HI}_{(\text{g})}]^2 (RT)^2}{[\text{I}_{2(\text{g})}] (RT) [\text{H}_{2(\text{g})}] (RT)} = \frac{[\text{HI}_{(\text{g})}]^2 (RT)^{(2-2)}}{[\text{I}_{2(\text{g})}] [\text{H}_{2(\text{g})}]} = K_c$$

In this example, $K_p = K_c$ i.e., both equilibrium constants are equal. However, this is not always the case. For example in reaction, $\text{N}_{2(\text{g})} + 3\text{H}_{2(\text{g})} \rightleftharpoons 2\text{NH}_{3(\text{g})}$,

$$K_c = \frac{[\text{NH}_{3(\text{g})}]^2}{[\text{N}_{2(\text{g})}] [\text{H}_{2(\text{g})}]^3} \text{ and } K_p = \frac{(P_{\text{NH}_{3(\text{g})}})^2}{(P_{\text{N}_{2(\text{g})}}) (P_{\text{H}_{2(\text{g})}})^3}$$

Assuming ideal behaviour,

$$\begin{aligned} K_p &= \frac{[\text{NH}_{3(\text{g})}]^2 (RT)^2}{[\text{N}_{2(\text{g})}] (RT) [\text{H}_{2(\text{g})}]^3 (RT)^3} \\ &= \frac{[\text{NH}_{3(\text{g})}]^2 (RT)^{(2-4)}}{[\text{N}_{2(\text{g})}] [\text{H}_{2(\text{g})}]^3} \\ &= \frac{[\text{NH}_{3(\text{g})}]^2 (RT)^{(-2)}}{[\text{N}_{2(\text{g})}] [\text{H}_{2(\text{g})}]^3} \end{aligned}$$

and hence we can write,

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

With the impression derived from the above two examples, we can now consider a general case for a gas phase reaction, $a\text{A}_{(\text{g})} \rightleftharpoons b\text{B}_{(\text{g})}$,

$$K_c = \frac{[\text{B}_{(\text{g})}]^b}{[\text{A}_{(\text{g})}]^a} \text{ and } K_p = \frac{(P_{\text{B}_{(\text{g})}})^b}{(P_{\text{A}_{(\text{g})}})^a}$$

where P_A and P_B are the partial pressures of A and B. Assuming ideal gas behavior in a closed rigid container of volume $V \text{ dm}^3$ at temperature $T \text{ (K)}$,

$$P_A V = n_A RT \text{ and } P_B V = n_B RT.$$

Therefore we can write

$$P_A = C_A RT \text{ and } P_B = C_B RT \text{ and when the } C_A \text{ and } C_B \text{ are expressed in mol dm}^{-3},$$

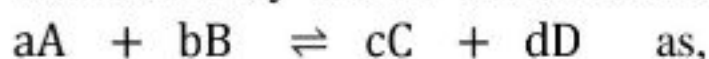
$P_A = [A]RT$ and $P_B = [B]RT$ substituting in K_p expression above,

$$K_p = \frac{([B]RT)^b}{([A]RT)^a} = \frac{[B]^b}{[A]^a} (RT)^{b-a} = K_c (RT)^{b-a}$$

$$= K_c (RT)^{\Delta n}, \text{ where } \Delta n = b - a$$

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

As a summary we can write the relation between K_p and K_c for a reaction,



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

Δn = amount of moles of gaseous products - amount of moles of gaseous reactants

In general, $K_p \neq K_c$ except in the special case(s) as shown above for the example with $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ system in which $\Delta n = 0$.

Note: It is general practice not to include units for the equilibrium constant. In thermodynamics, K is defined as having no units because every concentration (molarity) or pressure (atm/ Pa) term is actually a ratio to a standard value, which is 1 mol dm^{-3} or $1 \text{ atm}/ 101325 \text{ Pa}$ ($\sim 100 \text{ kPa}$). This procedure eliminates all units but does not alter the numerical parts of the concentration or pressure. Consequently, K has no units.

However, in the case when every concentration (molarity) or pressure (atm/ Pa) term is not a ratio to the standard value, that procedure will append appropriate units for the equilibrium constant(s).

i.e. Equilibrium constants can also be expressed as dimensionless quantities if the standard state of reactants and products are specified. For a pure gas, the standard state is 1 bar ($P^\ominus = 1 \text{ atm}$, 100 kPa). Therefore a pressure of 400 kPa in standard state can be expressed as $400 \text{ kPa}/100 \text{ kPa} = 4$, which is a dimensionless number. Standard state (C^\ominus) for a solute in a solution is 1.0 mol dm^{-3} . All concentrations can be measured with respect to it. The numerical value of equilibrium constant depends on the standard state chosen. Though the equilibrium constants are considered dimensionless/ unitless quantities, in this text we consider the concentrations and pressures with their respective units unless the standard state is mentioned.

The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol dm^{-3} and for K_p partial pressure can be substituted in **Pa, kPa, bar** or **atm**. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are the same.

For the reactions,

$\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$, K_c and K_p have no unit.

$\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$, K_c has unit mol dm^{-3} and K_p has unit **Pa**.

Example 2.3

Methane gas (CH_4) reacts with hydrogen sulfide gas at 1000 K to yield H_2 and carbon disulfide as $\text{CH}_4(\text{g}) + 2\text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{CS}_2(\text{g}) + 4\text{H}_2(\text{g})$

What are the value of K_p and K_c at 1000 K if the partial pressures in an equilibrium mixture at 1000 K are 0.20×10^5 Pa of CH_4 , 0.25×10^5 Pa of H_2S , 0.52×10^5 Pa of CS_2 and 0.10×10^5 Pa of H_2 ?

Answer

$$K_p = \frac{(P_{\text{H}_2(\text{g})})^4 (P_{\text{CS}_2(\text{g})})}{(P_{\text{CH}_4(\text{g})}) (P_{\text{H}_2\text{S}(\text{g})})^2} = \frac{(0.1 \text{ Pa})^4 (0.52 \text{ Pa})}{(0.20 \text{ Pa}) (0.25 \text{ Pa})^2} (1.0 \times 10^5 \text{ Pa})^2$$

$$= 4.2 \times 10^{-3} \times 10^{10} \text{ Pa}^2 = 4.2 \times 10^7 \text{ Pa}^2$$

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

$$\Delta n = 5 - 3 = 2$$

$$\text{Therefore, } K_p = K_c (RT)^2 \text{ and } K_c = \frac{K_p}{(RT)^2}$$

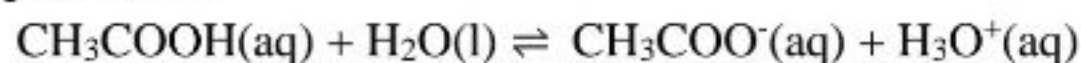
$$K_c = \frac{K_p}{(RT)^2} = \frac{4.2 \times 10^7 \text{ Pa}^2}{(8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 1000 \text{ K})^2} = \frac{4.2 \times 10^7 (10^{-3} \text{ J dm}^{-3})^2}{(8314 \text{ J mol}^{-1})^2}$$

$$= 6 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$$

However, if the partial pressures are defined as P/P^\ominus , where P^\ominus is the standard pressure of 1 atm or 1.0×10^5 Pa, we will have

$$K_p = \frac{\left(\frac{P_{\text{H}_2(\text{g})}}{P^\ominus}\right)^4 \left(\frac{P_{\text{CS}_2(\text{g})}}{P^\ominus}\right)}{\left(\frac{P_{\text{CH}_4(\text{g})}}{P^\ominus}\right) \left(\frac{P_{\text{H}_2\text{S}(\text{g})}}{P^\ominus}\right)^2} = \frac{(0.1)^4 (0.52)}{(0.20) (0.25)^2} = 4.2 \times 10^{-3}$$

Consider the ionization of acetic acid (CH_3COOH) in water as another example for a homogeneous equilibrium.



The equilibrium constant is; $K_c = \frac{[\text{CH}_3\text{COO}^-(\text{aq})] [\text{H}_3\text{O}^+(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})] [\text{H}_2\text{O}(\text{l})]}$

Here, liquid water, $\text{H}_2\text{O}(\text{l})$ is present as a medium for the reaction. In 1 dm^3 (1 L, or 1000 g of water, there are $1000 \text{ g}/(18 \text{ g mol}^{-1})$ or 55.5 moles, of water. Therefore, the “concentration” of water or $[\text{H}_2\text{O}(\text{l})]$ is 55.5 mol dm^{-3} . This is a large quantity compared to the concentrations of other species in solution (usually 1 mol dm^{-3} or smaller), and we

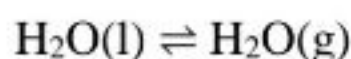
can assume that it does not change appreciably during the course of a reaction. Thus we may treat $[\text{H}_2\text{O(l)}]$ as a constant. Therefore, we can write the equilibrium constant as;

$$K_c = \frac{[\text{CH}_3\text{COO}^-(\text{aq})] [\text{H}_3\text{O}^+(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]}$$

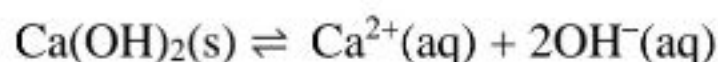
Where, $K_c = K'_c [\text{H}_2\text{O(l)}]$

2.1.8 Heterogeneous equilibria

Equilibrium in a system having more than one phase is called a heterogeneous equilibrium. The equilibrium between water vapour and liquid water in a closed container is an example of a heterogeneous equilibrium.



In this example, there is a gas phase and a liquid phase. In the same way, equilibrium between a solid and its saturated solution is a heterogeneous equilibrium.



Heterogeneous equilibria often involve pure solids or liquids. We can simplify equilibrium expressions for the heterogeneous equilibria involving a pure liquid or a pure solid, as the molar concentration of a pure solid or liquid is constant (i.e., independent of the amount present). Let us consider thermal decomposition of calcium carbonate as an example for heterogeneous chemical equilibrium.



Considering the stoichiometric equation, we can write,

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

Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, their concentrations are treated as constants, which allows us to simplify equilibrium constant expressions that involve pure solids or liquids. The reference states for pure solids and liquids are those forms stable at 100 kPa/1 atm, which are assigned an activity (effective mass) of 1. i.e. the “concentration” of a solid, like its density, is an intensive property and does not depend on how much of the substance is present.

In the above example, since $[\text{CaCO}_3(\text{s})]$ and $[\text{CaO(s)}]$ are both constants, the modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K_c = [\text{CO}_2(\text{g})],$$

where,

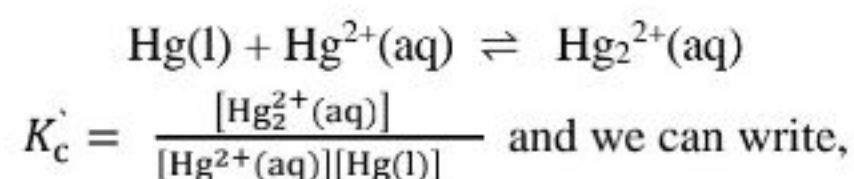
$$K_c = K'_c \frac{[\text{CaCO}_3(\text{s})]}{[\text{CaO(s)}]} \text{ is a constant.}$$

Likewise we can write

$$K_p = P_{\text{CO}_2(\text{g})}$$

For reactions carried out in solution, the concentration of the solvent is omitted from the equilibrium constant expression even when the solvent appears in the balanced chemical equation for the reaction. The concentration of the solvent is also typically much greater than the concentration of the reactants or products (recall that for pure water it is about 55.5 mol dm^{-3} and for pure ethanol it is about 17 mol dm^{-3}). Consequently, the solvent concentration is essentially constant during chemical reactions, and the solvent is therefore treated as a pure liquid. The equilibrium constant expression for a reaction contains only those species whose concentrations could change significantly during the reaction.

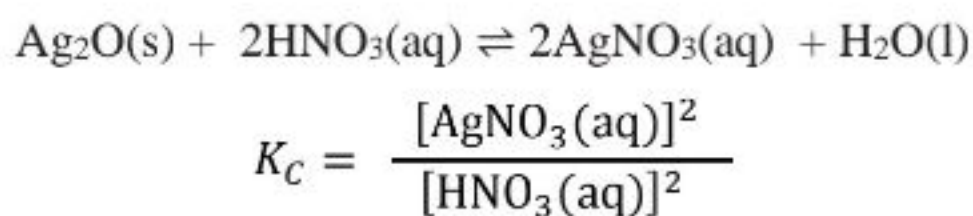
In the reaction,



$$K_c = \frac{[\text{Hg}_2^{2+}(\text{aq})]}{[\text{Hg}^{2+}(\text{aq})]} \text{ where, } K_c = K_c' [\text{Hg(l)}]$$

In this case, it's not appropriate to write an expression for K_p because none of the reactants and products is a gas.

In summary, it is clear that in a systems of a heterogeneous equilibrium, pure solids or liquids must be present for the equilibrium to exist, but their concentrations or partial pressures do not appear in the expression of the equilibrium constant. In the reaction below, we can see that though a solid reactant is present and liquid water is produced, the equilibrium constant expression does not contain both.



Note: The concentrations of pure solids, pure liquids, and solvents are omitted from equilibrium constant expressions because they do not change significantly during reactions when enough is present to reach equilibrium.

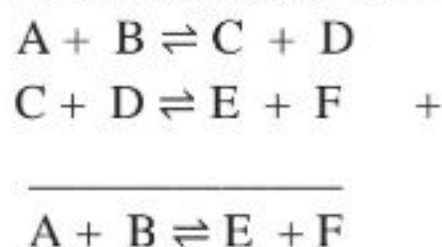
2.1.9 Equilibrium constant expressions for multi-step reactions

It is essential to know the equilibrium constant for a reaction that has not been previously studied or the desired reaction occurs in several steps. In such cases, the desired reaction can often be written as the sum of other reactions for which the equilibrium constants are known. The equilibrium constant for the unknown reaction can then be calculated from the tabulated or available values of the other reactions.

For example, consider the system $A + B \rightleftharpoons C + D$ in which the products formed in the first reaction, C and D, react further to form products E and F. At equilibrium we can write two separate equilibrium constants for the reactions,

$$\begin{aligned} A + B &\rightleftharpoons C + D \\ C + D &\rightleftharpoons E + F \\ K_c' &= \frac{[C][D]}{[A][B]} \text{ and } K_c'' = \frac{[E][F]}{[C][D]} \end{aligned}$$

We can see that the sum of the two reactions results the overall reaction and hence,



The equilibrium constant for the overall reaction is,

$$K_c = \frac{[E][F]}{[A][B]}$$

We can see that the expression of K_c is the product of K_c' and K_c''

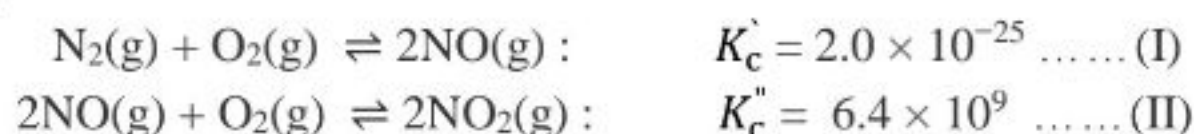
$$K_c' K_c'' = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]}$$

Therefore,

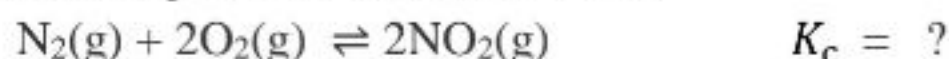
$$K_c = K_c' K_c''$$

Note: If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

For example, let's consider the reaction of $N_2(g)$ with $O_2(g)$ to give $NO_2(g)$ at $100^\circ C$. The reaction normally occurs in two distinct steps. In the first reaction (I), $N_2(g)$ reacts with $O_2(g)$ to give $NO(g)$. The $NO(g)$ produced then reacts with additional $O_2(g)$ to give $NO_2(g)$ as in reaction (II). Assume also that the concentrations are measured with respect to the standard molarity i.e. $C^\ominus = 1.0 \text{ mol dm}^{-3}$.



Summing reactions (I) and (II) gives the overall reaction:



$$K_c' = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]} = 2.0 \times 10^{-25} \text{ and } K_c'' = \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]} = 6.4 \times 10^9$$

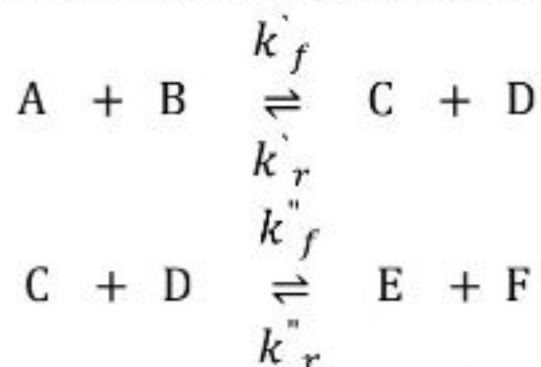
$$K_c' \times K_c'' = \frac{[NO(g)]^2}{[N_2(g)][O_2(g)]} \times \frac{[NO_2(g)]^2}{[NO(g)]^2[O_2(g)]} = \frac{[NO_2(g)]^2}{[O_2(g)]^2[N_2(g)]} = K_c$$

Therefore, $K_c = K_c' \times K_c'' = (2.0 \times 10^{-25})(6.4 \times 10^9) = 1.28 \times 10^{-15}$

Note: The relation among equilibrium constants of multi-step reactions can also be understood by the principles of chemical kinetics as described in Unit 11.

Consider the above example of the reaction $A + B \rightleftharpoons E + F$.

Suppose the same reaction has a mechanism with two elementary steps.



We can write, $K_c' = \frac{k_f'}{k_r'} = \frac{[C][D]}{[A][B]}$ and $K_c'' = \frac{k_f''}{k_r''} = \frac{[E][F]}{[C][D]}$

$$K_c' K_c'' = \frac{k_f'}{k_r'} \times \frac{k_f''}{k_r''} = \frac{[C][D]}{[A][B]} \times \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]} = K_c$$

In summary the followings are the key points to remember.

- The equilibrium constant is a constant at a given temperature, or it depends on the temperature.
- The concentrations of the reacting species in the condensed phase are expressed in mol dm^{-3} . In the gaseous phase, the concentrations can be expressed in mol dm^{-3} or in Pa (atm). K_c is related to K_p by a simple equation of

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

- The concentrations of pure solids, pure liquids (in heterogeneous equilibria), and solvents (in homogeneous equilibria) do not appear in the equilibrium constant expressions.
- The equilibrium constant (K_c or K_p) is a dimensionless quantity when the standard condition is used.
- In quoting a value for the equilibrium constant, we must specify the balanced equation and the temperature.
- If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.
- The value of K also depends on how the equilibrium equation is balanced. According to the law of mass action, each concentration term in the equilibrium constant expression is raised to a power equal to its stoichiometric coefficient. Thus if you double a chemical equation throughout, the corresponding equilibrium constant will be the square of the original value; if you triple the equation, the equilibrium constant

will be the cube of the original value, and so on. i.e. In general, if all the coefficients in a balanced chemical equation are subsequently multiplied by n , then the new equilibrium constant is the original equilibrium constant raised to the n^{th} power.

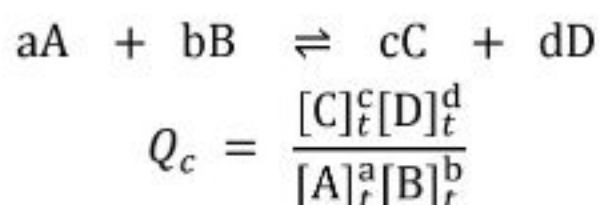
2.1.10 Predicting the direction of reaction and calculations based on equilibrium constant

We have seen that the equilibrium constant for a given reaction can be calculated from known equilibrium concentrations. Given the equilibrium constant and the initial concentrations of reactants, we can calculate the concentration of one or more substances at equilibrium only if the temperature does not change. In general, the *magnitude of the equilibrium constant* helps us to predict the direction in which a reaction mixture will proceed to achieve equilibrium and to calculate the concentrations of reactants and products once the equilibrium is reached. These uses of the equilibrium constant will be explored in this section.

Predicting the direction of a reaction

The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calculate the **reaction quotient Q** by substituting the initial concentrations in the equilibrium constant expression. The reaction quotient, Q (Q_c with molar concentrations and Q_p with partial pressures) is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily to be equilibrium values.

For a general reaction:



Here subscript t means that the concentrations are measured at an arbitrary time t and not necessarily at equilibrium. The reaction quotient Q is useful because it helps us predict the direction of reaction by comparing the values of Q_c and K_c . If Q_c is less than K_c ($Q_c < K_c$), movement toward equilibrium increases by converting reactants to products (that is, net reaction proceeds from left to right). If Q_c is greater than K_c ($Q_c > K_c$), movement toward equilibrium decreases by converting products to reactants (that is, net reaction proceeds from right to left). If Q_c equals K_c ($Q_c = K_c$), the reaction mixture is already at equilibrium, and no net reaction occurs. Thus, we can make the following generalizations concerning the direction of the reaction:

- $Q_c > K_c$: *The ratio of initial concentrations of products to reactants is too large. To reach equilibrium, products must be converted to reactants. The system*

proceeds from right to left (consuming products, forming reactants) to reach equilibrium.

- $Q_c = K_c$: The initial concentrations are equilibrium concentrations. The system is at equilibrium.
- $Q_c < K_c$: The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.

This can be illustrated by the conceptual diagram shown in Figure 2.7.

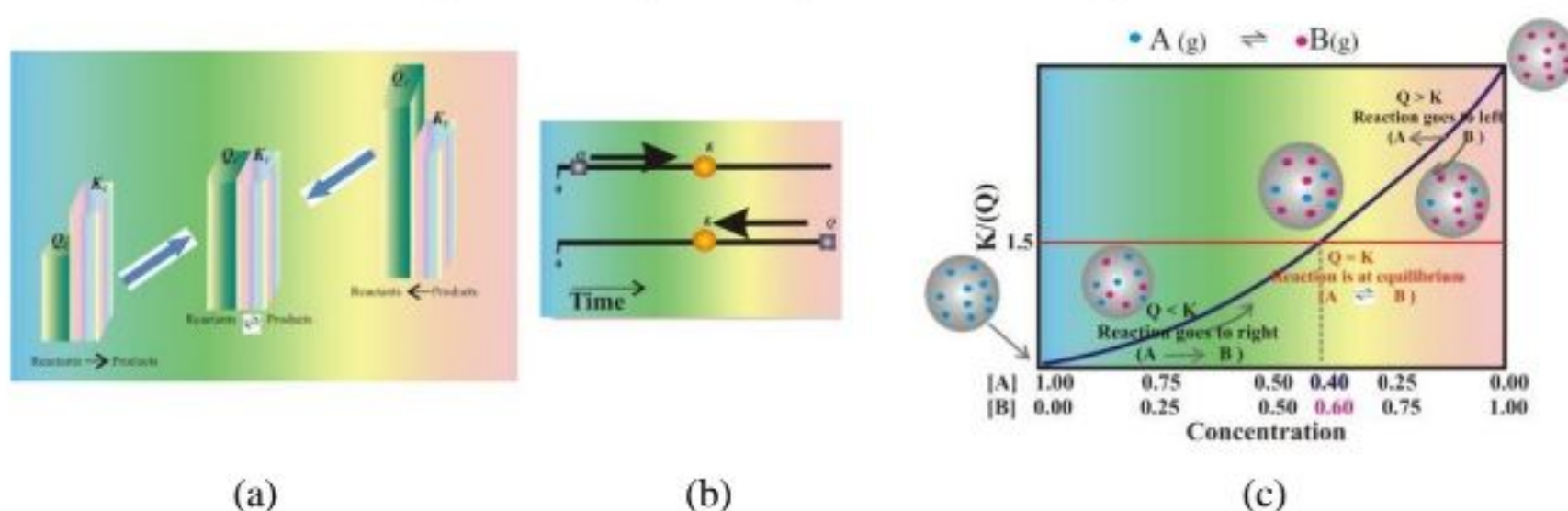


Figure 2.7 Different views for the interpretation of the magnitudes of K and Q : (a) compares the magnitudes of K and Q , (b) indicates the way that how the direction or equilibrium position of the reaction tends to move with the relative size of Q and (c) compares the composition of the reaction mixture at different positions where it can be noted that at equilibrium, $Q = K = 1.5$ with the presence of appropriate number of reactant and product molecules in the reaction mixture.

Example 2.4

The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3} . At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4} \text{ mol dm}^{-3}$. In which direction will the reaction proceed?

Answer

For the reaction the reaction quotient Q_c is given by,

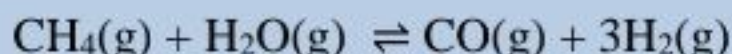
$$Q_c = \frac{[B][C]}{[A]^2} = \frac{(3 \times 10^{-4})(3 \times 10^{-4})}{(3 \times 10^{-4})^2} = 1$$

$$Q_c > K_c$$

Therefore, the reaction will proceed in the reverse direction.

Example 2.5

At elevated temperatures, methane ($\text{CH}_4(\text{g})$) reacts with water to produce hydrogen and carbon monoxide as:



Equilibrium constant for the reaction is $K = 2.4 \times 10^{-4}$ at 900 K. If, 1.2×10^{-2} moles of CH_4 , 8.0×10^{-3} moles of H_2O , 1.6×10^{-2} moles of CO and 6.0×10^{-3} moles of H_2 are placed in a 2.0 dm^3 closed rigid reactor and heated to 900 K, will the reaction be at equilibrium or will it proceed to the right to produce CO and H_2 or to the left to form CH_4 and H_2O ?

Answer

First let's find the initial concentrations of the substances present.

For example, we have 1.2×10^{-2} moles of CH_4 in a 2.0 dm^3 container, so

$$[\text{CH}_4(\text{g})] = 1.2 \times 10^{-2} \text{ mol} / 2.0 \text{ dm}^3 = 6.0 \times 10^{-3} \text{ mol dm}^{-3}$$

Similarly, we can calculate $[\text{H}_2\text{O}(\text{g})] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{CO}(\text{g})] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$, and $[\text{H}_2(\text{g})] = 3.0 \times 10^{-3} \text{ mol dm}^{-3}$.

$$\begin{aligned} Q_c &= \frac{[\text{CO}(\text{g})][\text{H}_2(\text{g})]^3}{[\text{CH}_4(\text{g})][\text{H}_2\text{O}(\text{g})]} \\ &= \frac{(8 \times 10^{-3})(3 \times 10^{-3})^3}{(6 \times 10^{-3})(4 \times 10^{-3})} \\ &= 9.0 \times 10^{-6} \end{aligned}$$

$$Q_c < K (2.4 \times 10^{-4})$$

Thus the ratio of the concentrations of products to the concentrations of reactants is less than the ratio for an equilibrium mixture. The reaction will therefore proceed to the right as written, forming H_2 and CO at the expense of H_2O and CH_4 .

Example 2.6

A mixture of 1.5 mol of N_2 , 2.0 mol of H_2 , and 8.0 mol of NH_3 is introduced into a 20.0 dm^3 closed rigid reaction vessel at 500 K. At this temperature, the equilibrium constant for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$, is 1.7×10^2 . Is the reaction mixture at equilibrium? If not, what is the direction of the net reaction?

Answer

The initial concentration of $[\text{N}_2(\text{g})]$ is $1.5/20 = 7.5 \times 10^{-2} \text{ mol dm}^{-3}$. Similarly, $[\text{H}_2(\text{g})] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$ and $[\text{NH}_3(\text{g})] = 4.0 \times 10^{-1} \text{ mol dm}^{-3}$. Substituting these concentrations into the Q expression gives

$$Q_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} = \frac{(4 \times 10^{-1})^2}{(7.5 \times 10^{-2})(1.0 \times 10^{-1})^3} = 2.1 \times 10^4$$

Because Q_c does not equal to K_c , the reaction mixture is not at equilibrium.

$$Q_c > K_c$$

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 $Q_c = K_c$.

With the knowledge from above examples, we can simply explain how Q_c varies with time as shown in Figure 2.8.

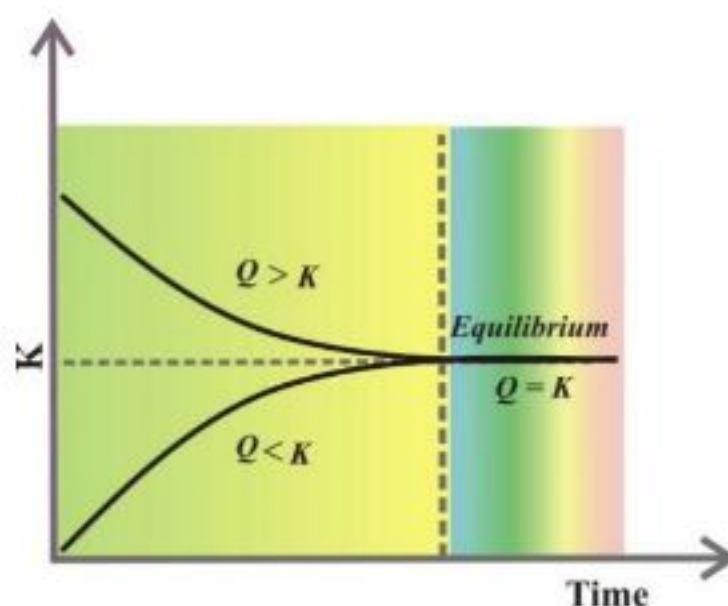


Figure 2.8 The figure explaining the variation of Q over time: If the initial Q is less than K it increases with time favouring the forward reaction; if it is greater than K , it decreases with time favouring the backward reaction until the condition is reached at which $Q = K$.

With the help of Figures 2.5 and 2.8, we can note that;

Before equilibrium, $\Delta G < 0$ and $Q < K$. The reaction is spontaneous in the forward direction.

At equilibrium, $\Delta G = 0$ and $Q = K$.

Beyond the equilibrium position, $\Delta G > 0$ and $Q > K$. The reaction is spontaneous in the reverse direction.

Note: *The reaction quotient (Q) is used to determine whether a system is at equilibrium and if it is not, to predict the direction of reaction.*

2.1.11 Calculating equilibrium concentrations

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

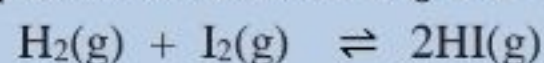
- (a) *the initial concentration,*
- (b) *the change in concentration (x) on going to equilibrium, and*
- (c) *the equilibrium concentration.*

In constructing the table, define x (or α) as the concentration (mol dm^{-3}) (or degree of dissociation) of one of the substances that reacts when going to equilibrium, and then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x .

Step 3. Substitute the equilibrium concentrations into the equilibrium expression for the reaction and solve for x . If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense. Calculate the equilibrium concentrations from the calculated value of x .

Example 2.7

The equilibrium constant K_c for the reaction of $\text{H}_2(\text{g})$ with $\text{I}_2(\text{g})$ is 64.0 at 800 K:



If 1.00 mol of $\text{H}_2(\text{g})$ is allowed to react with 1.00 mol of $\text{I}_2(\text{g})$ in a 10.0 dm^3 closed-rigid-reaction vessel at 800 K, what are the concentrations of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$ at equilibrium? What is the composition of the equilibrium mixture in moles?

Answer

The initial concentrations are $[\text{H}_2(\text{g})] = [\text{I}_2(\text{g})] = 1.00 \text{ mol}/10.0 \text{ dm}^3$
 $= 0.10 \text{ mol dm}^{-3}$.

For convenience, define an unknown, x , as the concentration (mol dm^{-3}) of $\text{H}_2(\text{g})$ that reacts. According to the balanced equation for the reaction, $x \text{ mol dm}^{-3}$ of $\text{H}_2(\text{g})$ reacts with $x \text{ mol dm}^{-3}$ of $\text{I}_2(\text{g})$ to give $2x \text{ mol dm}^{-3}$ of $\text{HI}(\text{g})$. This reduces the initial concentrations of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ from 0.10 mol dm^{-3} to $(0.10 - x) \text{ mol dm}^{-3}$ at equilibrium.

These can be summarized in a table under the balanced equation:

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
Initial/ mol dm^{-3}	0.1		0.1		0
Change/ mol dm^{-3}	$-x$		$-x$		$+2x$
Equilibrium/ mol dm^{-3}	$(0.10 - x)$		$(0.10 - x)$		$2x$

The equilibrium constant, $K_c = \frac{[\text{HI}(\text{g})]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]}$

Substituting the values; $64.0 = \frac{(2x)^2}{(0.10-x)(0.10-x)} = \frac{(2x)^2}{(0.10-x)^2} = \left[\frac{2x}{0.10-x}\right]^2$

Taking square roots of both sides: $\pm 8.0 = \frac{2x}{(0.10-x)}$

Taking + 8.0;

$$0.80 - 8x = 2x$$

$$x = 0.08 \text{ mol dm}^{-3}$$

(If we take $-8.0 = \frac{2x}{(0.10-x)}$; we get $x = 0.13 \text{ mol dm}^{-3}$

which is unacceptable as the initial concentration is 0.10 mol dm^{-3})

$$\therefore [\text{H}_2(\text{g})] = [\text{I}_2(\text{g})] = 0.02 \text{ mol dm}^{-3} \text{ and } [\text{HI}(\text{g})] = 0.16 \text{ mol dm}^{-3}$$

\therefore The composition in moles: $\text{H}_2(\text{g}) = \text{I}_2(\text{g}) = 0.02 \text{ mol dm}^{-3} \times 10.0 \text{ dm}^3 = 0.2 \text{ mol}$

And $\text{HI}(\text{g}) = 1.6 \text{ mol}$

Example 2.8

For the same reaction and temperature as in the previous example, suppose that the initial concentrations of $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$ are $0.006 \text{ mol dm}^{-3}$, $0.004 \text{ mol dm}^{-3}$, and 0.02 mol dm^{-3} respectively. Calculate the concentrations of these species at equilibrium.

Answer

As the initial concentrations do not correspond to the equilibrium concentrations, let x be the depletion in concentration (mol dm^{-3}) of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$, at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be $2x$.

	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{HI}(\text{g})$
Initial/ mol dm^{-3}	0.006		0.004		0.02
Change/ mol dm^{-3}	$-x$		$-x$		$+2x$
Equilibrium/ mol dm^{-3}	$(0.006 - x)$		$(0.004 - x)$		$(0.02 + 2x)$

The equilibrium constant, $K_c = \frac{[\text{HI(g)}]^2}{[\text{H}_2(\text{g})][\text{I}_2(\text{g})]} = 64 = \frac{(0.02 + 2x)^2}{(0.006 - x)(0.004 - x)}$

Multiplication gives us a quadratic equation;

$$60x^2 - 0.72x + 11.34 \times 10^{-4} = 0$$

This is of the type: $ax^2 + bx + c = 0$ and its solutions for x is given by,

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

By applying this to the quadratic equation we have, we get $x = 0.01 \text{ mol dm}^{-3}$ or $0.002 \text{ mol dm}^{-3}$. The value 0.01 mol dm^{-3} is unacceptable as the equilibrium concentration cannot be higher than the initial concentration. Therefore the accepted value of x is $0.002 \text{ mol dm}^{-3}$.

Now the equilibrium concentrations are:

$$[\text{H}_2(\text{g})] = (0.006 - 0.002) = 0.004 \text{ mol dm}^{-3}$$

$$[\text{I}_2(\text{g})] = (0.004 - 0.002) = 0.002 \text{ mol dm}^{-3}$$

$$[\text{HI(g)}] = (0.02 + 0.004) = 0.024 \text{ mol dm}^{-3}$$

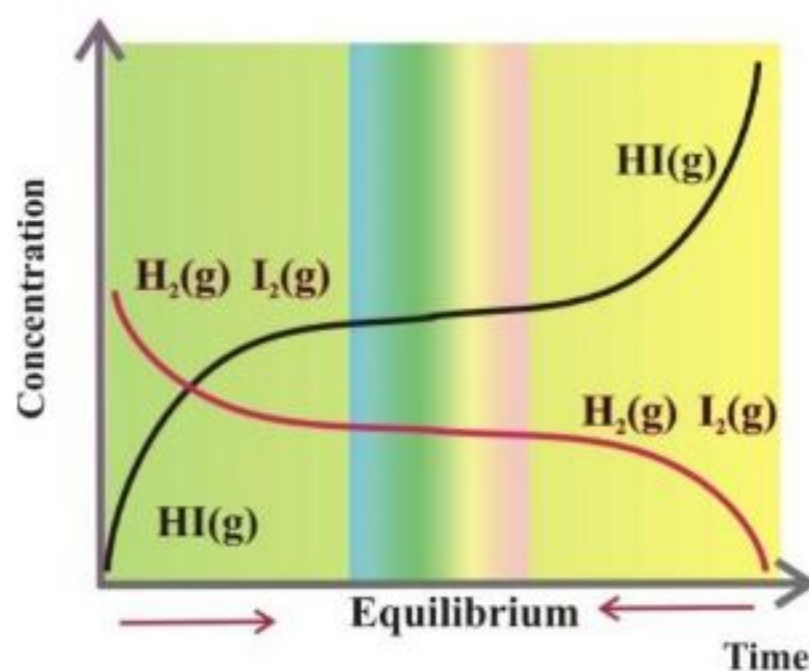


Figure 2.9 Chemical equilibrium in the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ can be attained from either direction. This explains that the reaction can start from either side (right and left) with a mixture of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ or with $\text{HI}(\text{g})$. When it starts with $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ mixture eventually those decrease in amount while the amount of $\text{HI}(\text{g})$ increases. In the other way, if the reactions starts with $\text{HI}(\text{g})$, amounts of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ increase with the time while the amount of $\text{HI}(\text{g})$ decreases.

Example 2.9

0.15 moles of N_2O_4 gas was placed in a 1.0 dm^3 closed rigid reaction vessel at 400 K and allowed to attain the equilibrium $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$. The total pressure at equilibrium was found to be $9.0 \times 10^5 \text{ Pa}$. Calculate partial pressures of each and hence K_p and K_c at equilibrium.

Answer

Assuming ideal behaviour for $\text{N}_2\text{O}_4(\text{g})$;

$$PV = nRT$$

$$P_{\text{N}_2\text{O}_4} = 0.15 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 400 \text{ K} \approx 5.0 \times 10^5 \text{ Pa}$$

Therefore, initial pressure = $4.98 \times 10^5 \text{ Pa}$

Consider the reaction,

	$\text{N}_2\text{O}_4(\text{g})$	\rightleftharpoons	2NO_2
Initial Pressure/ Pa:	5.0×10^5		0
Pressure change/ Pa:	x		$2x$
Pressure at equilibrium/ Pa:	$(5.0 \times 10^5 - x)$		$2x$

At equilibrium, total pressure; $P_{\text{total}} = P_{\text{N}_2\text{O}_4} + P_{\text{NO}_2}$

$$9.0 \times 10^5 \text{ Pa} = [(5.0 \times 10^5 - x) + 2x] \text{ Pa}$$

$$x = 4.0 \times 10^5 \text{ Pa}$$

$$P_{\text{N}_2\text{O}_4} = 1.0 \times 10^5 \text{ Pa} \text{ and } P_{\text{NO}_2} = 8.0 \times 10^5 \text{ Pa}$$

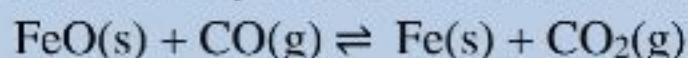
$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{(8.0 \times 10^5 \text{ Pa})^2}{(1.0 \times 10^5 \text{ Pa})} = 6.4 \times 10^6 \text{ Pa}$$

$$K_p = K_c (RT)^{\Delta n}; \text{ and } \Delta n = 2 - 1 = 1$$

$$K_c = \frac{K_p}{(RT)} = \frac{6.4 \times 10^6 \text{ Pa} \times 10^{-3}}{8.314 \times 400 \text{ J mol}^{-1}} = 1.9 \text{ mol dm}^{-3}$$

Example 2.10

The reduction of iron(II) oxide by carbon monoxide gives iron metal and carbon dioxide. The equilibrium constant K_p for the reaction at 1000 K is 0.25.



What are the equilibrium partial pressures of $\text{CO}(\text{g})$ and $\text{CO}_2(\text{g})$ at 1000 K if the initial partial pressures are $P_{\text{CO}(\text{g})} = 1.0 \times 10^5 \text{ Pa}$ and $P_{\text{CO}_2(\text{g})} = 0.50 \times 10^5 \text{ Pa}$. Comment on the value calculated.

Answer

We can calculate equilibrium partial pressures from initial partial pressures and in the same way that we calculate equilibrium concentrations from initial concentrations and substitute partial pressures for concentrations.

	$\text{FeO(s)} + \text{CO(g)} \rightleftharpoons \text{Fe(s)} + \text{CO}_2\text{(g)}$	
Initial pressure/ Pa	1.0×10^5	0.50×10^5
Change pressure/ Pa	$-x$	$+x$
Equilibrium pressure (Pa)	$(1.0 \times 10^5 - x)$	$(0.50 \times 10^5 + x)$

$$K_p = \frac{(P_{\text{CO}_2\text{(g)}})}{(P_{\text{CO(g)}})} = 0.25 = \frac{(0.50 \times 10^5 + x)}{(1.0 \times 10^5 - x)}$$

$$0.25 \times 10^5 - 0.25x = 0.50 \times 10^5 + x$$

$$x = -0.20 \times 10^5 \text{ Pa}$$

$$\therefore P_{\text{CO(g)}} = 1.20 \times 10^5 \text{ Pa}$$

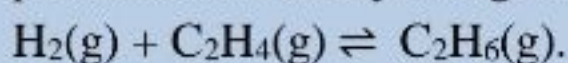
$$P_{\text{CO}_2\text{(g)}} = 0.30 \times 10^5 \text{ Pa}$$

A negative value for x means that the reaction goes from products to reactants to reach equilibrium. This makes sense because the initial reaction quotient, $Q_p = \frac{0.5}{1.0} = 0.5 > K_p$: is greater than the equilibrium constant, i.e. the net reaction always goes from products to reactants (right to left).

We can confirm this by the re-calculation of K_p using the derived values for $P_{\text{CO(g)}}$ and $P_{\text{CO}_2\text{(g)}}$. We get $K_p = \frac{0.30 \times 10^5 \text{ Pa}}{1.20 \times 10^5 \text{ Pa}} = 0.25$. So that the above given reaction proceeds to the left.

Example 2.11

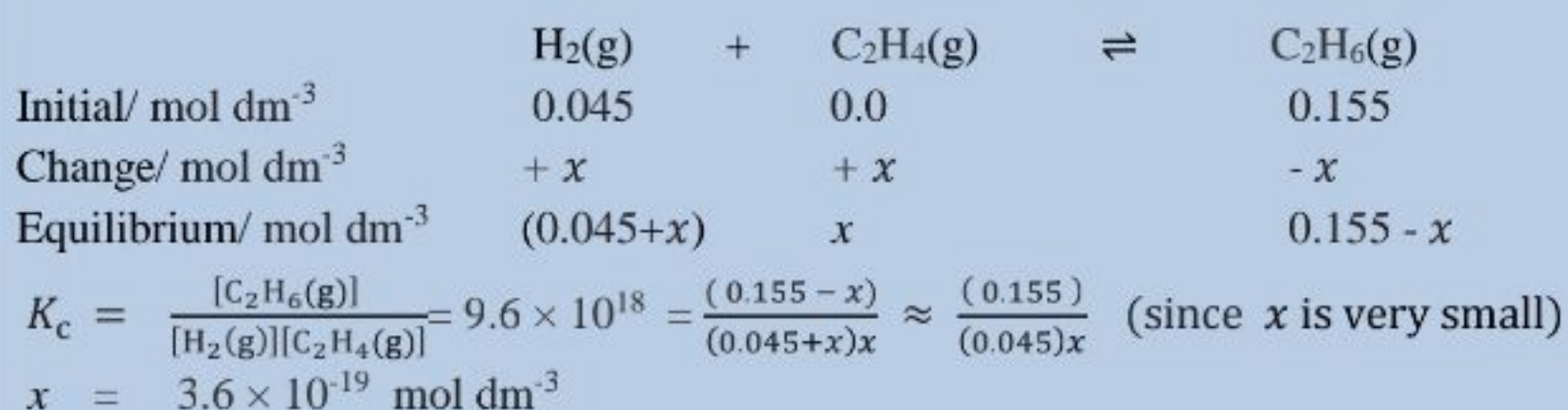
The chemical equation for the reaction of hydrogen with ethylene (C_2H_4) in the presence of a catalyst to give ethane (C_2H_6) is:



Equilibrium constant of the reaction $K_c = 9.6 \times 10^{18}$ at 25°C . If a mixture of $0.200 \text{ mol dm}^{-3} \text{ H}_2\text{(g)}$ and $0.155 \text{ mol dm}^{-3} \text{ C}_2\text{H}_4\text{(g)}$ is maintained at 25°C in the presence of a powdered nickel catalyst, what is the equilibrium concentration of each substance in the mixture?

Answer

Very large value of K_c shows that the reaction goes to completion. i.e. As the amount of $H_2(g)$ ($0.200 \text{ mol dm}^{-3}$) is higher than the amount of $C_2H_4(g)$ ($0.155 \text{ mol dm}^{-3}$), it is clear that all the $C_2H_4(g)$ is consumed to produce $0.155 \text{ mol dm}^{-3}$ of $C_2H_6(g)$. Therefore the remaining amount of $H_2(g)$ is $(0.200 - 0.155) \text{ mol dm}^{-3} = 0.045 \text{ mol dm}^{-3}$. As the K_c of the forward reaction is very large, the equilibrium constant for the reverse reaction should be very small. On this basis we can consider that the reverse reaction occurs in which the amount of $C_2H_6(g)$ consumed is x and the following equilibrium is built-up.



$$[H_2(g)] = 0.045 \text{ mol dm}^{-3}$$

$$[C_2H_4(g)] = 3.6 \times 10^{-19} \text{ mol dm}^{-3}$$

$$[C_2H_6(g)] = 0.155 \text{ mol dm}^{-3}$$

We can check and confirm the answer by substituting the values in K_c expression.

$$K_c = \frac{[C_2H_6(g)]}{[H_2(g)][C_2H_4(g)]} = \frac{0.155}{0.045 (3.6 \times 10^{-19})} = 9.6 \times 10^{18}$$

i. e. the assumptions made are correct.

2.1.12 Factors affecting the equilibrium

From the above discussions we now know that the chemical equilibrium is a balance between forward and reverse reactions at a constant temperature in a closed rigid system. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. When we say that an equilibrium position shifts to the right, for example, we mean that the net reaction is now from left to right or vice-versa. Variables that can be controlled experimentally are concentration, pressure, volume, and temperature. Here, we will examine how each of these variables affects a reacting system at equilibrium. The qualitative effect of the above

variables on the composition of an equilibrium mixture can be predicted using a principle first described by the French chemist Henri-Louis Le Châtelier.

Le Châtelier's principle:

Change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

This is applicable to all physical and chemical equilibria.

Effect of concentration change

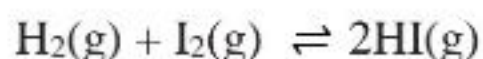
In general, when equilibrium is disturbed by the addition/removal of any reactant/product, Le Chatelier's principle predicts that:

- The concentration stress of an *added* reactant/product is relieved by net reaction in the direction that consumes the added substance.
- The concentration stress of a *removed* reactant/product is relieved by net reaction in the direction that *replenishes* the removed substance.

or in other words:

"When the concentration of any of the reactants or products in a reaction at equilibrium is changed, the composition of the equilibrium mixture changes so as to minimize the effect of concentration change".

Let us consider the reaction,



If $\text{H}_2(\text{g})$ is added to the reaction mixture at equilibrium, then the equilibrium of the reaction is disturbed. In order to restore it, the reaction proceeds in a direction wherein $\text{H}_2(\text{g})$ is consumed, i.e., more of $\text{H}_2(\text{g})$ and $\text{I}_2(\text{g})$ react to form $2\text{HI}(\text{g})$ and finally the equilibrium shifts to right (forward). This is in accordance with the Le Châtelier's principle which implies that in case of addition of a reactant/product, a new equilibrium will be set up in which the concentration of the reactant/product should be less than what it was after the addition but more than what it was in the original mixture. Figure 2.10 illustrates the system.

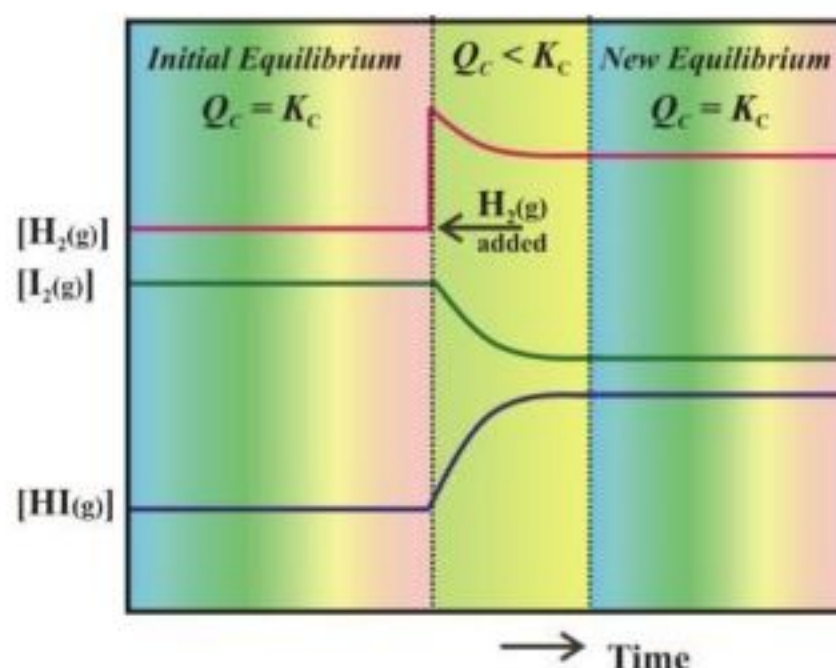


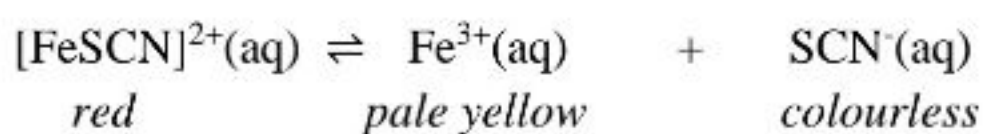
Figure 2.10 Effect of addition of H_2 on the change of concentration for the reactants and products in the reaction, $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$

This behaviour can be explained in terms of the reaction quotient, Q_c

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

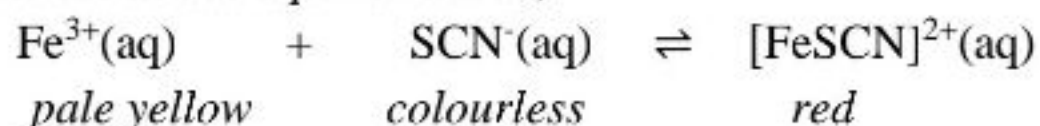
Addition of hydrogen at equilibrium results in the increase in the magnitude of the denominator which in turn decreases the value of Q_c below K_c . Thus, in order to release this stress, more $\text{H}_2(\text{g})$ will be consumed making the forward reaction predominant. Therefore, the system will readjust with time making the forward reaction to move forward to attain a new equilibrium. Similarly, we can understand that the removal of a product also boosts the forward reaction and increases the concentration of the products.

Another simple system that can be tested experimentally in the laboratory is the equilibrium in Iron(III) -thiocyanate system. $[\text{Fe}(\text{SCN})_3]$ dissolves readily in water to give a red solution. The red colour is due to the presence of hydrated $[\text{FeSCN}]^{2+}$ ion. The equilibrium between undissociated $[\text{FeSCN}]^{2+}$ and the Fe^{3+} and SCN^- ions is given by



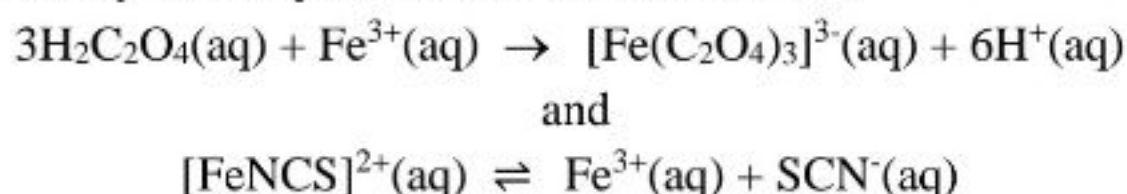
Once we add some sodium thiocyanate (NaSCN) to this solution, the stress applied to the equilibrium system increases the concentration of $\text{SCN}^-(\text{aq})$. To relieve this stress, some $\text{Fe}^{3+}(\text{aq})$ ions react with the added $\text{SCN}^-(\text{aq})$ ions, and the equilibrium shifts from right to left by deepening the red colour of the solution. Similarly, if we add $\text{Fe}^{3+}(\text{aq})$ ions to the original solution, the red colour would also deepen because the additional $\text{Fe}^{3+}(\text{aq})$ ions shift the equilibrium from right to left.

Further, if we write the above equilibrium as;

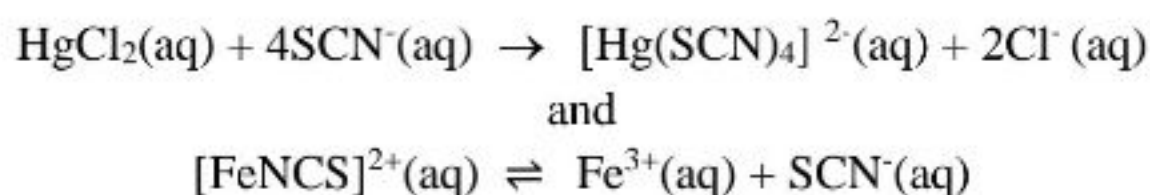


This equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product. The equilibrium can be shifted in the opposite direction by adding reagents that remove $\text{Fe}^{3+}(\text{aq})$ or $\text{SCN}^{-}(\text{aq})$ ions. For example, oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), reacts with $\text{Fe}^{3+}(\text{aq})$ ions to form the stable complex ion $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$, thus decreasing the concentration of free $\text{Fe}^{3+}(\text{aq})$. In accordance with the Le Chatelier's principle, the concentration stress of removed $\text{Fe}^{3+}(\text{aq})$ is relieved by dissociation of $[\text{Fe}(\text{SCN})]^{2+}$ to replenish the $\text{Fe}^{3+}(\text{aq})$ ions. Because the concentration of $[\text{Fe}(\text{SCN})]^{2+}$ decreases, the intensity of red color decreases.

This effect can be explained by the reactions shown below.

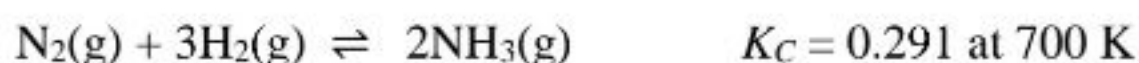


Addition of aq. HgCl_2 also decreases red colour because $\text{Hg}^{2+}(\text{aq})$ reacts with $\text{SCN}^{-}(\text{aq})$ ions to form the stable complex ion $[\text{Hg}(\text{SCN})_4]^{2-}$. Removal of free $\text{SCN}^{-}(\text{aq})$ shifts the equilibrium from right to left to replenish $\text{SCN}^{-}(\text{aq})$ ions. Addition of potassium KSCN on the other hand increases the colour intensity of the solution as it shift the equilibrium to right.



Example:

Let's consider the following equilibrium system in the Haber process for the synthesis of ammonia:



Suppose we have an equilibrium mixture of $0.50 \text{ mol dm}^{-3} \text{ N}_2(\text{g})$, $3.00 \text{ mol dm}^{-3} \text{ H}_2(\text{g})$, and $1.98 \text{ mol dm}^{-3} \text{ NH}_3(\text{g})$ at 700 K and that we disturb the equilibrium by increasing the $\text{N}_2(\text{g})$ concentration to 1.50 mol dm^{-3} . Le Châtelier's principle tells us that the reaction will occur to relieve the stress of the increased concentration of $\text{N}_2(\text{g})$ by converting some of the $\text{N}_2(\text{g})$ to $\text{NH}_3(\text{g})$. It is clear that the number of gaseous molecules decreases in the forward direction allowing the release in the stress. i.e. as the $\text{N}_2(\text{g})$ concentration decreases, the $\text{H}_2(\text{g})$ concentration must also decrease and the $\text{NH}_3(\text{g})$ concentration must increase in accordance with the stoichiometry of the balanced equation.

These changes can be explained by the following Figure 2.11.

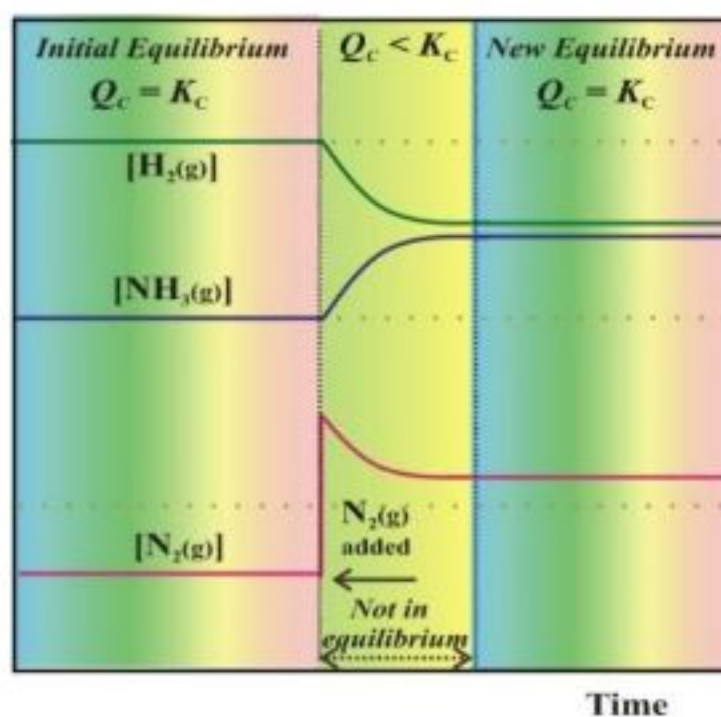
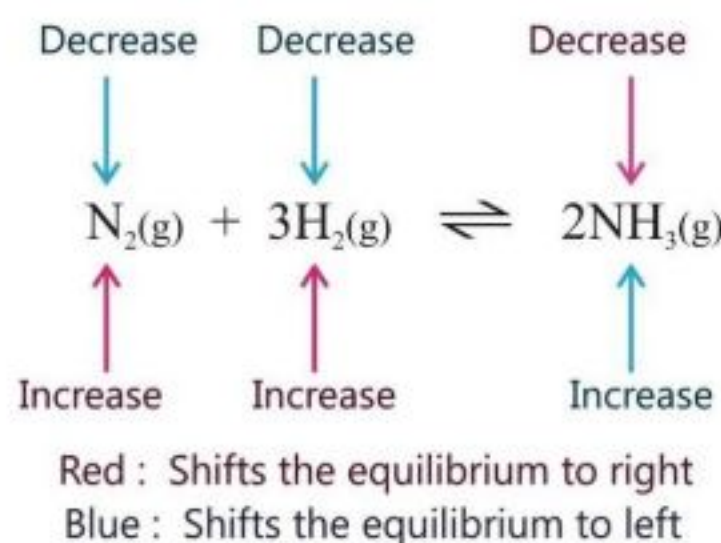


Figure 2.11 Effect of addition of N_2 on the change of concentration for the reactants and products in the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Now we can understand that once the rules of Le Châtelier's principle are applied to the equilibrium, the yield of ammonia is increased by an increase in the $N_2(g)$ or $H_2(g)$ concentration or by a decrease in the $NH_3(g)$ concentration and the sketch below gives us a kind of summary on the effect on the equilibrium position.



Sketch 1 An increase in the $N_2(g)$ or $H_2(g)$ concentration or a decrease in the $NH_3(g)$ concentration shifts the equilibrium from left to right. A decrease in the $N_2(g)$ or $H_2(g)$ concentration or an increase in the $NH_3(g)$ concentration shifts the equilibrium from right to left.

Though Le Châtelier's principle gives us to predict changes in the composition of an equilibrium mixture with the applying stress, it does not explain *why* those changes occur. However, we can understand the effect by considering the reaction quotient Q_c . For the initial equilibrium mixture of $0.50 \text{ mol dm}^{-3} N_2(g)$, $3.00 \text{ mol dm}^{-3} H_2(g)$, and $1.98 \text{ mol dm}^{-3} NH_3(g)$ at 700 K , Q_c equals the equilibrium constant K_c (0.291) because the system is at equilibrium:

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{[1.98]^2}{[0.5][3.0]^3} = 0.29 = K_c$$

When we disturb the equilibrium by increasing the $\text{N}_2(\text{g})$ concentration to 1.50 mol dm^{-3} , the denominator of the equilibrium constant expression increases and Q_c decreases to a value less than K_c :

$$Q_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} = \frac{[1.98]^2}{[1.5][3.0]^3} = 0.0968 < K_c$$

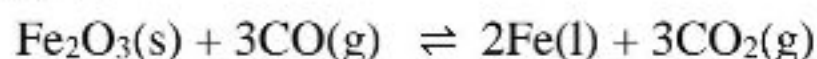
For the system to move to a new state of equilibrium, Q_c must increase; that is, the numerator of the equilibrium constant expression must increase and the denominator must decrease. This implies that the net conversion of $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$ to $\text{NH}_3(\text{g})$ occurs just as predicted by Le Châtelier's principle. When the new equilibrium is established as shown in Figure 2.11, the concentrations are 1.31 mol dm^{-3} $\text{N}_2(\text{g})$, 2.43 mol dm^{-3} $\text{H}_2(\text{g})$, and 2.36 mol dm^{-3} $\text{NH}_3(\text{g})$, and Q_c again equals K_c :

$$Q_c = \frac{[2.36]^2}{[1.31][2.43]^3} = 0.29 = K_c$$

Example:

Applying Le Châtelier's principle to solid \rightleftharpoons gas systems:

The reaction of iron(III) oxide with carbon monoxide occurs in a blast furnace when iron ore is reduced to iron metal:



Let's use Le Châtelier's principle to predict the direction of the net reaction when an equilibrium mixture is disturbed by:

- (a) Adding Fe_2O_3
- (b) Removing CO_2
- (c) Removing CO ; while accounting for the change using the reaction quotient Q_c .

- (a) Because Fe_2O_3 is a pure solid, its concentration is equal to 1 and does not change when more Fe_2O_3 is added. Therefore, there is no concentration stress and the original equilibrium is undisturbed.
- (b) Le Châtelier's principle predicts that the concentration stress of CO_2 removed will be relieved by net reaction shift from reactants to products to replenish CO_2 .
- (c) Le Châtelier's principle predicts that the concentration stress of CO removed will be relieved by net reaction shift from products to reactants to replenish CO . The reaction quotient is;

$$Q_c = \frac{[\text{CO}_2(\text{g})]^3}{[\text{CO}(\text{g})]^3}$$

When the equilibrium is disturbed by reducing $[\text{CO}]$, Q_c increases, so that $Q_c > K_c$. For the system to move to a new state of equilibrium, Q_c must decrease; that is, $[\text{CO}_2]$ must decrease and $[\text{CO}]$ must increase. Therefore, the net reaction goes from products to reactants, as predicted by Le Châtelier's principle.

Example 1:

Lead carbonate decomposes to lead oxide and carbon dioxide according to the following equation:



Because PbCO_3 and PbO are solids, the equilibrium constant is simply $K = [\text{CO}_2(\text{g})]$. At a given temperature, therefore, any system that contains solid PbCO_3 and solid PbO will have exactly the same concentration of $\text{CO}_2(\text{g})$ at equilibrium, regardless of the ratio or the amounts of the solids present. This can be understood by Figure 2.12, which shows a plot of $[\text{CO}_2(\text{g})]$ versus the amount of solid PbCO_3 added. Initially, the added PbCO_3 decomposes completely to $\text{CO}_2(\text{g})$ because the amount of PbCO_3 is not sufficient to give a $\text{CO}_2(\text{g})$ concentration equal to K . Thus the left portion of the graph represents a system that is not at equilibrium because it contains only $\text{CO}_2(\text{g})$ and $\text{PbO}(\text{s})$. In contrast, when just enough PbCO_3 has been added to give $[\text{CO}_2(\text{g})] = K$, the system has reached equilibrium, and adding more PbCO_3 has no effect on the $\text{CO}_2(\text{g})$ concentration: so the graph is a horizontal line. Thus any $\text{CO}_2(\text{g})$ concentration that is not on the horizontal line represents a non-equilibrium state, and the system will adjust its composition to achieve equilibrium, provided enough PbCO_3 and PbO are present. For example, the point labelled as **A** in Figure 2.12, the concentration of $\text{CO}_2(\text{g})$ lies above the horizontal line, so it corresponds to a $[\text{CO}_2(\text{g})]$ that is greater than the equilibrium concentration of $\text{CO}_2(\text{g})$ ($Q > K$). To reach equilibrium, the system must decrease $[\text{CO}_2(\text{g})]$, which it can do only by reacting $\text{CO}_2(\text{g})$ with solid PbO to form solid PbCO_3 . Thus the reaction will proceed to the left side, until $[\text{CO}_2(\text{g})] = K$. Conversely, the point labelled as **B** in the figure, the concentration of gaseous $\text{CO}_2(\text{g})$ lies below the horizontal line, so it corresponds to a $[\text{CO}_2(\text{g})]$ that is less than the equilibrium concentration of $\text{CO}_2(\text{g})$ ($Q < K$). To reach equilibrium, the system must increase $[\text{CO}_2(\text{g})]$, which it can do only by decomposing solid PbCO_3 to form $\text{CO}_2(\text{g})$ and solid PbO . The reaction will therefore proceed to the right as written, until $[\text{CO}_2(\text{g})] = K$.

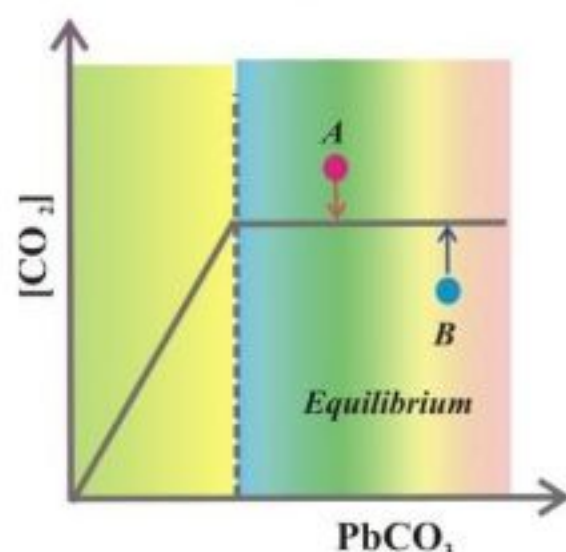
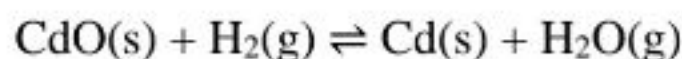


Figure 2.12 Initially the concentration of $\text{CO}_2(\text{g})$ increases linearly with the amount of solid PbCO_3 added, as PbCO_3 decomposes to $\text{CO}_2(\text{g})$ and solid PbO . Once the $\text{CO}_2(\text{g})$ concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid PbCO_3 has no effect on $[\text{CO}_2(\text{g})]$, as long as the temperature remains constant.

Example 2:

The reduction of cadmium oxide by hydrogen giving metallic cadmium and water vapour exhibits a manner which further gives us much understanding about the Le Châtelier's principle.



Equilibrium constant K_c is $[\text{H}_2\text{O(g)}] / [\text{H}_2\text{(g)}]$. For example, if $[\text{H}_2\text{O(g)}]$ is doubled at equilibrium, then $[\text{H}_2\text{(g)}]$ must also be doubled for the system to remain at equilibrium. A plot of $[\text{H}_2\text{O(g)}]$ versus $[\text{H}_2\text{(g)}]$ at equilibrium is a straight line with a slope of K_c . Again, only those pairs of concentrations of $\text{H}_2\text{O(g)}$ and $\text{H}_2\text{(g)}$ that lie on the line correspond to equilibrium states. Any point representing a pair of concentrations that does not lie on the line corresponds to a non-equilibrium state. In such cases, the reaction will proceed in whichever direction causes the composition of the system to move toward the equilibrium line. For example, point A in Figure 2.13 lies below the line, indicating that the $[\text{H}_2\text{O(g)}] / [\text{H}_2\text{(g)}]$ ratio is less than the ratio of an equilibrium mixture ($Q < K$). Thus the reaction will proceed to the right as written, consuming $\text{H}_2\text{(g)}$ and producing $\text{H}_2\text{O(g)}$, which causes the concentration ratio to move up and to the left toward the equilibrium line. Conversely, point B in Figure 2.13 lies above the line, indicating that the $[\text{H}_2\text{O(g)}] / [\text{H}_2\text{(g)}]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction will proceed to the left as written, consuming $\text{H}_2\text{O(g)}$ and producing $\text{H}_2\text{(g)}$, which causes the concentration ratio to move down and to the right toward the equilibrium line.

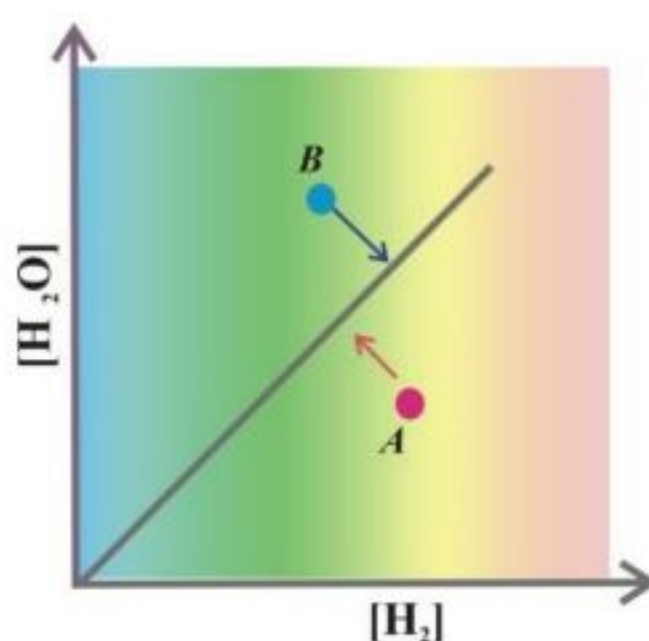
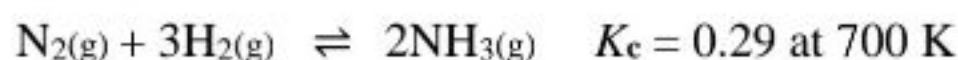


Figure 2.13 For any equilibrium concentration of $\text{H}_2\text{O(g)}$, there is only one equilibrium concentration of $\text{H}_2\text{(g)}$. Because the magnitudes of the two concentrations are directly proportional, a large $[\text{H}_2\text{O(g)}]$ at equilibrium requires a large $[\text{H}_2\text{(g)}]$ and vice versa. In this case, the slope of the line is equal to K_c .

Changes in pressure and volume

To illustrate how an equilibrium mixture is affected by a change in pressure as a result of a change in the volume, let's return to the Haber synthesis of ammonia. The balanced equation for the reaction has 4 moles of gas on the reactant side of the equation and 2 moles on the product side:



What happens to the composition of the equilibrium mixture if we increase the pressure by decreasing the volume? (the pressure of an ideal gas is inversely proportional to the volume at constant temperature and constant number of moles of gas). According to Le Châtelier's principle, net reaction will occur in the direction that relieves the stress of the increased pressure, which means that the number of moles of gas must decrease. Therefore, we predict that the net reaction will proceed from left to right because the forward reaction converts 4 moles of gaseous reactants to 2 moles of gaseous products. In general, Le Châtelier'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.*
- *A decrease in pressure by expanding the volume will bring about net reaction in the direction that increases the number of moles of gas.*

To see why Le Châtelier's principle works for pressure (volume) changes, let's look again at the reaction quotient for the equilibrium mixture of $0.50 \text{ mol dm}^{-3} \text{ N}_2(\text{g})$, $3.00 \text{ mol dm}^{-3} \text{ H}_2(\text{g})$ and $1.98 \text{ mol dm}^{-3} \text{ NH}_3(\text{g})$ at 700 K, where Q_c equals the equilibrium constant K_c (0.291) because the system is at equilibrium:

$$Q_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]^3} = \frac{[1.98]^2}{[0.5][3.0]^3} = 0.29 = K_c$$

If we disturb the equilibrium by reducing the volume by a factor of 2, we not only double the total pressure, we also double the partial pressure and thus the molar concentration of each reactant and product (molarity = $n/V = P/RT$). Because the balanced equation has more moles of gaseous reactants than the gaseous products, the increase in the denominator of the equilibrium constant expression is greater than the increase in the numerator and the new value of Q_c is less than the equilibrium constant.

$$Q_c = \frac{[\text{NH}_3(\text{g})]^2}{[\text{N}_2(\text{g})][\text{H}_2(\text{g})]} = \frac{[3.96]^2}{[1.0][6.0]^3} = 0.073 < K_c$$

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

Effect of inert gas addition

If the volume is kept constant by doing the experiment in a closed-rigid container and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressures or the molar concentrations of the substances involved in the reaction. The reaction quotient changes only if the added gas is a reactant or product involved in the reaction

Effect of temperature change

Whenever an equilibrium is disturbed by a change in the concentration, pressure or volume, the composition of the equilibrium mixture changes because the reaction quotient, Q_c no longer equals the equilibrium constant, K_c due to the change in equilibrium position and that does not change the value of equilibrium constant. However, when a change in temperature occurs, the value of equilibrium constant, K_c is changed. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- *The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.*

We can write the reaction as: reactants \rightleftharpoons products + heat ($\Delta H < 0$)

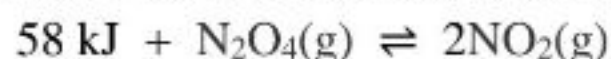
- *The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.*

We can write the reaction as : reactants + heat \rightleftharpoons products ($\Delta H > 0$)

According to above reactions, heat can be thought of as a product in an exothermic reaction and as a reactant in an endothermic reaction. Increasing the temperature of a system corresponds to adding heat. Le Chatelier's principle predicts that an exothermic reaction will shift to the left (toward the reactants) if the temperature of the system is increased (heat is added). Conversely, an endothermic reaction will shift to the right (toward the products) if the temperature of the system is increased. If a reaction is thermochemically neutral ($\Delta H_{rxn} = 0$), then a change in temperature will not affect the equilibrium composition.

Example:

We can examine the effects of temperature on the dissociation of $N_2O_4(g)$ to $NO_2(g)$, for which $\Delta H = +58 \text{ kJ mol}^{-1}$. This reaction can be written as follows:



$$K_c = \frac{[NO_2(g)]^2}{[N_2O_4(g)]}$$

Increasing the temperature (adding heat to the system) is a stress that will drive the reaction to the right. Thus increasing the temperature increases the ratio of $\text{NO}_2(\text{g})$ to $\text{N}_2\text{O}_4(\text{g})$ at equilibrium, which increases equilibrium constant K .

The effect of increasing the temperature on a system at equilibrium can be summarized as follows: increasing the temperature increases the magnitude of the equilibrium constant for an endothermic reaction, decreases the equilibrium constant for an exothermic reaction, and has no effect on the equilibrium constant for a thermally neutral reaction.

In summary, three types of stresses can alter the composition of an equilibrium system: adding or removing reactants or products, changing the total pressure or volume, and changing the temperature of the system. A reaction with an unfavourable equilibrium constant can be driven to completion by continually removing one of the products of the reaction. Equilibria that contain different numbers of gaseous reactant and product molecules are sensitive to changes in volume or pressure; higher pressures favour the side with fewer gaseous molecules. Removing heat from an exothermic reaction favours the formation of products, whereas removing heat from an endothermic reaction favours the formation of reactants.

The effect of catalyst on equilibrium

The addition of a catalyst to a reaction increases the rate by providing a new, lower-energy alternative pathway for the conversion of reactants to products. Because the forward and reverse reactions pass through the same transition state, a catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. If a reaction mixture is at equilibrium in the absence of a catalyst (that is, the forward and reverse rates are equal), it will still be at equilibrium after a catalyst is added because the forward and reverse rates, though faster, remain equal. If a reaction mixture is not at equilibrium, a catalyst accelerates the rate at which equilibrium is reached, but it does not affect the composition of the equilibrium mixture. Because a catalyst has no effect on the equilibrium concentrations, it does not appear in the balanced chemical equation or in the equilibrium constant expression (As the catalyst is not consumed in the reaction they are not considered in the overall rate equation and therefore do not affect the equilibrium of the reaction but only the rate). Even though a catalyst doesn't change the position of equilibrium it can nevertheless significantly influence the choice of optimum conditions for a reaction.

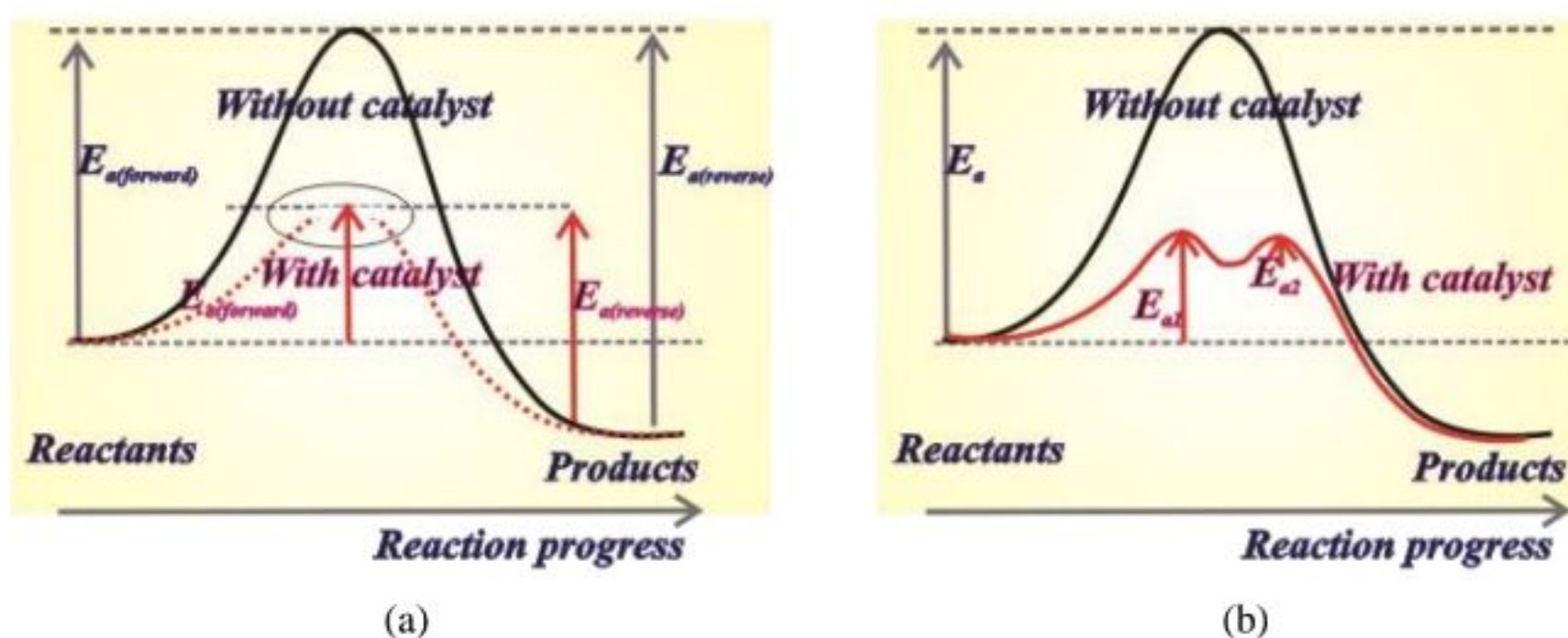


Figure 2.14 Comparison of the reaction profile with and without a catalyst. The addition of a catalyst to a reaction increases the rate by providing a new, lower-energy alternative pathway as shown in (a). Also the reaction may find the similar path with multi steps and proceed via an intermediate as shown in (b).

For example, in the Haber synthesis of ammonia, because the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ is exothermic, its equilibrium constant decreases with increasing temperature, and optimum yields of $\text{NH}_3(\text{g})$ are obtained at low temperatures. At those low temperatures, however, the rate at which equilibrium is reached is too slow for the reaction to be practical. Thus, low temperatures give good yields but slow rates, whereas high temperatures give satisfactory rates but poor yields. The answer to the dilemma is to find a catalyst. A catalyst consisting of iron mixed with certain metal oxides causes the reaction to occur at a satisfactory rate at temperatures where the equilibrium concentration of $\text{NH}_3(\text{g})$ is reasonably favourable. The yield of $\text{NH}_3(\text{g})$ can be improved further by running the reaction at high pressures. Typical reaction conditions for the industrial synthesis of ammonia are $400 - 500\text{ }^\circ\text{C}$ and $130 - 300\text{ atm}$.

Following table summarizes the shifts in equilibrium in response to stresses imposed on an equilibrium system.

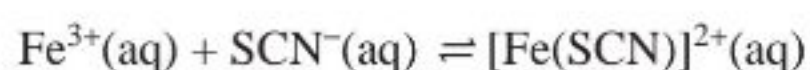
Table 2.1 Response of equilibrium system to the stresses applied

Stress	Response of the system	Effect on equilibrium constant
Increase in concentration at constant temperature	System shifts to decrease the reactant or the product added	Does not change. The concentrations of all reactants and products change to keep the ratio constant
Decrease in concentration at constant temperature	System shifts to increase the reactant or the product removed	Does not change. The concentrations of all reactants and products change to keep the ratio constant
Increase in volume (Decrease in pressure) at constant temperature	System shifts to the side with more gaseous species. (when the number of gaseous species are the same on both sides, consider the exo/endo-thermic nature)	Does not change. The concentrations of all reactants and products change to keep the ratio constant
Decrease in volume (Increase in pressure) at constant temperature	System shifts to the side with least gaseous species. (when the number of gaseous species are the same on both sides, consider the exo/endo-thermic nature)	Does not change. The concentrations of all reactants and products change to keep the ratio constant
Increase in temperature	Favours the endothermic reaction by using the added heat	Equilibrium constant changes because the equilibrium position shifts
Decrease in temperature	Favours the exothermic reaction by releasing more heat	Equilibrium constant changes because the equilibrium position shifts
Addition of a catalyst	No change in the system because the catalyst increases the rates of forward and backward reactions by the same extent. Only thing happens is that the system reaches the equilibrium faster	Does not change
Addition of an inert gas	No change in the system because it does not participate in the reaction	Does not change

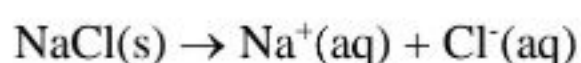
2.2 Ionic equilibrium in aqueous solutions

A solution can be defined as a homogeneous mixture of two or more substances. The solute is the substance present in a smaller amount or the substance that has been dissolved, and the solvent is the substance present in a larger amount. A solution may be gaseous (such as air), solid (such as an alloy), or liquid (seawater, for example). In this section we will discuss only *aqueous solutions*, in which the solute initially is a liquid or a solid and the solvent is water and once the solution is formed we consider the ionic form of the substances which are in equilibrium in aqueous phase.

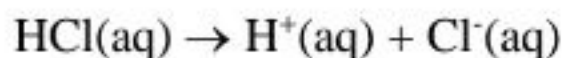
For example, under the effect of change of concentration on the direction of equilibrium, we have earlier considered the following equilibrium which involves ions:



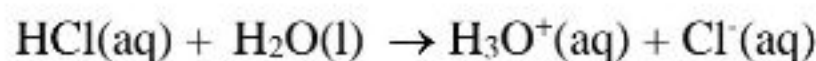
There are numerous equilibria that involve ions only. It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called *electrolytes* while the other does not and are thus, referred to as *nonelectrolytes*. Faraday further classified electrolytes into *strong* and *weak* electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is entirely composed of sodium ions and chloride ions, i.e.



Acids and bases are also electrolytes. Some acids, like hydrochloric acid (HCl) and nitric acid (HNO₃), are strong electrolytes. These acids ionize completely in water; for example, when hydrogen chloride gas dissolves in water, it forms hydrated H⁺ and Cl⁻ ions:



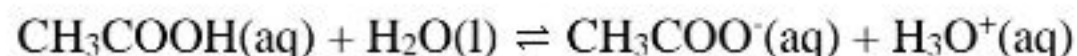
or we write the reaction as:



However, that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and protons, i.e.



or we write the reaction as:



We can see that the \rightarrow (single arrow) is used in the case of dissociation of HCl to show the complete or almost 100% ionization. Also we can understand that a solution of HCl does not have any free HCl(aq) molecules as they are completely dissociated to $\text{H}_3\text{O}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ ions. In the case of acetic acid, a \rightleftharpoons (double arrow) is used to show the partial or less than 5% ionization in water and the reaction is reversible. Initially, a number of CH_3COOH molecules break up into $\text{CH}_3\text{COO}^-(\text{aq})$ and $\text{H}^+(\text{aq})$ ions. As time goes on, some of the $\text{CH}_3\text{COO}^-(\text{aq})$ and $\text{H}^+(\text{aq})$ ions recombine into CH_3COOH molecules. Eventually, a state is reached in which the acid molecules ionize as fast as the ions recombine reaching a state of *chemical equilibrium*. It is very important to show the physical state of each species in the system where (aq) is used to show that the species are in aqueous phase. Further, as the amount of water (solvent) is in large excess, a bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give *trigonal pyramidal* hydrated proton called the *hydronium ion*, $\text{H}_3\text{O}^+(\text{aq})$. It has to be noted that the use of $\text{H}^+(\text{aq})$ and $\text{H}_3\text{O}^+(\text{aq})$ means the same i.e., a proton or a hydrated proton.

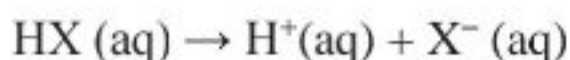
With the above simple explanations we can note that in weak electrolytes, equilibrium is established between ions and the unionized molecules. This type of equilibrium involving ions in aqueous solution is called **ionic equilibrium**. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

2.2.1 Acids, bases (and salts)

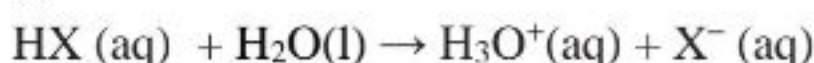
Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids. As most of the acids taste sour, the word “acid” has been derived from a latin word “*acidus*” meaning sour. Acids are known to turn blue litmus paper into red and liberate dihydrogen (H_2) on reacting with metals. Similarly, bases are known to turn red litmus paper blue, taste bitter and feel soapy. A common example of a base is washing soda used for washing purposes. When acids and bases are mixed in the right proportion they react with each other to give *salts*. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (<5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced.

Arrhenius concept of acids and bases

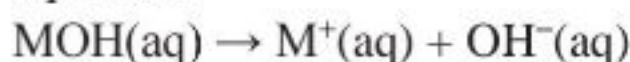
According to Arrhenius theory, *acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$ and bases are substances that produce hydroxyl ions $OH^-(aq)$* . The ionization of an acid $HX(aq)$ can be represented by the following equations:



or



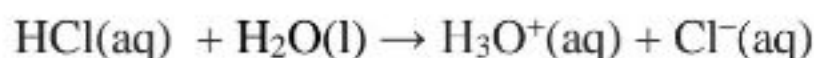
Similarly, a base molecule like $MOH(aq)$ ionizes in aqueous solution according to the equation:



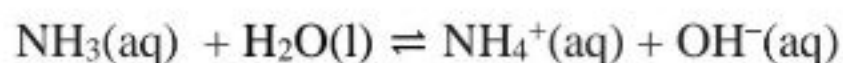
The hydroxyl ion also exists in the hydrated form in the aqueous solution (eg. $H_3O_2^-(aq)$). Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.

The Brønsted -Lowry definition of acids and bases

The Danish chemist, Johannes Brønsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brønsted-Lowry theory, *acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+* . In short, *acids are proton donors and bases are proton acceptors*. For example;



Here we can see that the $HCl(aq)$ molecule donates a proton to water forming $Cl^-(aq)$ and $H_3O^+(aq)$ ions. i.e. Therefore, $HCl(aq)$ is classified as a Brønsted acid because it can donate a H^+ ion. (We can also see that the $H_2O(l)$ molecule accepts that proton acting as a base; further insights of this nature will be explained in a latter section dealing with *conjugate acid-base pairs*).

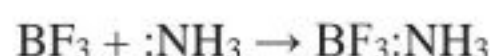


Here we can see that the $NH_3(aq)$ molecule accepts a proton from water forming $NH_4^+(aq)$ and $OH^-(aq)$ ions. i.e. Therefore, $NH_3(aq)$ is classified as a Brønsted base because it can accept a H^+ ion.

Lewis acids and bases

G.N. Lewis in 1923 defined an *acid as a species which accepts an electron pair and a base as a species which donates an electron pair*. As far as bases are concerned, there is not much difference between Brønsted-Lowry and Lewis concepts, as the base provides

a lone pair in both the cases. However, in Lewis concept many acids do not have protons. A typical example is reaction of electron deficient species BF_3 with NH_3 . BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,

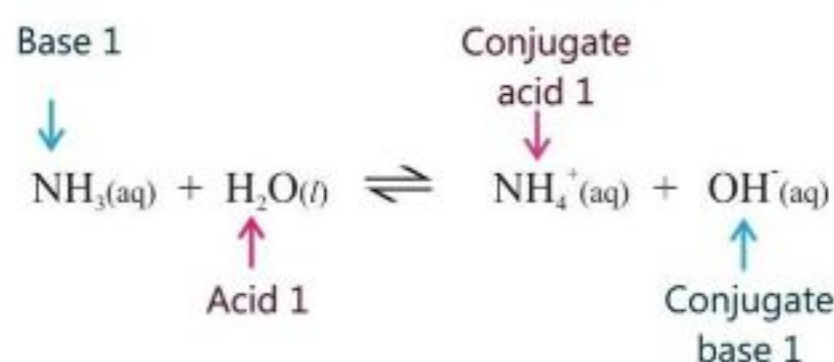


Electron deficient species like AlCl_3 , Co^{3+} , Mg^{2+} , etc. can act as Lewis acids while species like H_2O , NH_3 , OH^- etc. which can donate a pair of electrons, can act as Lewis bases.

2.2.2 Conjugate acid – base pairs

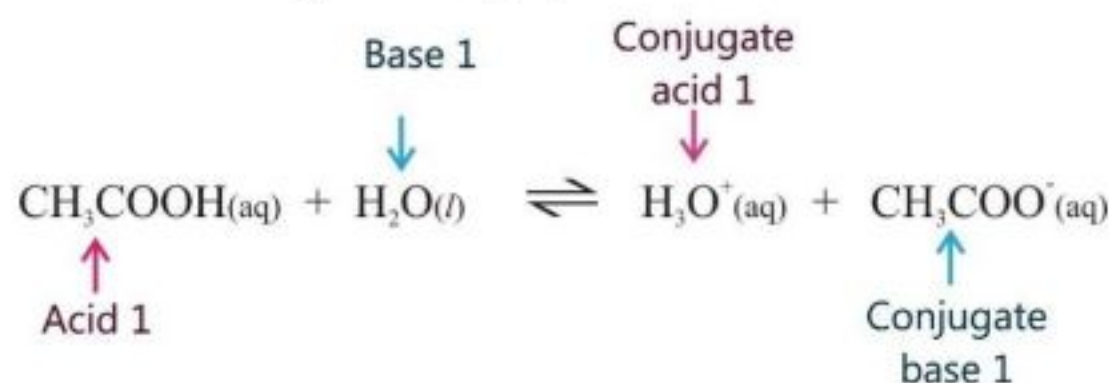
Brønsted definition of acids and bases can further be extended to the concept of the **conjugate acid-base pair**, which can be defined as *an acid and its conjugate base or a base and its conjugate acid*. The conjugate base of a Brønsted acid is the species that remains when one proton has been removed from the acid. Conversely, a conjugate acid results from the addition of a proton to a Brønsted base.

Consider the partial dissolution of $\text{NH}_3(\text{aq})$ in water.



A basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brønsted acid and base, respectively. In the reverse reaction, H^+ is transferred from $\text{NH}_4^+(\text{aq})$ to $\text{OH}^-(\text{aq})$. In this case, $\text{NH}_4^+(\text{aq})$ acts as a Brønsted acid while OH^- acted as a Brønsted base. The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. Therefore, $\text{OH}^-(\text{aq})$ is called the conjugate base of an acid H_2O and $\text{NH}_4^+(\text{aq})$ is called conjugate acid of the base $\text{NH}_3(\text{aq})$. If Brønsted acid is a strong acid, its conjugate base is a weak base and **vice versa**. It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of acetic acid $\text{CH}_3\text{COOH}(\text{aq})$ in water. $\text{CH}_3\text{COOH}(\text{aq})$ acts as an acid by donating a proton to H_2O molecule which acts as a base.



It can be seen in the above equation, that water acts as a base because it accepts the proton. The species $\text{H}_3\text{O}^+(\text{aq})$ is produced when water accepts a proton from $\text{CH}_3\text{COOH}(\text{aq})$. Therefore, $\text{CH}_3\text{COO}^-(\text{aq})$ is a conjugate base of $\text{CH}_3\text{COOH}(\text{aq})$ acid and $\text{CH}_3\text{COOH}(\text{aq})$ is the conjugate acid of base $\text{CH}_3\text{COO}^-(\text{aq})$. Similarly, H_2O is a conjugate base of the acid $\text{H}_3\text{O}^+(\text{aq})$ and $\text{H}_3\text{O}^+(\text{aq})$ is the conjugate acid of base H_2O .

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with CH_3COOH acid, water acts as a base while in case of ammonia it acts as an acid by donating a proton.

Example 2.12

- (i) What will be the conjugate bases for the following Brønsted acids: HF , H_2SO_4 and HCO_3^-

Answer

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F^- , HSO_4^- and CO_3^{2-} respectively.

- (ii) Write the conjugate acids for the following Brønsted bases: NH_2^- , NH_3 and HCOO^- .

Answer

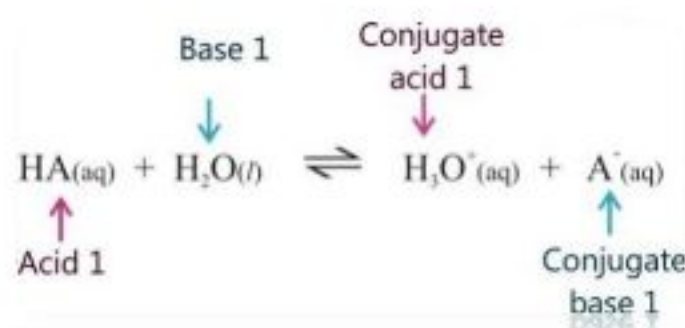
The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3 , NH_4^+ and HCOOH respectively.

2.2.3 Ionization of acids and bases

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid (HClO_4), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $\text{Ba}(\text{OH})_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH^- . According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H_3O^+ and OH^- ions respectively in the medium.

Alternatively, the strength of an acid or base may also be gauged in terms of Brønsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and

a strong base implies a good proton acceptor. Consider, the acid-base dissociation equilibrium of a weak acid HA,

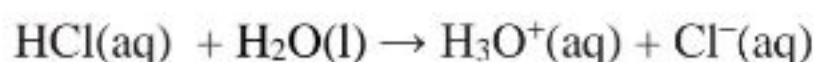


As we saw earlier, acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and $\text{H}_3\text{O}^+_{(\text{aq})}$ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is the stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed the stronger acid and the equilibrium will shift in the direction of the weaker acid. Say, if $\text{HA}_{(\text{aq})}$ is a stronger acid than $\text{H}_3\text{O}^+_{(\text{aq})}$, and then $\text{HA}_{(\text{aq})}$ will donate protons and not $\text{H}_3\text{O}^+_{(\text{aq})}$, and the solution will mainly contain $\text{A}^-_{(\text{aq})}$ and $\text{H}_3\text{O}^+_{(\text{aq})}$ ions. The equilibrium moves in the direction of formation of weaker acid and weaker base because *the stronger acid donates a proton to the stronger base*.

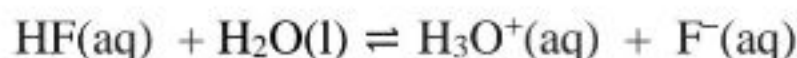
It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., *strong acids have very weak conjugate bases*. Strong acids like perchloric acid (HClO_4), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4^- , Cl^- , Br^- , I^- , NO_3^- and HSO_4^- , which are much weaker bases than H_2O . Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the *weak acids have very strong conjugate bases*. For example, NH_2^- , O^{2-} and H^- are very good proton acceptors and thus, much stronger bases than H_2O .

Therefore we can summarize the following on conjugate acid-base pairs.

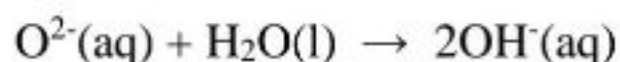
- If an acid is strong, its conjugate base has no measurable strength. Thus the Cl^- ion, which is the conjugate base of the strong acid HCl , is an extremely weak base.
- H_3O^+ is the strongest acid that can exist in aqueous solution. Acids stronger than H_3O^+ react with water to produce H_3O^+ and their conjugate bases. Thus HCl , which is a stronger acid than H_3O^+ , reacts with water completely to form H_3O^+ and Cl^- :



Acids weaker than H_3O^+ react with water to a much smaller extent, producing H_3O^+ and their conjugate bases. For example, the following equilibrium lies primarily to the left:



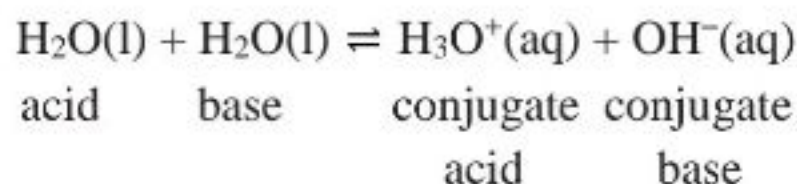
- The OH^- ion is the strongest base that can exist in aqueous solution. Bases stronger than OH^- react with water to produce OH^- and their conjugate acids. For example, the oxide ion (O^{2-}) is a stronger base than OH^- , so it reacts with water completely as follows:



For this reason the oxide ion does not exist in aqueous solutions.

2.2.4 The ionization constant of water and its ionic product

Water and some substances are unique in their ability of acting both as an acid and a base. We have seen this in case of water in the section above. In the presence of an acid HA, it accepts a proton and acts as the base while in the presence of a base, B^- it acts as an acid by donating a proton. In pure water, one H_2O molecule donates a proton and acts as an acid and another water molecule accepts a proton and acts as a base at the same time. The following equilibrium exists:



The dissociation constant for the reaction is represented by,

$$K = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{H}_2\text{O(l)}]^2}$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant (Concentration of water in 1.00 dm^3 of solution is $10^3 \text{ g dm}^{-3} / 18 \text{ g mol}^{-1} = 55.55 \text{ mol dm}^{-3}$ is a constant). Therefore, incorporation of $[\text{H}_2\text{O(l)}]$ into the equilibrium constant to give a new constant, K_w , which is called the **ionic product of water**.

$$\text{i.e., } K[\text{H}_2\text{O(l)}]^2 = K_w = [\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]$$

The concentrations of $\text{H}_3\text{O}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ have been found out experimentally as $1.0 \times 10^{-7} \text{ mol dm}^{-3}$ at 298 K. As dissociation of water produces equal number of $\text{H}_3\text{O}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ ions, the value of K_w at 298K is,

$$K_w = [\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})] = (1 \times 10^{-7} \text{ mol dm}^{-3})^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

It has to be noted that the K_w is temperature dependent and is an equilibrium constant. When $[\text{H}_3\text{O}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$, the aqueous solution is said to be neutral. In an acidic solution there is an excess of hydronium ions and $[\text{H}_3\text{O}^+(\text{aq})] > [\text{OH}^-(\text{aq})]$. In a basic solution there is an excess of hydroxide ions, so $[\text{H}_3\text{O}^+(\text{aq})] < [\text{OH}^-(\text{aq})]$.

2.2.5 The pH scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the **pH scale**. The pH of a solution is defined as the negative logarithm to base 10 of the activity ($a_{\text{H}_3\text{O}^+(\text{aq})}$) or ($a_{\text{H}^+(\text{aq})}$) of the hydronium or hydrogen ion. In dilute solutions ($< 0.01 \text{ mol dm}^{-3}$), activity of hydrogen ion is equal in magnitude to molarity represented by $[\text{H}_3\text{O}^+(\text{aq})]$. It should be noted that activity has no units and is defined as:

$$(a_{\text{H}_3\text{O}^+(\text{aq})}) \text{ or } (a_{\text{H}^+(\text{aq})}) = [\text{H}_3\text{O}^+(\text{aq})] / 1 \text{ mol dm}^{-3}$$

Therefore, from the definition of pH is

$$\text{pH} = -\log (a_{\text{H}_3\text{O}^+(\text{aq})}) = -\log \{ [\text{H}_3\text{O}^+(\text{aq})] / 1 \text{ mol dm}^{-3} \}$$

As the $[\text{H}_3\text{O}^+(\text{aq})]$ has units mol dm^{-3} ,

$$\text{pH} = -\log \{ [\text{H}_3\text{O}^+(\text{aq})] \text{ mol dm}^{-3} / \text{mol dm}^{-3} \}$$

$$\text{pH} = -\log \{ [\text{H}_3\text{O}^+(\text{aq})] \}$$

That is, pH value has no units.

Thus, an acidic solution of HCl ($10^{-2} \text{ mol dm}^{-3}$) will have a $\text{pH} = 2$. Similarly, a basic solution of NaOH having $[\text{OH}^-] = 10^{-4} \text{ mol dm}^{-3}$ and $[\text{H}_3\text{O}^+] = 10^{-10} \text{ mol dm}^{-3}$ will have a $\text{pH} = 10$. At 25°C , pure water has a concentration of hydronium or hydrogen ions, $[\text{H}_3\text{O}^+]$ or $[\text{H}^+] = 10^{-7} \text{ mol dm}^{-3}$. Hence, the pH of pure water is given as:

$$\text{pH} = -\log(10^{-7} \text{ mol dm}^{-3} / \text{mol dm}^{-3}) = 7$$

Acidic solutions possess a concentration of hydrogen ions, $[\text{H}^+] > 10^{-7} \text{ mol dm}^{-3}$, while basic solutions possess a concentration of hydrogen ions, $[\text{H}^+] < 10^{-7} \text{ mol dm}^{-3}$. Thus, we can summarise that

Acidic solution has $\text{pH} < 7$

Basic solution has $\text{pH} > 7$

Neutral solution has $\text{pH} = 7$

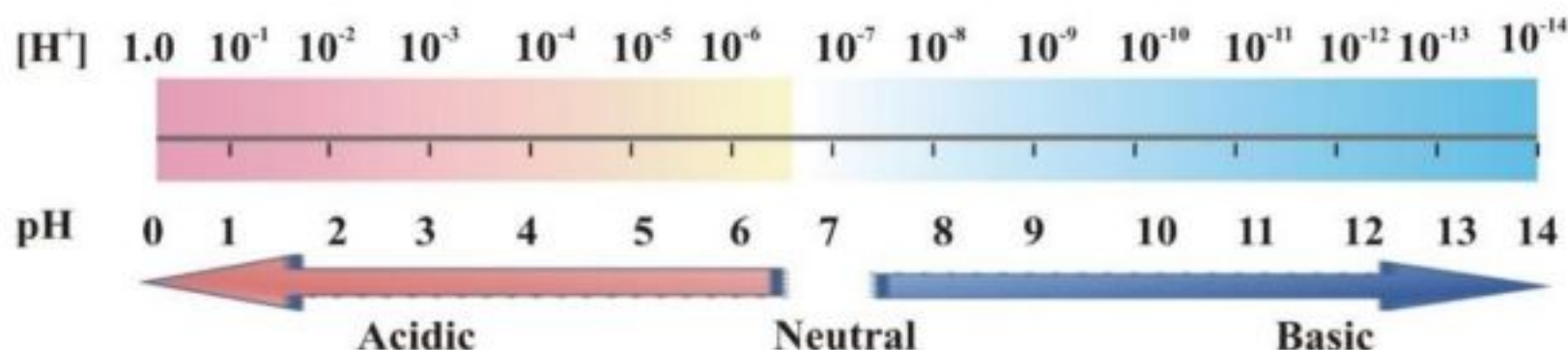


Figure 2.15 Simple visualization of the pH scale. At pH 7.0 solutions are said to be neutral. Proceeding to the lower pH values increases the acidity while the otherway increases the basicity of solutions.

$$K_w = [\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]$$

Taking negative logarithm on both sides of equation, we obtain

$$\begin{aligned} -\log K_w &= -\log\{[\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]\} \\ pK_w &= -\log[\text{H}_3\text{O}^+(\text{aq})] - \log[\text{OH}^-(\text{aq})] \\ pK_w &= \text{pH} + \text{pOH} \\ \text{or} \\ \text{pH} + \text{pOH} &= 14 \end{aligned}$$

Note that although K_w may change with temperature, the variations in pH with temperature are so small that we often ignore it. pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in $[\text{H}^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[\text{H}^+]$ changes by a factor of 100, the value of pH changes by 2 units. Now you can realize why the change in pH with temperature is often ignored.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that gives different colours in solutions of different pH. The pH in the range of 1-14 can be determined with an accuracy of ~ 0.5 using a pH paper. In the laboratory, the pH of a solution is also measured with a pH meter.

Let's consider following examples involving calculations based on pH.

Example 2.13

Calculate pH of a $1.0 \times 10^{-4} \text{ mol dm}^{-3}$ solution of HCl.

Answer

$$\text{pH} = -\log(10^{-4} \text{ mol dm}^{-3} / \text{mol dm}^{-3}) = 4$$

Example 2.14

In a NaOH solution $[\text{OH}^-]$ is $1.0 \times 10^{-4} \text{ mol dm}^{-3}$. Calculate the pH of the solution.

Answer

$$[\text{OH}^-] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log(10^{-4} \text{ mol dm}^{-3} / \text{mol dm}^{-3}) = 4 \text{ Therefore, } \text{pH} = 14 - 4 = 10$$

or

$$[\text{OH}^-] = 1.0 \times 10^{-4} \text{ mol dm}^{-3} \text{ gives } [\text{H}^+] = 1.0 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log(10^{-10} \text{ mol dm}^{-3} / \text{mol dm}^{-3}) = 10$$

Example 2.15

Calculate pH of a $1.0 \times 10^{-8} \text{ mol dm}^{-3}$ solution of HCl.

Answer

In this calculation some may make a wrong approach by taking pH as
 $\text{pH} = -\log(10^{-8} \text{ mol dm}^{-3} / \text{mol dm}^{-3}) = 8$

One should note that here the $[\text{H}^+]$ from HCl is less than that coming from the self-ionization of water (i.e. $1.0 \times 10^{-7} \text{ mol dm}^{-3}$). Therefore, we should consider the $[\text{H}^+]$ generated from both HCl and water. That is, $[\text{H}^+]$ from the given HCl solution is $1.0 \times 10^{-8} \text{ mol dm}^{-3}$ and take that from water as x .

Therefore, $[\text{OH}^-] = x$ and $[\text{H}_3\text{O}^+] = 10^{-8} + x$

$$K_w = [\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})] = 10^{-14} = (10^{-8} + x)x$$

$$x^2 + 10^{-8}x - 10^{-14} = 0$$

Solving the above quadratic equation, we get

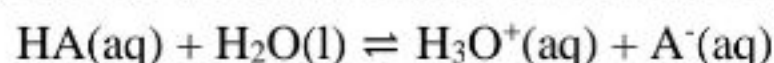
$$[\text{OH}^-] = 9.5 \times 10^{-8} \text{ mol dm}^{-3} \text{ and hence } \text{pOH} = 7.02$$

Therefore, $\text{pH} = 6.98$

In the above calculations in examples, it was easy to decide the concentration of $[\text{H}^+]$ and $[\text{OH}^-]$ as we know that HCl and NaOH are a strong acid and a base, respectively, giving rise to complete ionization. However, when we have aqueous solutions of weak acids or bases, it needs some more information on the system as they undergo partial dissociation. In the next section we consider dissociation of weak acids and bases with the emphasis on their equilibria.

2.2.6 Weak acids and their ionization (dissociation) constant

Consider a weak monoprotic acid, HA. Its ionization in water is represented by



The equilibrium expression for this ionization is

$$K = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})][\text{H}_2\text{O}(\text{l})]}$$

We can write,

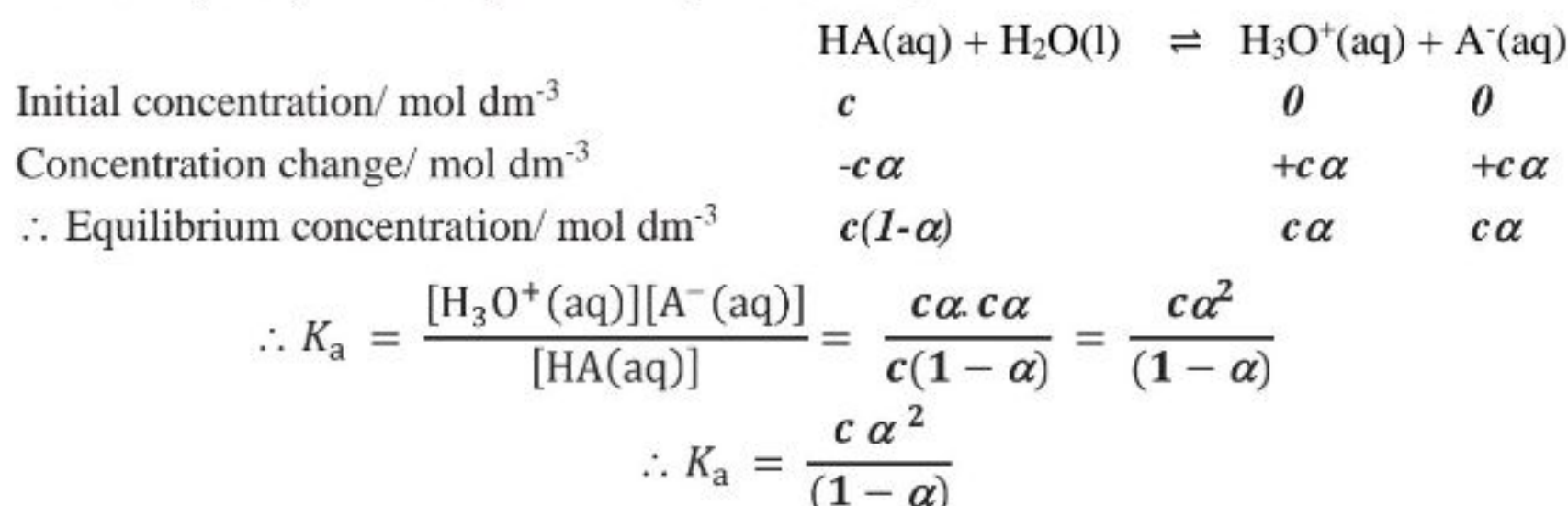
$$K[\text{H}_2\text{O}(\text{l})] = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

Taking $K[\text{H}_2\text{O}(\text{l})] = K_a$, as a constant, because $[\text{H}_2\text{O}(\text{l})]$ is a constant, we can write

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

K_a is called the *dissociation or ionization constant* of the weak acid which is the *equilibrium constant for the ionization of the acid*. At a given temperature, the strength of the acid HA is measured quantitatively by the magnitude of K_a . Large K_a , indicates that the acid is stronger, which means a greater the concentration of $[\text{H}_3\text{O}^+(\text{aq})]$ or $[\text{H}^+(\text{aq})]$ ions at equilibrium due to its ionization in aqueous solution. Only weak acids have K_a values associated with them.

The above definition of the acid ionization constant can also be treated as follows considering the partial ionization of HA in aqueous solution. Assuming that the initial concentration of the undissociated acid is c and its extent of ionization (or degree of ionization) is α , we can express the equilibrium as,



As the ionization of a weak acid is very small, we can assume that α is very small or $(1-\alpha) \sim 1$. Hence, $\therefore K_a = c\alpha^2$

This is called Ostwald's law of dilution.

Note: This is valid for weak bases in aqueous solutions too.

The values of the ionization constants of some weak acids at 298 K are given in the following table.

Table 2.2 The ionization constants of some selected weak acids (at 298K)

Acid	K_a
Hydrofluoric Acid (HF)	3.5×10^{-4}
Nitrous Acid (HNO ₂)	4.5×10^{-4}
Acetic Acid (CH ₃ COOH)	1.74×10^{-5}
Benzoic Acid (C ₆ H ₅ COOH)	6.50×10^{-5}
Hypochlorous Acid (HClO)	3.00×10^{-8}
Hydrocyanic Acid (HCN)	4.90×10^{-10}
Phenol (C ₆ H ₅ OH)	1.30×10^{-10}

Note: K_a is a dimensionless quantity with the understanding that the standard state concentration of all species is 1 mol dm^{-3} . That is all the concentration terms appearing in the equilibrium constant expression is divided by 1 mol dm^{-3} . Otherwise we indicate the units as relevant to the equilibrium constant expression.

The pH scale for the hydrogen ion concentration has been so useful that besides pK_w ($-\log K_w$), it has been extended to other species and quantities. Thus, we have:

$$pK_a = -\log (K_a)$$

Knowing the ionization constant, K_a of an acid and its initial concentration c , it is possible to calculate the equilibrium concentration of all species and also the degree of ionization of the acid and the pH of the solution.

A general step-wise approach can be adopted to evaluate the pH of a weak electrolyte as follows:

- Step 1.** The species present before dissociation are identified as Brönsted-Lowry acids/ bases.
- Step 2.** Balanced equations for all possible reactions i.e., with a species acting both as acids as well as bases are written.
- Step 3.** The reaction with the higher K_a is identified as the primary reaction whilst the other is a subsidiary reaction.
- Step 4.** Enlist in a tabular form the following values for each of the species in the primary reaction.
 - (a) Initial concentration, c
 - (b) Change in concentration on proceeding to equilibrium in terms of α , degree of ionization
 - (c) Equilibrium concentration
- Step 5.** Substitute equilibrium concentrations into equilibrium constant equation for the principal reaction and solve for α .
- Step 6.** Calculate the concentration of species in the principal reaction.
- Step 7.** Calculate $\text{pH} = -\log[\text{H}_3\text{O}^+]$ or calculate $[\text{H}_3\text{O}^+]$ once pH is known using $[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$

The following example(s) illustrate(s) the above mentioned approach in calculating pH.

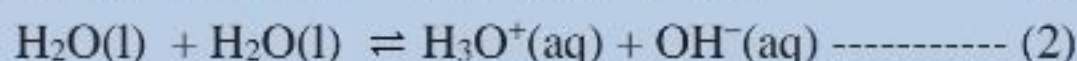
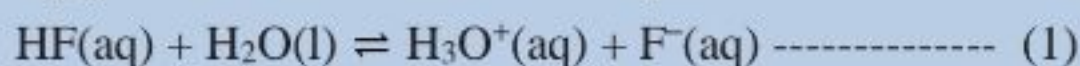
Example 2.16

The ionization constant of HF is 3.2×10^{-4} at 298 K. Calculate the degree of dissociation of HF in its 0.20 mol dm^{-3} solution. Calculate the concentration of all species present (H_3O^+ , F^- and HF) in the solution and its pH.

Answer

Procedure I:

The following proton transfer reactions are possible:



As $K_a (3.2 \times 10^{-4}) \gg K_w (1.0 \times 10^{-14})$, we can understand that reaction (1) is the major reaction.

	HF(aq) +	H ₂ O(l)	\rightleftharpoons	H ₃ O ⁺ (aq)	+	F ⁻ (aq)
Initial concentration/ mol dm^{-3}	0.2			0		0
Concentration change/ mol dm^{-3}	-0.2 α			+0.2 α		+0.2 α
\therefore Equilibrium concentration/ mol dm^{-3}	0.2(1- α)			+0.2 α		+0.2 α

Substituting equilibrium concentrations in the equilibrium reaction for the principal reaction gives:

$$\therefore K_a = \frac{0.2\alpha \times 0.2\alpha}{0.2(1-\alpha)} = \frac{(0.2\alpha)^2}{0.2(1-\alpha)}$$

As the acid considered is weak, we can assume that the ionization is small compared to the initial concentration of the acid $\therefore (1-\alpha) \sim 1$ or $0.2(1-\alpha) \sim 0.2$

$$\text{Substituting in } K_a = \frac{0.2\alpha \times 0.2\alpha}{0.2(1-\alpha)} \sim \frac{(0.2\alpha)^2}{0.2} = 3.2 \times 10^{-4}$$

$$\alpha^2 = 1.6 \times 10^{-3}$$

$$\alpha = 4.0 \times 10^{-2}$$

$$[\text{H}_3\text{O}^+] = [\text{F}^-] = c\alpha = 0.2 \text{ mol dm}^{-3} \times 0.04 = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{HF}] = c(1-\alpha) = 0.2 \text{ mol dm}^{-3} (1-0.04) = 19.2 \times 10^{-2} \text{ mol dm}^{-3}$$

Hence, $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(8.0 \times 10^{-3}) = 2.10$

Validity of the approximation we made can be checked by calculating the percent value of the ionization with respect to the initial concentration of the acid. When the percent value is less than 5% we usually accept the approximation and otherwise it is necessary to solve the quadratic equation to obtain the value of α .

From the above estimated value 0.04 we get,

$$\frac{0.04}{0.20} \times 100\% = 2.0\%$$

Thus the approximation used can be accepted.

We can further confirm/clarify the above approximation by obtaining the value of α after solving the quadratic equation and taking the relative percent deviation of it.

For the above example: $K_a = \frac{0.2\alpha \times 0.2\alpha}{0.2(1-\alpha)} = 3.2 \times 10^{-4}$

We obtain the following quadratic equation:

$$\alpha^2 + 1.6 \times 10^{-3}\alpha - 1.6 \times 10^{-3} = 0$$

Note: The values for x of the quadratic equation, $ax^2 + bx + c = 0$ are given by

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

The quadratic equation with α can be solved and the two values of α are:

$$\alpha = +3.92 \times 10^{-2} \text{ and } -4.08 \times 10^{-2}$$

The negative value is not acceptable and hence

$$\alpha = 3.92 \times 10^{-2}$$

Now we can calculate the relative percent deviation as

$$\frac{0.04 - 3.92 \times 10^{-2}}{0.04} \times 100\% = 2.0\%$$

We can see that the close similarity in the above two methods and therefore usually we make the said approximation for this type of calculations.

Note: The above approximation can be applied in the cases when the initial concentration of the acid/base is much larger (at least 3 orders of magnitude) than the acid ionization constant K_a of the acid.

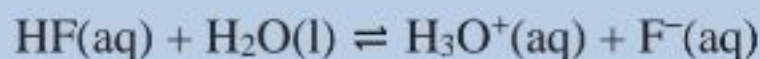
In the above example: initial concentration is 0.2 mol dm^{-3} and $K_a = 3.2 \times 10^{-4}$, so the ratio is

$$\frac{2.0 \times 10^{-1}}{3.2 \times 10^{-4}} \sim 10^3$$

Therefore, we can make the approximation.

Procedure II:

The example above can also be treated as follows. We know that the major reaction in system is,



Now taking the dissociated concentration or change in concentration as x , we can write,

	HF(aq) +	H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	+	F ⁻ (aq)
Initial concentration/ mol dm ⁻³	0.2			0		0
Concentration change (mol dm ⁻³)	- x			+ x		+ x
∴ Equilibrium concentration/ mol dm ⁻³	0.2 - x			+ x		+ x

Substituting equilibrium concentrations in the equilibrium reaction gives:

$$\therefore K_a = \frac{x \times x}{(0.2 - x)} = \frac{(x)^2}{(0.2 - x)}$$

As the acid considered is weak, we can assume that the ionization is small compared to the initial concentration of the acid $0.2 - x \sim 0.2$

$$\text{Substituting in } K_a \sim \frac{(x)^2}{0.2} = 3.2 \times 10^{-4}$$

$$x^2 = 6.4 \times 10^{-5}$$

$$x = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

And we have

$$[\text{H}_3\text{O}^+] = [\text{F}^-] = x = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{HF}] = 0.20 - x = 0.2 - 0.008 = 19.2 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{Hence, pH} = -\log[\text{H}_3\text{O}^+] = -\log(8.0 \times 10^{-3}) = 2.10$$

Note that the procedure II gives us the values of equilibrium concentrations directly.

Example 2.17

The pH of 0.10 mol dm⁻³ monobasic acid HA(aq) is 4.50. Calculate the concentration of species H⁺(aq), A⁻(aq) and HA(aq) at equilibrium. Also, determine the value of K_a and pK_a of the monobasic acid.

Answer

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$\text{Therefore, } [\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.50} = 3.16 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+] = [\text{A}^-] = 3.16 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{HA}]_{\text{eqbm}} = 0.1 - (3.16 \times 10^{-5}) \sim 0.1 \text{ mol dm}^{-3}$$

We can summarize these as follows

	$\text{HA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{A}^-(\text{aq})$		
Initial concentration/ mol dm^{-3}	0.1	0	0
Concentration change/ mol dm^{-3}	-3.16×10^{-5}	3.16×10^{-5}	3.16×10^{-5}
\therefore Equilibrium concentration/ mol dm^{-3}	$(0.10 - 3.16 \times 10^{-5})$	3.16×10^{-5}	3.16×10^{-5}
\therefore Equilibrium concentration/ mol dm^{-3}	0.10	3.16×10^{-5}	3.16×10^{-5}

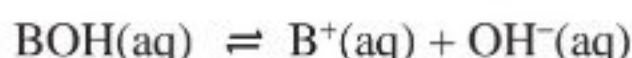
$$\text{Thus, } K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA(aq)}]}$$

$$\therefore K_a = (3.16 \times 10^{-5})^2 / 0.1 = 1.0 \times 10^{-8} \text{ mol dm}^{-3}$$

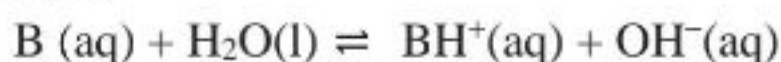
$$\text{p}K_a = -\log(10^{-8}) = 8$$

2.2.7 Weak bases and base ionization constant

The ionization of base MOH can be represented by equation:



We can write this reaction as,



In a weak base there is partial ionization of $\text{MOH}_{(\text{aq})}$ into $\text{M}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$, is similar to that of acid-dissociation equilibrium. The equilibrium constant for base ionization is called **base ionization constant** and is represented by K_b . It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation:

$$K = \frac{[\text{BH}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{B(aq)}][\text{H}_2\text{O(l)}]}$$

Similar to treatment in weak acids,

$$K[\text{H}_2\text{O(l)}] = \frac{[\text{BH}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{B(aq)}]}$$

$$K_b = \frac{[\text{BH}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{B(aq)}]}$$

or for the reaction, $\text{BOH(aq)} \rightleftharpoons \text{B}^+(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{B}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{BOH(aq)}]}$$

Alternatively, if c = initial concentration of base and α = degree of ionization of base, when equilibrium is reached, the equilibrium constant can be written as:

$$\therefore K_b = \frac{c\alpha^2}{(1-\alpha)}$$

The production of hydroxide ions in this *base ionization reaction* means that $[\text{OH}^-(\text{aq})] > [\text{H}^+(\text{aq})]$ and therefore $\text{pH} > 7$.

The values of the ionization constants of some weak bases at 298 K are given in the following table.

Table 2.3 The ionization constants of some selected weak bases (at 298K)

Base	K_b
Dimethylamine, $(\text{CH}_3)_2\text{NH}$	5.40×10^{-4}
Triethylamine, $(\text{C}_2\text{H}_5)_3\text{N}$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Pyridine, $\text{C}_5\text{H}_5\text{N}$	1.77×10^{-9}
Aniline, $\text{C}_6\text{H}_5\text{NH}_2$	4.27×10^{-10}
Urea, $\text{CO}(\text{NH}_2)_2$	1.30×10^{-14}

In solving problems involving weak bases, we follow the same procedure we used for weak acids. The main difference is that we calculate $[\text{OH}^-(\text{aq})]$ first rather than $[\text{H}^+(\text{aq})]$ and the following example shows this approach.

Example 2.18

Calculate the pH of a 0.40 mol dm^{-3} ammonia solution. $K_b = 1.80 \times 10^{-5}$

Answer

The following equilibrium reaction exists and let x be the equilibrium concentration of $\text{NH}_4^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ ions in mol dm^{-3} , we summarize:

	$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
Initial concentration/ mol dm^{-3}	0.4		0
Concentration change/ mol dm^{-3}	$-x$		$+x$
\therefore Equilibrium concentration/ mol dm^{-3}	$(0.4-x)$		$+x$

$$K_b = \frac{[\text{NH}_4^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_3(\text{aq})]} = 1.80 \times 10^{-5}$$

$$\frac{(x)(x)}{(0.4 - x)} = 1.80 \times 10^{-5}$$

Applying the approximation $0.40 - x \sim 0.40$, we obtain

$$\frac{(x^2)}{0.4} = 1.80 \times 10^{-5}$$

$$x = [\text{OH}^-(\text{aq})] = 2.7 \times 10^{-3} \text{ mol dm}^{-3}$$

Note: To test the approximation, $\{[2.7 \times 10^{-3}]/0.4\} \times 100\% = 0.68\%$, i.e. the assumption is valid.

$$\therefore \text{pOH} = -\log (2.7 \times 10^{-3}) = 2.57$$

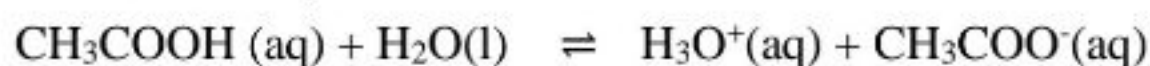
Applying the relationship $\text{pH} + \text{pOH} = 14.00$, we get

$$\text{pH} = 14.00 - 2.57 = 11.43$$

$$(\text{or } [\text{OH}^-(\text{aq})] = (2.7 \times 10^{-3}), \therefore [\text{H}^+(\text{aq})] = 10^{-14}/2.7 \times 10^{-3} = 3.7 \times 10^{-12} \therefore \text{pH} = 11.43)$$

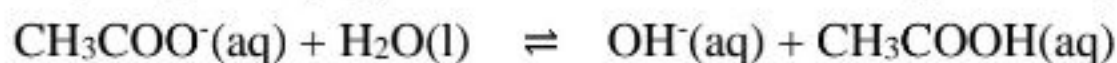
2.2.8 Relation between K_a and K_b

K_a and K_b represent the strength of an acid and a base, respectively. In case of a conjugate acid-base pair, they are related in a simple manner so that if one is known, the other can be deduced. Consider the example:



$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]}$$

The conjugate base, $\text{CH}_3\text{COO}^-(\text{aq})$, reacts with water according to the equation



The base ionization constant for the reaction,

$$K_b = \frac{[\text{OH}^-(\text{aq})][\text{CH}_3\text{COOH}(\text{aq})]}{[\text{CH}_3\text{COO}^-(\text{aq})]}$$

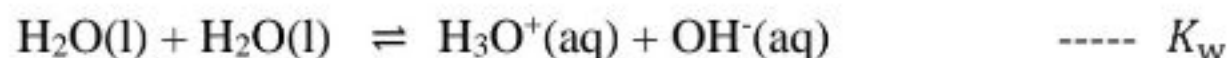
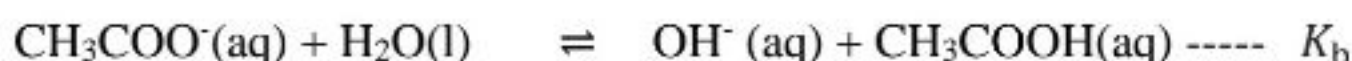
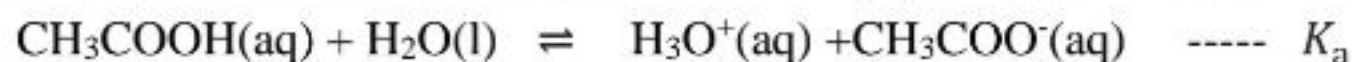
Consider the product of these two ionization constants.

$$K_a \times K_b = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]} \times \frac{[\text{OH}^-(\text{aq})][\text{CH}_3\text{COOH}(\text{aq})]}{[\text{CH}_3\text{COO}^-(\text{aq})]}$$

$$K_a \times K_b = [\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]$$

i.e. $K_a \times K_b = K_w$

When the two reactions are added we see that it is simply the autoionization of water.



This follows the general rule in chemical equilibrium as we have discussed earlier,

Note: If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

Note that the relation $K_a K_b = K_w$ can also be obtained by considering the ionization of a weak base too.

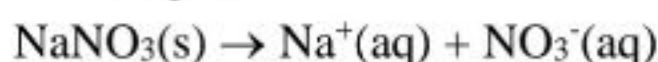
From this we have $K_a \times K_b = K_w$ and thus,

$$K_a = \frac{K_w}{K_b} \text{ and } K_b = \frac{K_w}{K_a}$$

From this we can see that the stronger the acid (the larger K_a), the weaker is the conjugate base (the smaller K_b), and vice versa.

2.2.9 Hydrolysis of salts and the pH of their solutions

Salts formed by the reactions between acids and bases in definite proportions, undergo ionization in water. The cations/anions formed on ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to reform corresponding acids/bases depending on the nature of salts. The process of interaction between water and cations/anions or both of salts is called **hydrolysis**. The pH of the solution gets affected by this interaction. The cations (e.g.: Na^+ , K^+ , Ca^{2+} , Ba^{2+} , etc.) of strong bases and anions (e.g.: Cl^- , Br^- , NO_3^- , ClO_4^- etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7. For example;



However, the other categories of salts do undergo hydrolysis.

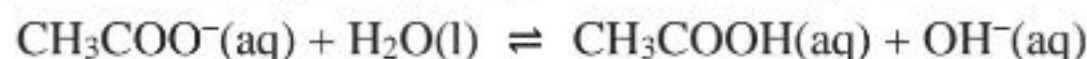
We now consider the hydrolysis of the salts of the following types:

- (i) salts of a weak acid and a strong base, e.g.: CH_3COONa .
- (ii) salts of a strong acid and a weak base, e.g.: NH_4Cl .
- (iii) salts of a weak acid and a weak base, e.g.: $\text{CH}_3\text{COONH}_4$.

In the first case, CH_3COONa being a salt of the weak acid CH_3COOH and the strong base NaOH , gets completely ionised in aqueous solution.



Acetate ion thus formed undergoes hydrolysis in water to give acetic acid and OH^- ions



Acetic acid being a weak acid ($K_a = 1.8 \times 10^{-5}$) remains mainly unionized/undissociated in solution. This results in increase of OH^- ion concentration in the solution making it basic. The pH of such a solution is more than 7.

Example 2.19

Calculate the pH of a 0.10 mol dm^{-3} solution of sodium acetate (CH_3COONa).

$$K_{\text{b}}(\text{CH}_3\text{COO}^-) = 5.6 \times 10^{-10}$$

Answer

As CH_3COONa completely ionizes into $\text{CH}_3\text{COO}^-(\text{aq})$ and $\text{Na}^+(\text{aq})$ in solution, $\text{CH}_3\text{COO}^-(\text{aq})$ ion undergoes hydrolysis.



Initial concentration/ mol dm^{-3}	0.10	0	0
Concentration change/ mol dm^{-3}	-x	+x	+x
\therefore Equilibrium concentration/ mol dm^{-3}	$0.10 - x$	+x	+x

Now we can write the equilibrium constant for the hydrolysis or the base ionization constant as.

$$K_{\text{b}} = \frac{[\text{OH}^-(\text{aq})][\text{CH}_3\text{COOH}(\text{aq})]}{[\text{CH}_3\text{COO}^-(\text{aq})]}$$

Substituting above values at equilibrium,

$$K_{\text{b}} = \frac{x^2}{(0.10 - x)} = 5.6 \times 10^{-10}$$

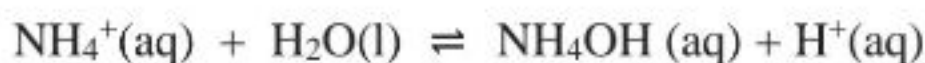
Since K_{b} is very small and the initial concentration of the base is large, we can apply the approximation $0.10 - x \sim 0.10$

$$\begin{aligned} \frac{x^2}{0.10} &\sim 5.6 \times 10^{-10} \\ x^2 &= 5.6 \times 10^{-11} \\ x = [\text{OH}^-(\text{aq})] &= 7.5 \times 10^{-6} \text{ mol dm}^{-3} \\ \therefore \text{pOH} &= 5.13 \\ \text{pH} &= 14.00 - 5.13 = 8.87 \end{aligned}$$

Similarly, NH_4Cl formed from the weak base, NH_4OH and the strong acid, HCl , dissociates completely in water.

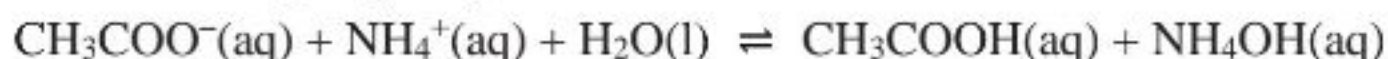


Ammonium ions undergo hydrolysis with water to form $\text{NH}_4\text{OH}(\text{aq})$ and $\text{H}^+(\text{aq})$ ions

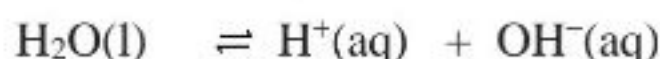


Ammonium hydroxide is a weak base ($K_b = 1.77 \times 10^{-5}$) and therefore remains almost unionised in solution. This results in increase of H^+ ion concentration in solution making the solution acidic. Thus, the pH of NH_4Cl solution in water is less than 7.

Consider the hydrolysis of $\text{CH}_3\text{COONH}_4$ salt formed from a weak acid and a weak base. The ions formed undergo hydrolysis as follow:



CH_3COOH and NH_4OH , also remain in partially dissociated form:



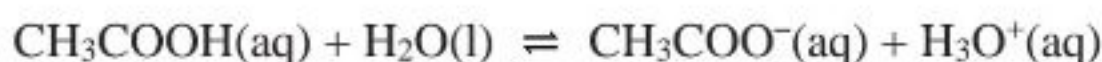
However, whether a solution containing such a salt is acidic, basic, or neutral depends on the relative strengths of the weak acid and the weak base. We can make qualitative predictions about these solutions as follows.

- $K_b > K_a$ ($\text{p}K_b < \text{p}K_a$); i.e if K_b for the anion is greater than K_a for the cation, then the solution must be basic because the anion will hydrolyze to a greater extent than the cation. At equilibrium, there will be more OH^- ions than H^+ ions.
- $K_b < K_a$ ($\text{p}K_b > \text{p}K_a$); i.e, if K_b for the anion is smaller than K_a for the cation, the solution will be acidic because cation hydrolysis will be more extensive than anion hydrolysis.
- $K_a \sim K_b$ ($\text{p}K_b \sim \text{p}K_a$); If K_a is approximately equal to K_b , the solution will be nearly neutral.

2.2.10 Aqueous solutions containing a common ion

In previous sections in acid-base ionization and salt hydrolysis we have discussed the properties of solutions containing a single solute. In the solutions of two dissolved solutes containing the same ion or a *common ion*, properties will be different. A common ion suppresses the ionization of a weak acid or a weak base.

For example, when both sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and ionize to produce CH_3COO^- ions as shown in the following equations where $\text{CH}_3\text{COONa}(\text{aq})$ dissociates completely while $\text{CH}_3\text{COOH}(\text{aq})$ undergoes partial dissociation.

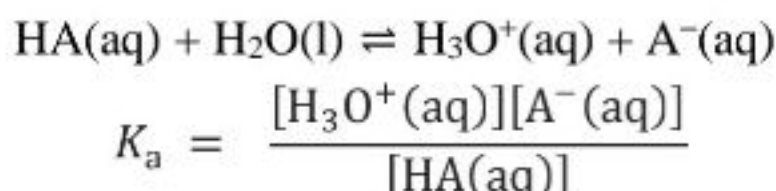


According to Le Chatelier's principle, the addition of CH_3COO^- ions from CH_3COONa to a solution of CH_3COOH will suppress the ionization of CH_3COOH by shifting the equilibrium from right to left causing decrease in the hydrogen ion concentration. Therefore a solution containing both CH_3COOH and CH_3COONa will be *less* acidic than a solution containing only CH_3COOH at the same concentration. The shift in equilibrium of the ionization of acetic acid is caused by the acetate ions from the salt. CH_3COO^- is the common ion because it is supplied by both CH_3COOH and CH_3COONa .

The **common ion effect** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substances.

The common ion effect plays an important role in determining the pH of a solution and the solubility of a slightly soluble salt.

Let us consider the pH of a solution containing a weak acid, HA, and a soluble salt of the weak acid, such as NaA.



We can write,

$$[\text{H}_3\text{O}^+(\text{aq})] = K_a \frac{[\text{HA(aq)}]}{[\text{A}^-(\text{aq})]}$$

Taking -log on both sides,

$$-\log [\text{H}_3\text{O}^+(\text{aq})] = -\log K_a - \log \frac{[\text{HA(aq)}]}{[\text{A}^-(\text{aq})]}$$

$$-\log [\text{H}_3\text{O}^+(\text{aq})] = -\log K_a + \log \frac{[\text{A}^-(\text{aq})]}{[\text{HA(aq)}]}$$

We can write,

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-(\text{aq})]}{[\text{HA(aq)}]}$$

or

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

The above expression is called **Henderson-Hasselbalch equation**.

If we know K_a and the concentrations of the acid and the salt of the acid, we can calculate the pH of the solution.

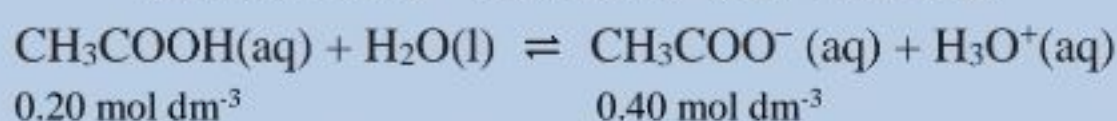
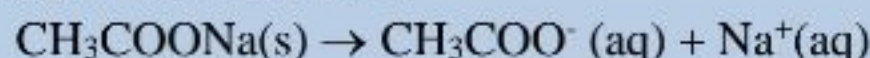
In problems that involve the common ion effect, we are usually given the starting concentrations of a weak acid HA and its salt, such as NaA. As long as the concentrations of these species are reasonably high (0.10 mol dm^{-3}), we can neglect the ionization of the acid and the hydrolysis of the salt. This is a valid approximation because HA is a weak acid and the extent of the hydrolysis of the $\text{A}^{-}(\text{aq})$ ion is generally very small. Moreover, the presence of common ion $\text{A}^{-}(\text{aq})$ from the salt NaA further suppresses the ionization of HA and the presence of unionized HA further suppresses the hydrolysis of $\text{A}^{-}(\text{aq})$. Thus we can use the starting concentrations as the equilibrium concentrations in the Henderson-Hasselbalch equation.

Example 2.20

- Calculate the pH of a solution containing $0.20 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ and $0.40 \text{ mol dm}^{-3} \text{ CH}_3\text{COONa}$.
- What would be the pH of a $0.20 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH}$ solution if no salt was present? $K_{\text{a}}(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$

Answer

- $\text{CH}_3\text{COONa}(\text{s})$ is a strong electrolyte and hence it dissociates completely giving $[\text{CH}_3\text{COO}^{-}(\text{aq})]$ as 0.40 mol dm^{-3} and we can neglect the $[\text{CH}_3\text{COO}^{-}(\text{aq})]$ from the CH_3COOH acid as its dissociation is suppressed. Therefore, we can take $[\text{CH}_3\text{COO}^{-}(\text{aq})]$ as 0.40 mol dm^{-3} and $[\text{CH}_3\text{COOH}(\text{aq})]$ as 0.20 mol dm^{-3} .



$$K_{\text{a}} = \frac{[\text{H}_3\text{O}^{+}(\text{aq})][\text{CH}_3\text{COO}^{-}(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]} = 1.8 \times 10^{-5}$$

$$[\text{H}_3\text{O}^{+}(\text{aq})] = \frac{(0.20)}{(0.40)} \times 1.8 \times 10^{-5} = 9.0 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^{+}(\text{aq})] = 5.04$$

or we can use

$$\text{pH} = \text{p}K_{\text{a}} + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = -\log(K_{\text{a}}) + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pH} = 4.74 + \log \frac{0.40}{0.20}$$

$$\text{pH} = 4.74 + \log 2$$

$$\text{pH} = 5.04$$

(ii) without common ion we have only the equilibrium of

	$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
Initial concentration/ mol dm ⁻³	0.20	0	0
Concentration change/ mol dm ⁻³	- x	+x	+x
∴ Equilibrium concentration/ mol dm ⁻³	0.20 - x	+x	+x

Substituting with the assumption $0.20 - x \sim 0.20$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]} = 1.8 \times 10^{-5}$$

$$\frac{(x)^2}{0.20} = 1.8 \times 10^{-5}$$

$$x = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\therefore [\text{H}_3\text{O}^+(\text{aq})] = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = 2.70$$

This shows clearly that the presence of the common ion CH_3COO^- suppresses the ionization of the acid CH_3COOH .

Following example shows an important situation, when the concentration of the acid and salt are the same.

Example 2.21

Calculate the pH of a 1.0 dm³ solution made by adding 0.10 mol of acetic acid and 0.10 mol of sodium acetate.

Answer

In this case the $[\text{CH}_3\text{COO}^-(\text{aq})]$ is the concentration of CH_3COONa because it ionizes completely and therefore we can write:

	$\text{CH}_3\text{COOH}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
Initial concentration/ mol dm ⁻³	0.10	0	0.10
Change in concentration/ mol dm ⁻³	- x	+x	+x
∴ Equilibrium concentration/ mol dm ⁻³	0.10 - x	+x	0.10 + x

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]} = 1.8 \times 10^{-5}$$

$$\frac{x(0.10 + x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

As x is small, we can write,

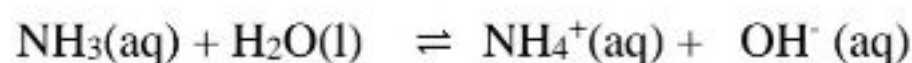
$$\frac{x(0.10)}{(0.10)} = 1.8 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+(\text{aq})] = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

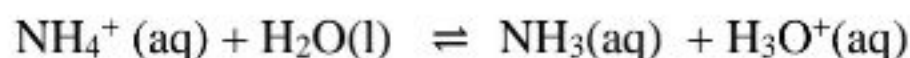
$$\therefore \text{pH} = 4.74$$

$$\text{i.e. pH} = \text{p}K_a$$

The common ion effect also operates in a solution containing a weak base, such as NH_3 , and a salt of the base, say NH_4Cl . At equilibrium



Here, $\text{NH}_4^+(\text{aq})$ is predominant over $\text{NH}_3(\text{aq})$ as it comes from the complete ionization of NH_4Cl and hence the equilibrium $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$ is suppressed. Therefore, in this solution, pH is mainly controlled by the equilibrium



We can write,

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = \frac{K_a [\text{NH}_4^+(\text{aq})]}{[\text{NH}_3(\text{aq})]}$$

$$-\log [\text{H}_3\text{O}^+(\text{aq})] = -\log K_a - \log \frac{[\text{NH}_4^+(\text{aq})]}{[\text{NH}_3(\text{aq})]}$$

$$-\log [\text{H}_3\text{O}^+(\text{aq})] = -\log K_a + \log \frac{[\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$$

We can write

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$$

$$\text{pH} = -\log(K_a) + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

A solution containing both NH_3 and its salt NH_4Cl is less basic than a solution containing only NH_3 at the same concentration. The common ion NH_4^+ suppresses the ionization of NH_3 in the solution containing both the base and the salt.

2.2.11 Volumetric titrations

Titration is a procedure for determining the concentration of a solution using another solution of known concentration, called the standard solution. In this usually we perform the volume measurements and find the required volume of the one necessary to react completely with the other. The determination of the volume depends on the way we find the completion of the reaction.

Equivalence points and end points

For a titration to be accurate we must add a stoichiometrically equivalent amount of the titrant (a solution with known concentration in a burette) to a solution containing the analyte (a solution with unknown concentration in a titration flask). We call the volume of the titrant required to reach this stoichiometric mixture the **equivalence point**, V_{eq} .

Knowing the stoichiometry of the titration reaction(s), we can calculate the amount of moles of the analyte. Unfortunately, in most titrations we usually have no obvious indication that the equivalence point has been reached. Instead, we stop adding titrant when we reach an **end point** of our choosing. Often this end point is indicated by a change in the color of a substance added to the solution containing the analyte. Such substances are known as **indicators**. Usually, indicators change their colour along with the change in pH of the solution, so that the volume of the titrant needed to reach the end point is little in excess compared to the equivalence point volume (1 drop of the titrant or 0.05 cm^3). The difference between the end point and the equivalence point is called the **titration error**. Though the difference in volume is very small, we can see that this causes a significant change in pH. Hence the pH values at the end point and equivalence point are not comparable. In the case when we know the concentrations of both the titrant and the analyte, we can construct the pattern of change in a measured property (for example pH) with the volume of the titrant and by this way the equivalence point is clearly defined. Following figures show the set-up of the titration and the comparison between equivalence and end points.

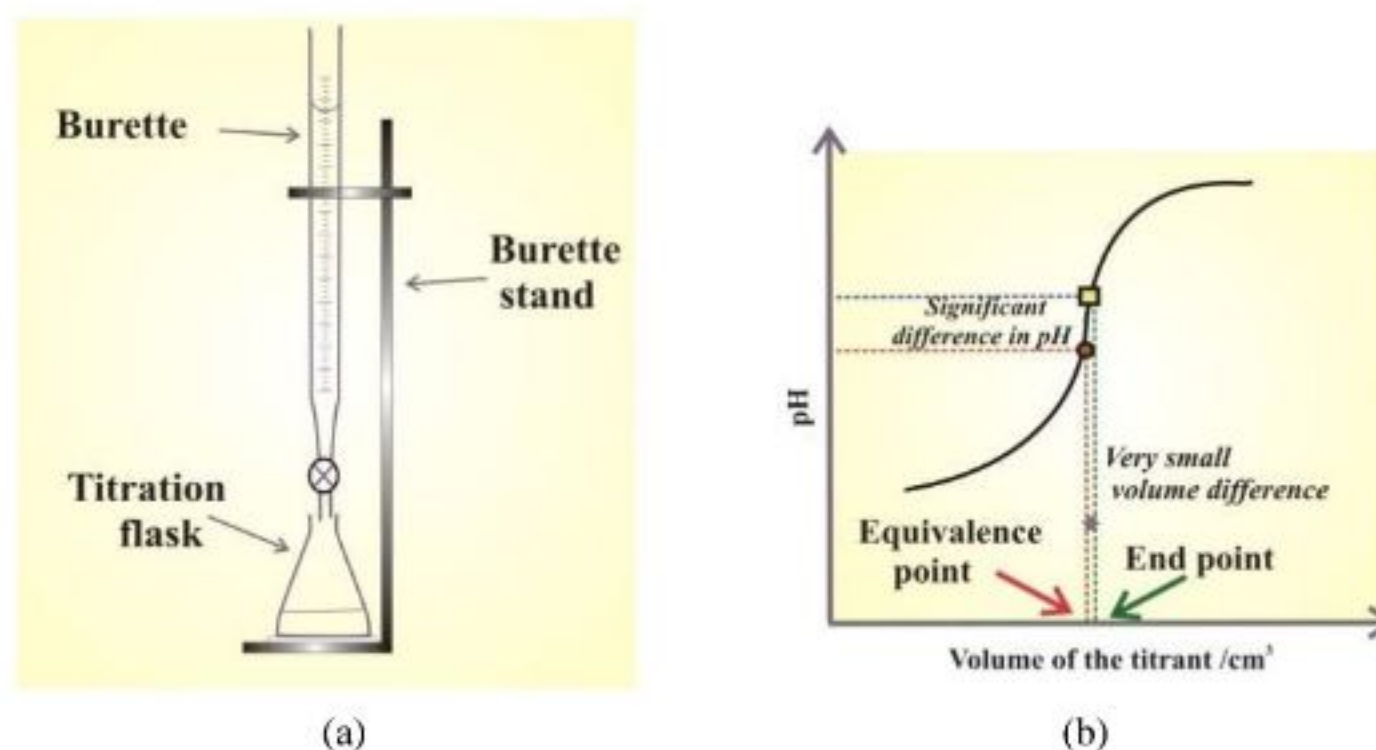


Figure 2.16 (a) A sketch of a titration set up: A solution with unknown concentration is placed in a titration flask and the solution is titrated against the titrant in the burette by adding it slowly. (b) shows the difference in end point and equivalence point where end point is determined by using an indicator in which we need some excess of the titrant ($\sim 0.05 \text{ cm}^3$) to observe the colour change in the indicator. In the case of equivalence point it is the point at which stoichiometric amounts are exactly reacted. Therefore, equivalence point volume is always less than that of end point volume. This small difference in volumes, however, causes very large difference in pH.

Acid-base titrations

Under this section, we will consider four types of titrations involving:

- a strong acid and a strong base,
- a weak acid and a strong base,
- a strong acid and a weak base, and
- a weak acid and a weak base.

Titration involving a weak acid and a weak base are complicated by the hydrolysis of both the cation and the anion of the salt formed.

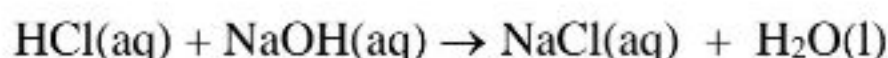
In the following section, we will consider the above types of titrations with the understanding of their respective equivalence points and the variation and calculation of pH along the titration (along the volume of the titrant). It has to be noted that it is simply an understanding of pH variation theoretically by considering the titration between the analyte of known concentration and the titrant with a known concentration. With these considerations, we can construct the **titration curves (volume vs pH)** theoretically. i.e. A **titration curve** provides us with a visual picture of how a property, such as pH, changes as we add the titrant.

- **Strong acid – strong base titrations**

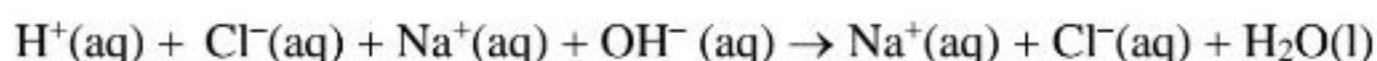
Consider the titration of 25.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ HCl with $0.100 \text{ mol dm}^{-3}$ NaOH.

(Note: The volumes are measured with burette and pipette with the accuracy of 0.00 cm^3 .)

Reaction taking place is,



As HCl(aq), NaOH(aq) and NaCl(aq) are strong electrolytes, we can write the above reaction as,



We can see that the pH of the solution depends on the relative concentrations of $\text{H}^+(\text{aq})$ and $\text{OH}^-(\text{aq})$ ions present at each stage of the volume of NaOH added and therefore it is possible to consider the situations like pH at the equivalence point, pH before the equivalence point, and pH after the equivalence point.

Let us first calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point,

moles HCl = amount of moles NaOH (as the stoichiometry between HCl and NaOH is 1 : 1)

Applying the simple formula $C_a V_a = C_b V_b$

where the subscript 'a' indicates the acid, HCl, and the subscript 'b' indicates the base, NaOH:

(i) The volume of NaOH needed to reach the equivalence point, therefore, is

$$\begin{aligned} 0.100 \times 25.00 &= 0.100 \times V_b \\ \therefore V_b &= 25.00 \text{ cm}^3 \end{aligned}$$

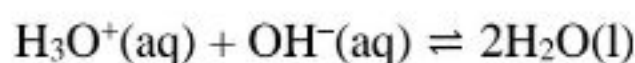
(ii) Initially the solution is $0.100 \text{ mol dm}^{-3}$ in HCl. Since HCl is a strong acid, means that the pH is

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[\text{HCl}] = -\log(0.100) = 1.00$$

(iii) Before the equivalence point, HCl is present in excess and the pH is determined by the concentration of excess HCl. After adding 10.00 cm^3 of NaOH, i.e. stoichiometrically lesser amount of NaOH compared to the amount of HCl present, the concentration of excess (or remaining) HCl has to be estimated.

$$\begin{aligned}
 \text{Initial amount of HCl (in moles)} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 2.50 \times 10^{-3} \text{ mol} \\
 \text{Amount of NaOH added} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 10.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 1.0 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of HCl reacted} &= 1.0 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of HCl remaining} &= (2.50 \times 10^{-3} - 1.00 \times 10^{-3}) \text{ mol} \\
 &= 1.50 \times 10^{-3} \text{ mol} \\
 \therefore \text{Concentration of HCl (H}_3\text{O}^+) \text{ remaining} &= \frac{1.5 \times 10^{-3} \text{ mol}}{35.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} \\
 &= 0.043 \text{ mol dm}^{-3} \\
 \therefore \text{pH} &= -\log (0.043) = 1.37
 \end{aligned}$$

(iv) At the equivalence point (after addition of 25.00 cm^3 of NaOH) all the H^+ and OH^- ions are consumed. Also the salt NaCl present as Na^+ and Cl^- does not undergo hydrolysis. Therefore, for the reaction of a strong base with a strong acid at the equivalence point the only equilibrium reaction (net reaction) of importance is,



At the equivalence point, $[\text{H}^+(\text{aq})] = [\text{OH}^-(\text{aq})]$ and the pH of the solution is 7.00.

(v) After adding 35.00 cm^3 of NaOH, i.e. stoichiometrically higher amount of NaOH compared to the amount of HCl present, the concentration of excess (or remaining) NaOH has to be estimated.

$$\begin{aligned}
 \text{Initial amount of HCl (in moles)} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 2.50 \times 10^{-3} \text{ mol} \\
 \text{Amount of NaOH added} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 35.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 3.50 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of HCl reacted} &= 2.5 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of NaOH remaining} &= (3.50 \times 10^{-3} - 2.50 \times 10^{-3}) \text{ mol} \\
 &= 1.0 \times 10^{-3} \text{ mol} \\
 \therefore \text{Concentration of NaOH (OH}^-) \text{ remaining} &= \frac{1.0 \times 10^{-3} \text{ mol}}{60.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} \\
 &= 0.017 \text{ mol dm}^{-3} \\
 \therefore \text{pOH} &= -\log (0.017) = 1.77 \\
 \therefore \text{pH} &= 14.00 - 1.77 = 12.23
 \end{aligned}$$

Important: Now we can see that the pH curve has some deflection around $\text{pH}=7$. Let's see the changes in pH in the vicinity of the equivalence point.

Addition of 24.90 cm³ of NaOH:

After adding 24.90 cm³ of NaOH, i.e. stoichiometrically lesser amount of NaOH compared to the amount of HCl present, the concentration of excess (or remaining) HCl has to be estimated.

$$\begin{aligned}
 \text{Initial amount of HCl (in moles)} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 2.50 \times 10^{-3} \text{ mol} \\
 \text{Amount of NaOH added} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 24.90 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 2.49 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of HCl reacted} &= 2.49 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of HCl remaining} &= (2.50 \times 10^{-3} - 2.49 \times 10^{-3}) \text{ mol} \\
 &= 1.00 \times 10^{-5} \text{ mol} \\
 \therefore \text{Concentration of HCl (H}_3\text{O}^+) \text{ remaining} &= \frac{1.00 \times 10^{-5} \text{ mol}}{49.90 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} \\
 &= 2.00 \times 10^{-4} \text{ mol dm}^{-3} \\
 \therefore \text{pH} = -\log (2.00 \times 10^{-4}) &= 3.7
 \end{aligned}$$

Addition of 25.10 cm³ of NaOH:

$$\begin{aligned}
 \text{Initial amount of HCl (in moles)} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 2.50 \times 10^{-3} \text{ mol} \\
 \text{Amount of NaOH added} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.10 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 2.51 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of HCl reacted} &= 2.50 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of NaOH remaining} &= (2.51 \times 10^{-3} - 2.50 \times 10^{-3}) \text{ mol} \\
 &= 1.0 \times 10^{-5} \text{ mol} \\
 \therefore \text{Concentration of NaOH (OH}^-) \text{ remaining} &= \frac{1.0 \times 10^{-5} \text{ mol}}{50.10 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} \\
 &= 2.00 \times 10^{-4} \text{ mol dm}^{-3} \\
 \therefore \text{pOH} = -\log (2.00 \times 10^{-4}) &= 3.7 \\
 \therefore \text{pH} = 14.00 - 3.70 &= 10.30
 \end{aligned}$$

After addition of NaOH volumes higher than 25.00 cm³, i.e. stoichiometrically higher amount of NaOH compared to the amount of HCl present, the concentration of excess (or remaining) NaOH has to be estimated.

In this strong acid vs strong base titration we can see that there is a drastic change in pH in the vicinity of the equivalence point (6.6 pH unit change within the 0.020 cm³ volume interval). By plotting the calculated pH values against different volumes of NaOH added,

we can obtain the pH curve in Figure 2.17(a) and 2.17(b) shows the behaviour of pH curves with the variation of initial concentration of the acid and base.

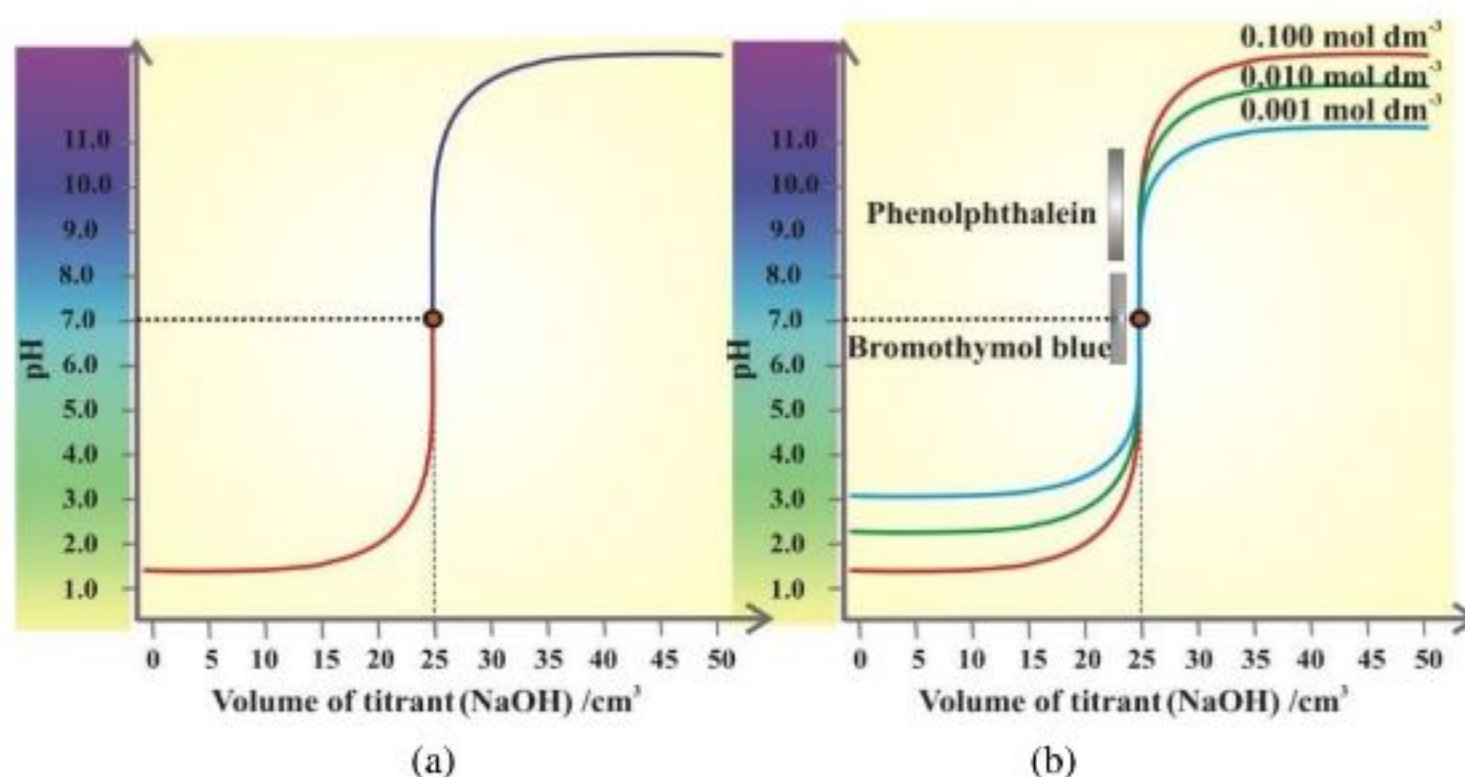
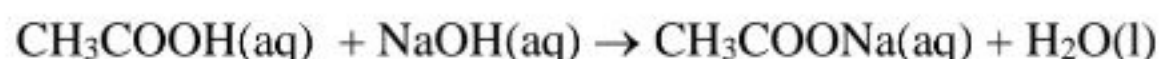


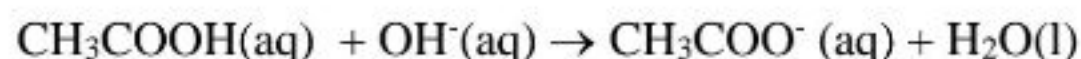
Figure 2.17 (a) Titration curve for the titration of 25.00 cm³ of 0.100 mol dm⁻³ HCl with 0.100 mol dm⁻³ NaOH. A steep change in pH occurs in the vicinity of equivalence point at which pH = 7.0 with 25.00 cm³ of NaOH. (b) Shows the variation in pH curves with the initial concentrations of HCl and NaOH. When the initial concentration decreases the spread of the pH curve decreases. Role of indicators phenolphthalein and bromothymol blue will be discussed in a separate section.

- **Weak acid – strong base titrations**

Consider the reaction between acetic acid (a weak acid) and sodium hydroxide (a strong base):

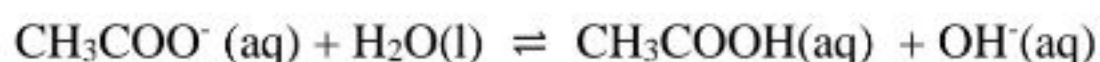


As NaOH is a strong base we can rewrite the reaction as,



As we have discussed earlier, the $\text{CH}_3\text{COO}^-(\text{aq})$ undergoes hydrolysis and the reaction will determine the pH at the equivalence point of the titration.

The acetate ion undergoes hydrolysis as follows:



Therefore, at the equivalence point, where we have only sodium acetate, the pH will be greater than 7 as a result of the excess $\text{OH}^-(\text{aq})$ ions formed due to the hydrolysis of acetate ions. Let's try to understand the titration curve of this type of a titration where a weak acid is titrated with a strong base.

Consider the titration of 25.00 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ CH}_3\text{COOH(aq)}$ with $0.100 \text{ mol dm}^{-3} \text{ NaOH}$. $K_a(\text{CH}_3\text{COOH}) = 1.80 \times 10^{-5}$

We can see that the pH of the solution depends on the relative concentrations of the undissociated $\text{CH}_3\text{COOH(aq)}$ acid and $\text{CH}_3\text{COO}^-(\text{aq})$ ions (formed as $\text{CH}_3\text{COONa(aq)}$) present) at each stage of the volume of NaOH added. Similar to the titration between a strong acid and a strong base, it is possible to consider the situations like pH at the equivalence point, pH before the equivalence point, and pH after the equivalence point.

Let us first calculate the volume of NaOH needed to reach the equivalence point. At the equivalence point ,

Amount of moles CH_3COOH = Amount of moles NaOH (as the stoichiometry between CH_3COOH and NaOH is 1 : 1)

Applying simple formula $C_a V_a = C_b V_b$

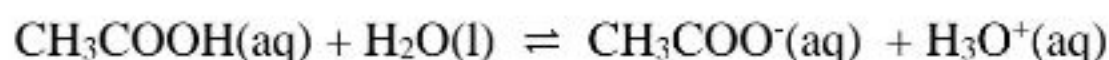
where the subscript 'a' indicates the acid, CH_3COOH , and the subscript 'b' indicates the base, NaOH.

(i) The volume of NaOH needed to reach the equivalence point, therefore, is

$$0.100 \times 25.00 = 0.100 \times V_b$$

$$\therefore V_b = 25.00 \text{ cm}^3$$

(ii) Initially the solution is $0.100 \text{ mol dm}^{-3}$ in CH_3COOH . Since CH_3COOH is a weak acid, $[\text{H}_3\text{O}^+]$ will be determined by its partial ionization, i.e



$[\text{H}_3\text{O}^+]$ is calculated from K_a as,

	$\text{CH}_3\text{COOH(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
Initial concentration/ mol dm^{-3}	0.1	0	0
Change in concentration/ mol dm^{-3}	x	$+x$	$+x$
\therefore Equilibrium concentration/ mol dm^{-3}	$(0.10 - x)$	$+x$	$+x$
\therefore Equilibrium concentration/ mol dm^{-3}	0.10	$+x$	$+x$

(with the assumption $(0.10 - x) \sim 0.1$)

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH(aq)}]} = \frac{x^2}{(0.1)} = 1.80 \times 10^{-5}$$

$$x^2 = 1.80 \times 10^{-6}$$

$$x = 1.34 \times 10^{-3}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[1.34 \times 10^{-3}] = 2.87$$

Or
$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH(aq)}]}$$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})]^2}{C_0}$$

where initial concentration of the acid is C_0

$$[\text{H}_3\text{O}^+(\text{aq})] = (K_a C_0)^{1/2}$$

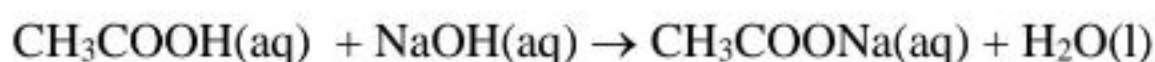
$$-\log [\text{H}_3\text{O}^+(\text{aq})] = -\log(K_a)^{1/2} - \log(C_0)^{1/2}$$

$$-\log [\text{H}_3\text{O}^+(\text{aq})] = -\frac{1}{2} \log(K_a) - \frac{1}{2} \log(C_0)$$

$$\text{pH} = -\frac{1}{2} \text{p}K_a - \frac{1}{2} \log(C_0)$$

(iii) Before the equivalence point, the added amount of NaOH is stoichiometrically lesser than the amount of CH_3COOH acid present in the solution. Therefore, the solution contains undissociated CH_3COOH acid and the salt CH_3COONa . In other words, now we have a mixture of a weak acid and its salt (conjugate base), i.e. a buffer solution. To calculate pH, we can use the **Henderson-Hasselbalch** equation with our knowledge of buffer solutions.

Let's consider the reaction after the addition of 10.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ NaOH.

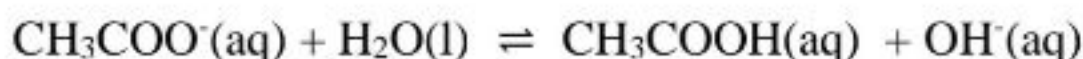


Initial amount of CH_3COOH	$= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3}$ $= 2.50 \times 10^{-3} \text{ mol}$
Amount of NaOH added	$= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 10.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3}$ $= 1.0 \times 10^{-3} \text{ mol}$
\therefore Amount of CH_3COOH reacted	$= 1.0 \times 10^{-3} \text{ mol}$
\therefore Amount of CH_3COOH remaining	$= (2.50 \times 10^{-3} - 1.00 \times 10^{-3}) \text{ mol}$ $= 1.50 \times 10^{-3} \text{ mol}$
\therefore Concentration of CH_3COOH remaining	$= \frac{1.5 \times 10^{-3} \text{ mol}}{35.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3}$ $= 0.043 \text{ mol dm}^{-3}$
Amount of CH_3COONa formed	$= \text{Amount of NaOH added} = 1.0 \times 10^{-3} \text{ mol}$
Concentration of CH_3COONa formed	$= \frac{1.0 \times 10^{-3} \text{ mol}}{35.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3}$ $= 0.029 \text{ mol dm}^{-3}$

Substituting these values in,

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \\ \text{pH} &= 4.74 + \log \frac{(0.029)}{(0.043)} \\ \text{pH} &= 4.57 \end{aligned}$$

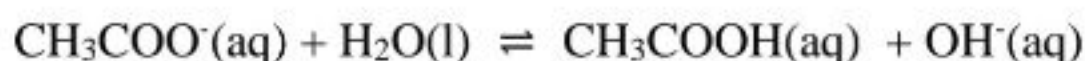
(iv) At the equivalence point (after addition of 25.00 cm³ of NaOH) all the CH₃COOH and NaOH are consumed. The salt CH₃COONa present undergoes hydrolysis as,



According to the reaction, CH₃COOH(aq) + NaOH(aq) → CH₃COONa(aq) + H₂O(l)

The amount of CH₃COONa (CH₃COO⁻(aq)) formed = 2.50 × 10⁻³ mol

$$\begin{aligned} \therefore \text{The concentration of the salt} &= \frac{2.5 \times 10^{-3} \text{ mol}}{50.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} \\ &= 0.05 \text{ mol dm}^{-3} \end{aligned}$$



Initial concentration/ mol dm ⁻³	0.05	0	0
Change in concentration/ mol dm ⁻³	-x	+x	+x
∴ Equilibrium concentration/ mol dm ⁻³	(0.05 - x)	+x	+x
∴ Equilibrium concentration/ mol dm ⁻³	0.05	+x	+x

(with the assumption (0.05 - x) ~ 0.05)

For the above hydrolysis reaction we can write the expression for K_b as,

$$\begin{aligned} K_b &= \frac{[\text{OH}^-(\text{aq})][\text{CH}_3\text{COOH}(\text{aq})]}{[\text{CH}_3\text{COO}^-(\text{aq})]} = \frac{x^2}{(0.05)} = \frac{K_w}{K_a} = 5.6 \times 10^{-10} \\ x &= [\text{OH}^-(\text{aq})] = 5.3 \times 10^{-6} \text{ mol dm}^{-3} \\ \therefore \text{pOH} &= 5.28 \\ \therefore \text{pH} &= 14.00 - 5.28 \\ \therefore \text{pH} &= 8.72 \end{aligned}$$

Or,

$$\begin{aligned} K_b &= \frac{[\text{OH}^-(\text{aq})][\text{CH}_3\text{COOH}(\text{aq})]}{[\text{CH}_3\text{COO}^-(\text{aq})]} \\ K_b &= \frac{[\text{OH}^-(\text{aq})]^2}{S}, \end{aligned}$$

where S is the concentration of the salt

$$\begin{aligned} [\text{OH}^-(\text{aq})] &= (K_b S)^{1/2} \\ -\log[\text{OH}^-(\text{aq})] &= -\log(K_b)^{1/2} - \log(S)^{1/2} \\ -\log[\text{OH}^-(\text{aq})] &= -\frac{1}{2}\log(K_b) - \frac{1}{2}\log S \end{aligned}$$

$$\begin{aligned} \text{pOH} &= -\frac{1}{2}\text{p}K_b - \frac{1}{2}\log S \\ \text{Substituting, } \text{pH} + \text{pOH} &= \text{p}K_w \text{ and } \text{p}K_a + \text{p}K_b = \text{p}K_w \\ \text{p}K_w - \text{pH} &= -\frac{1}{2}(\text{p}K_w - \text{p}K_a) - \frac{1}{2}\log S \\ \therefore \text{pH} &= \frac{1}{2}\text{p}K_a + \frac{1}{2}\text{p}K_w + \frac{1}{2}\log S \end{aligned}$$

- (v) After the equivalence point the total amount of CH_3COOH initially present gets converted to the salt CH_3COONa and excess NaOH will present as OH^- . Therefore, the pH of the mixture is determined by the excess concentration of $[\text{OH}^-(\text{aq})]$.

After adding 35.00 cm^3 of NaOH , i.e. stoichiometrically higher amount of NaOH compared to the amount of CH_3COOH present, the concentration of excess (or remaining) NaOH has to be estimated.

$$\begin{aligned}
 \text{Initial amount of } \text{CH}_3\text{COOH} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 2.50 \times 10^{-3} \text{ mol} \\
 \text{Amount of } \text{NaOH} \text{ added} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 35.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\
 &= 3.50 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of } \text{CH}_3\text{COOH} \text{ reacted} &= 2.5 \times 10^{-3} \text{ mol} \\
 \therefore \text{Amount of } \text{NaOH} \text{ remaining} &= (3.50 \times 10^{-3} - 2.50 \times 10^{-3}) \text{ mol} \\
 &= 1.0 \times 10^{-3} \text{ mol} \\
 \therefore \text{Concentration of } \text{NaOH} (\text{OH}^-) \text{ remaining} &= \frac{1.0 \times 10^{-3} \text{ mol}}{60.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} \\
 &= 0.017 \text{ mol dm}^{-3} \\
 \therefore \text{pOH} &= -\log(0.017) = 1.77 \\
 \therefore \text{pH} &= 14.00 - 1.77 = 12.23
 \end{aligned}$$

Or, After the equivalence point, $[\text{H}_3\text{O}^+(\text{aq})] = \frac{K_w}{[\text{OH}^-(\text{aq})]}$

$[\text{OH}^-(\text{aq})]$ is the excess concentration of the strong base

And taking excess $[\text{OH}^-(\text{aq})] = B'$

$$\begin{aligned}
 [\text{H}_3\text{O}^+(\text{aq})] &= \frac{K_w}{B'} \\
 -\log[\text{H}_3\text{O}^+(\text{aq})] &= -\log(K_w) - (-\log B') \\
 \text{pH} &= \text{p}K_w + \log(B')
 \end{aligned}$$

At the half-equivalence point:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Concentrations of the acid and the conjugate base are equal.

$$\therefore \text{pH} = \text{p}K_a$$

We can summarize the above in the following pH curve in **Figure 2.18**.

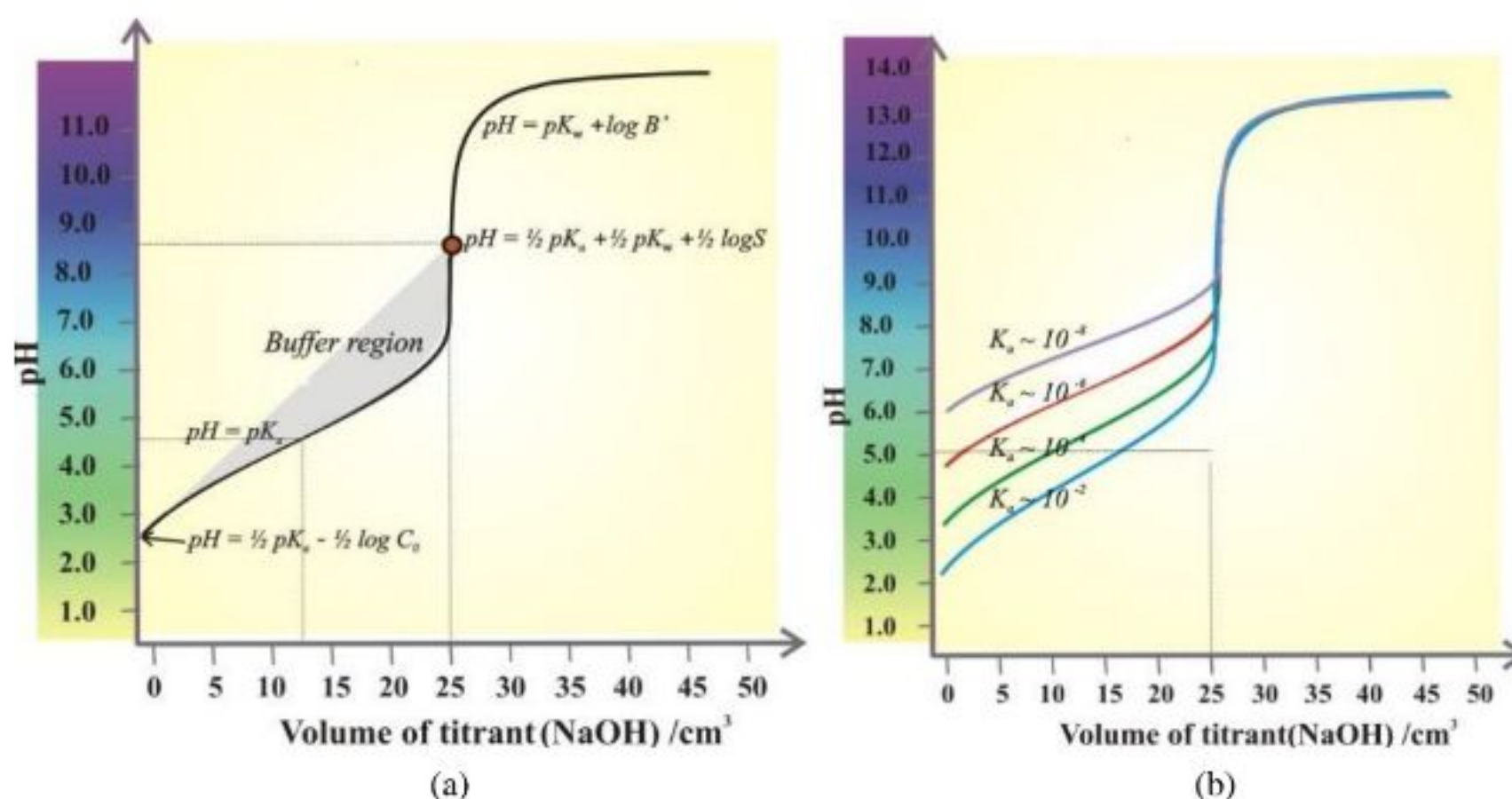
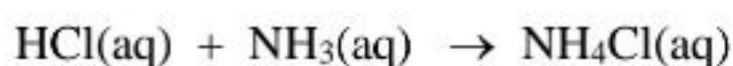


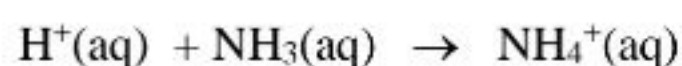
Figure 2.18 (a) Titration curve for the titration of 25.00 cm³ of 0.100 mol dm⁻³ CH₃COOH with 0.100 mol dm⁻³ NaOH. Equivalence point occurs in basic region with pH of 8.72. In these titrations a buffer solution is formed below the equivalence point (will be explained in a separate section 12.3). Characteristics points with the pH functions are also marked. In (b) variations of pH curves with the strength of the weak acid are compared. Weaker the acid, the equivalence point shifts more to the basic side.

- Strong acid – weak base titrations**

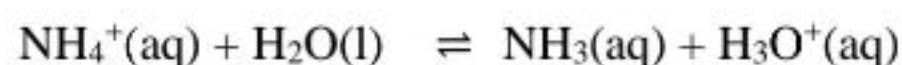
Let us consider the titration between NH₃, a weak base and HCl, a strong acid: the reaction taking place is;



or simply



We can see that the pH at the equivalence point is *less than 7* due to the hydrolysis of the NH₄⁺(aq)



Because of the volatility of an aqueous ammonia solution, it is more convenient to add HCl acid from a burette to the ammonia solution.

Example:

Let 25.00 cm^3 of $0.10 \text{ mol dm}^{-3} \text{ NH}_3$, a weak base be titrated with $0.10 \text{ mol dm}^{-3} \text{ HCl}$, a strong acid.

We can see that the pH of the solution depends on the relative concentrations of the undissociated NH_4Cl and NH_3 at each stage of the volume of HCl added. Therefore, like the case considered for the weak acid-strong base titration, it is possible to consider pH at the equivalence point, pH before the equivalence point, and pH after the equivalence point.

Let us first calculate the volume of HCl needed to reach the equivalence point. At the equivalence point,

Amount of moles of NH_3 = Amount of moles of HCl (as the stoichiometry between NH_3 and HCl is 1 : 1)

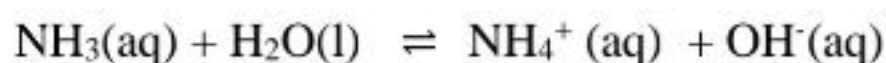
Applying the formula $C_a V_a = C_b V_b$

(i) The volume of HCl needed to reach the equivalence point, therefore, is

$$0.100 \times 25.00 = 0.100 \times V_b$$

$$\therefore V_b = 25.00 \text{ cm}^3$$

(ii) Initially the solution is $0.100 \text{ mol dm}^{-3}$ in NH_3 . Since NH_3 is a weak base, $[\text{OH}^-]$ will be determined considering its partial ionization, i.e



$[\text{OH}^-]$ is calculated from K_b as,

	$\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$	\rightleftharpoons	$\text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
Initial concentration/ mol dm^{-3}	0.1		0 0
Change in concentration/ mol dm^{-3}	-x		+x +x
\therefore Equilibrium concentration/ mol dm^{-3}	(0.10 -x)		+x +x
\therefore Equilibrium concentration/ mol dm^{-3}	0.10		+x +x

(with the assumption $(0.10 - x) \sim 0.1$)

$$K_b = \frac{[\text{NH}_4^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_3(\text{aq})]} = \frac{x^2}{(0.1)} = 1.80 \times 10^{-5}$$

$$x^2 = 1.80 \times 10^{-6}$$

$$x = 1.34 \times 10^{-3}$$

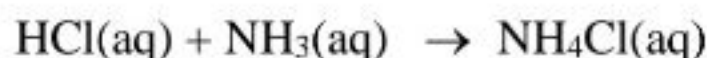
$$\text{pOH} = -\log[\text{OH}^-(\text{aq})] = -\log[1.34 \times 10^{-3}] = 2.87$$

$$\therefore \text{pH} = 14.00 - 2.87 = 11.13$$

(iii) Before the equivalence point, the added amount of HCl is stoichiometrically lesser than the amount of NH_3 present in the solution. Therefore, the solution contains undissociated NH_3 and the salt NH_4Cl . In other words, now we have a mixture of a

weak base and its salt (conjugate acid), i.e. a buffer solution. To calculate pH, we can use our knowledge of buffer solutions.

Let's consider the reaction after the addition of 10.00 cm^3 of $0.100 \text{ mol dm}^{-3}$ HCl.



$$\begin{aligned} \text{Initial amount of NH}_3 &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\ &= 2.50 \times 10^{-3} \text{ mol} \\ \text{Amount of HCl added} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 10.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\ &= 1.0 \times 10^{-3} \text{ mol} \\ \therefore \text{Amount of NH}_3 \text{ reacted} &= 1.0 \times 10^{-3} \text{ mol} \\ \therefore \text{Amount of NH}_3 \text{ remaining} &= (2.50 \times 10^{-3} - 1.00 \times 10^{-3}) \text{ mol} \\ &= 1.50 \times 10^{-3} \text{ mol} \\ \therefore \text{Concentration of NH}_3 \text{ remaining} &= \frac{1.5 \times 10^{-3} \text{ mol}}{35.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} \\ &= 0.043 \text{ mol dm}^{-3} \end{aligned}$$

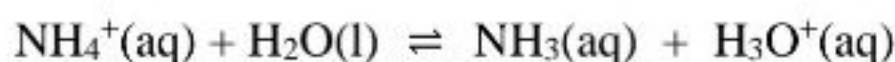
Amount of NH_4Cl formed = Amount of HCl added = $1.0 \times 10^{-3} \text{ mol}$

$$\text{Concentration of NH}_4\text{Cl formed} = \frac{1.0 \times 10^{-3} \text{ mol}}{35.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} = 0.029 \text{ mol dm}^{-3}$$

Substituting these values in,

$$\begin{aligned} \text{pOH} &= \text{pK}_b + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \\ \text{pOH} &= 4.74 + \log \frac{(0.029)}{(0.043)} \\ \text{pOH} &= 4.57 \\ \therefore \text{pH} &= 14.00 - 4.57 = 9.43 \end{aligned}$$

- (iv) At the equivalence point (after addition of 25.00 cm^3 of HCl) all the NH_3 and HCl are consumed. The salt NH_4Cl present undergoes hydrolysis as,



According to the reaction, $\text{HCl(aq)} + \text{NH}_3(\text{aq}) \rightarrow \text{NH}_4\text{Cl(aq)}$

The amount of NH_4Cl ($\text{NH}_4^+(\text{aq})$) formed = $2.50 \times 10^{-3} \text{ mol}$

$$\therefore \text{The concentration of the salt} = \frac{2.5 \times 10^{-3} \text{ mol}}{50.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} = 0.05 \text{ mol dm}^{-3}$$

	$\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O(l)} \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$		
Initial concentration/ mol dm^{-3}	0.05	0	0
Change in concentration/ mol dm^{-3}	-x	+x	+x
\therefore Equilibrium concentration/ mol dm^{-3}	(0.05 - x)	+x	+x
\therefore Equilibrium concentration/ mol dm^{-3}	0.05	+x	+x
(with the assumption (0.05 - x) \sim 0.05)			

For the above hydrolysis reaction we can write the expression for K_b as,

$$K_b = \frac{[\text{NH}_3(\text{aq})][\text{H}_3\text{O}^+(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.05} \quad (\text{with the assumption})$$

$$x^2 = 28 \times 10^{-12}$$

$$x = [\text{H}_3\text{O}^+(\text{aq})] = 5.3 \times 10^{-6}$$

$$\therefore \text{pH} = 5.28$$

(v) After the equivalence point the total amount of NH_3 initially present gets converted to the salt NH_4Cl and excess HCl will be present as H_3O^+ . Therefore, the pH of the mixture is determined by the excess concentration of $[\text{H}_3\text{O}^+(\text{aq})]$.

In order to calculate pH after adding 35.00 cm^3 of HCl , i.e. stoichiometrically a higher amount of HCl compared to the amount of NH_3 present, the concentration of excess (or remaining) HCl has to be estimated.

$$\begin{aligned} \text{Initial amount of } \text{NH}_3 &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\ &= 2.50 \times 10^{-3} \text{ mol} \\ \text{Amount of HCl added} &= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 35.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3} \\ &= 3.50 \times 10^{-3} \text{ mol} \\ \therefore \text{Amount of } \text{NH}_3 \text{ reacted} &= 2.5 \times 10^{-3} \text{ mol} \\ \therefore \text{Amount of HCl remaining} &= (3.50 \times 10^{-3} - 2.50 \times 10^{-3}) \text{ mol} \\ &= 1.0 \times 10^{-3} \text{ mol} \\ \therefore \text{Concentration of HCl (H}_3\text{O}^+(\text{aq})) \text{ remaining} &= \frac{1.0 \times 10^{-3} \text{ mol}}{60.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3} \\ &= 0.017 \text{ mol dm}^{-3} \\ \therefore \text{pH} &= -\log(0.017) = 1.77 \end{aligned}$$

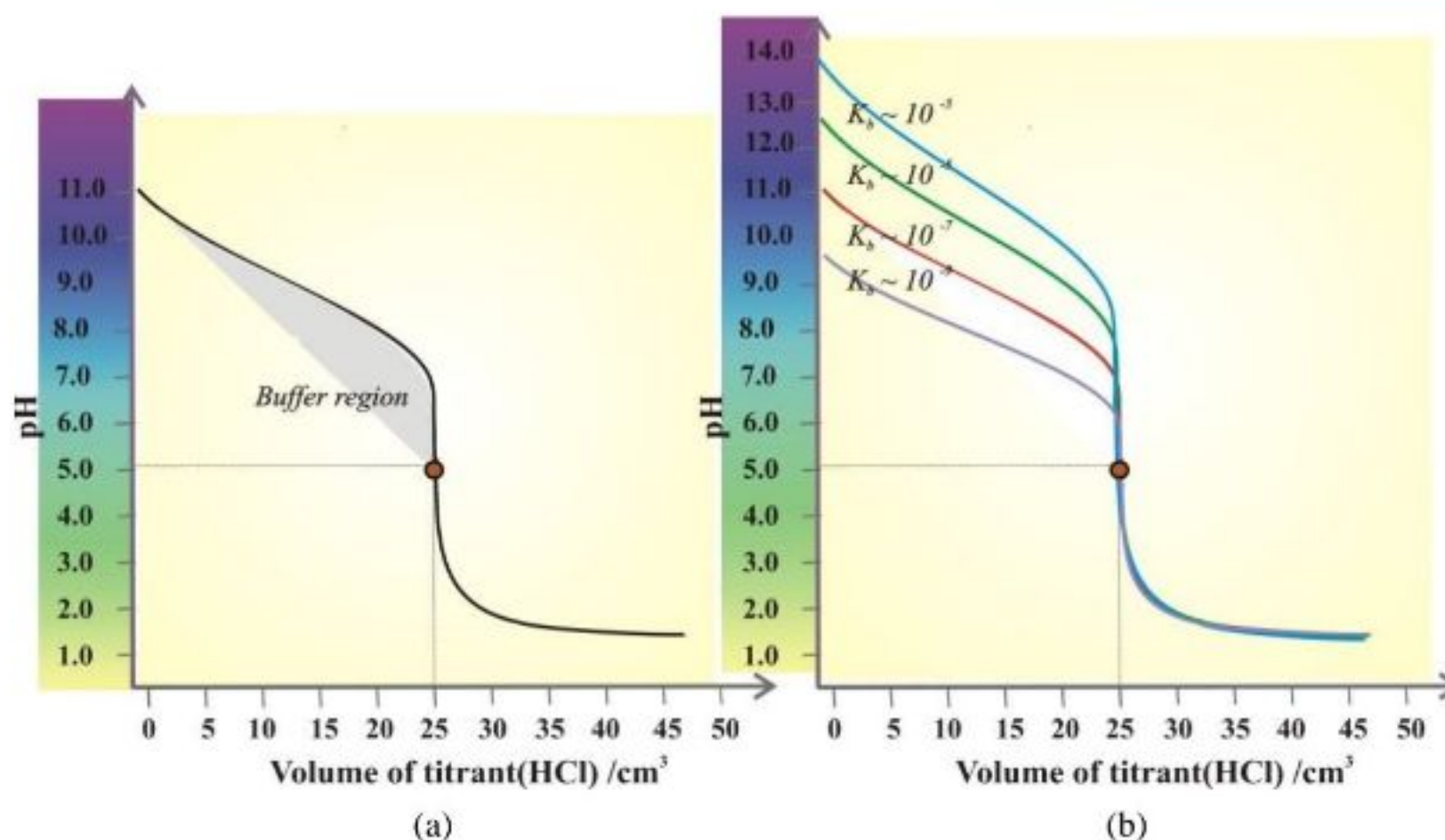


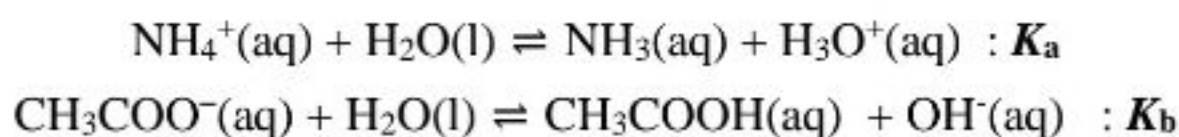
Figure 2.19 (a) Titration curve for the titration of 25.00 cm³ of 0.100 mol dm⁻³ NH₃ with 0.100 mol dm⁻³ HCl. Equivalence point occurs in acidic region with pH of 5.28. In these titrations a buffer solution is formed too below the equivalence point. In (b) variations of pH curves with the strength of the weak base are compared. Weaker the base, the equivalence point shifts more to acidic side.

• Weak acid- weak base titration

When acetic acid, which is a weak acid, reacts with ammonia, the reaction taking place is,



Now we can see that the products contain the base CH₃COO⁻ and the acid NH₄⁺. Therefore, the pH at the equivalence point is determined by the strength of the hydrolysis of these. We can write,



From these reactions, we see that H₃O⁺ and OH⁻ ions are formed and they undergo neutralization. Though neutralization occurs, still we may not have equal amount of H₃O⁺ and OH⁻ and hence pH ≠ 7 at the equivalence point. It depends on the relative strengths

of K_a and K_b : *if $K_a > K_b$, the solution is acidic and if $K_a < K_b$, the solution is basic .*

Another important feature in this kind of a titration is that there is no steep pH changing region in the pH curve and it mainly shows a deflecting point, resulting in difficulty to use an indicator to locate the equivalence point. Therefore, the titrations between a weak acid and a weak base are hardly carried out. Figure 2.20 shows the variation of pH in this type of a titration.

Note: It has to be noted that the pH of such solutions is determined by using pK values of the acid and the base using the mathematical formula,

$$\text{pH} = 7 + \frac{1}{2} (\text{p}K_{\text{a}} - \text{p}K_{\text{b}})$$

The pH of the solution can be greater than 7, if the difference is positive and it will be less than 7, if the difference is negative.

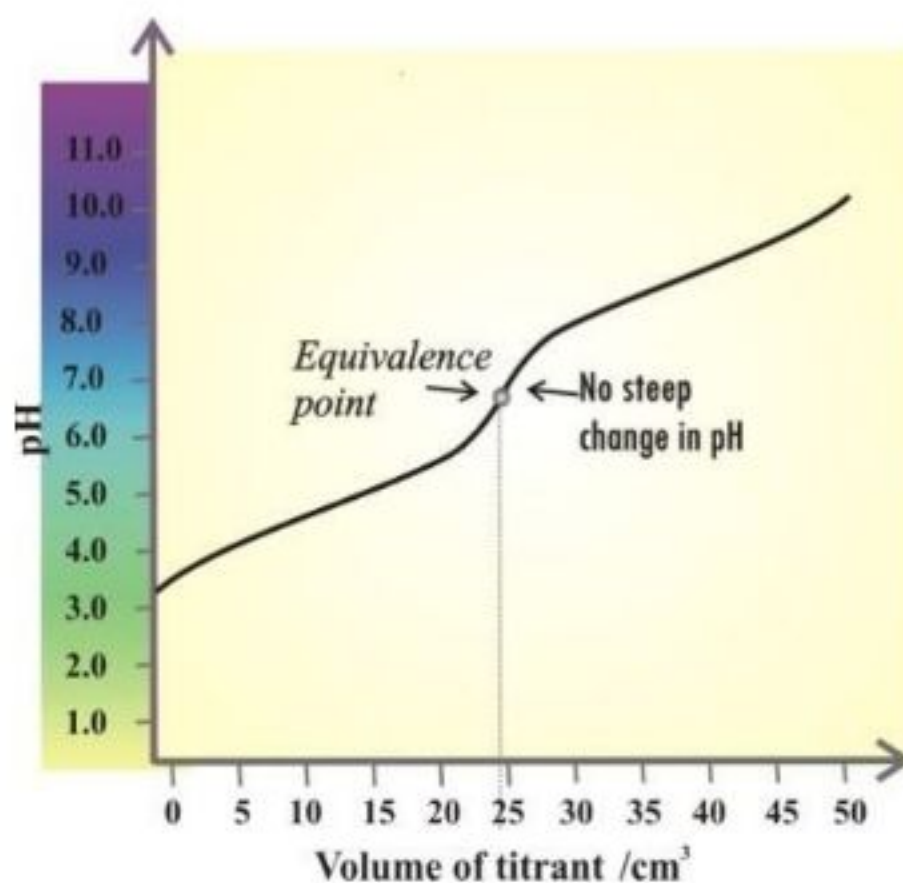


Figure 2.20 Titration curve for the titration of 25.00 cm³ of 0.100 mol dm⁻³ CH₃COOH with 0.100 mol dm⁻³ NH₃. It is difficult to judge the location of the equivalence point as it depends on the relative strengths of the acid and the base. There is no steep change in pH in these types of systems.

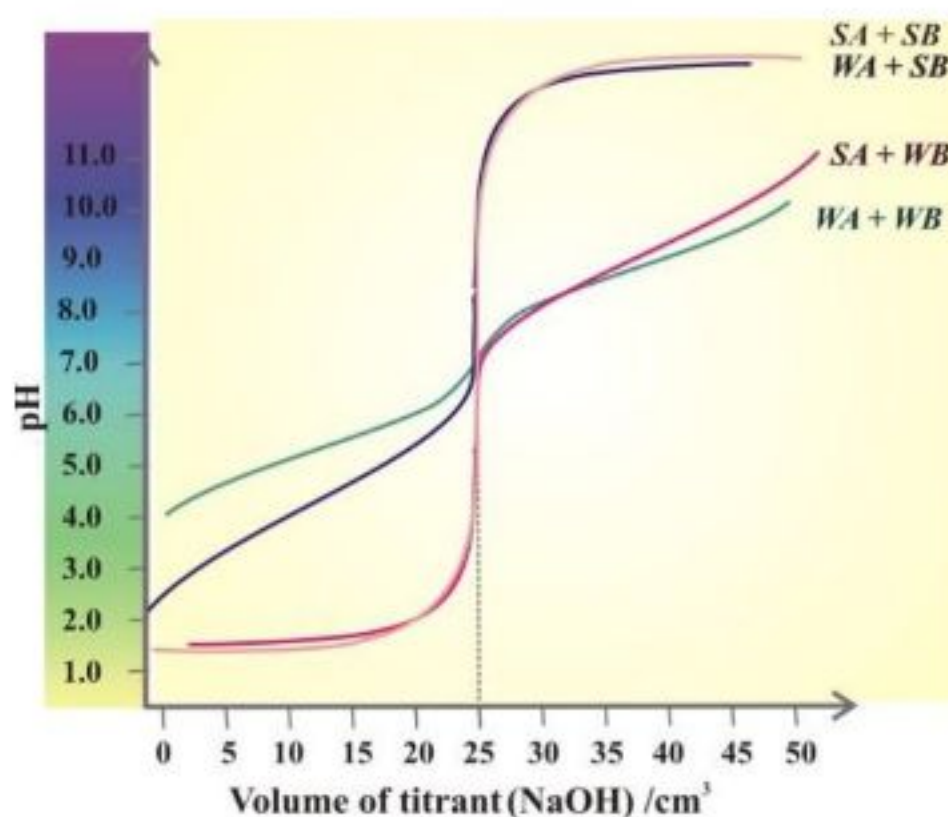
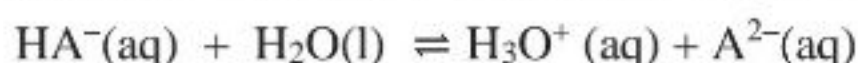
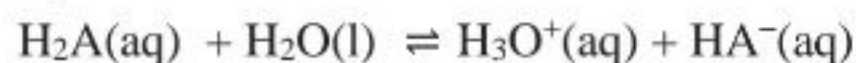


Figure 2.21 Summary of the four types of titrations with 0.100 mol dm⁻³ acid (mono basic) and 0.100 mol dm⁻³ base (mono acidic) discussed above. (SA-strong acid, SB-strong base, WA-Weak acid and WB-Weak base)

2.2.12 Di- and polybasic acids and di- and polyacidic bases

Some of the acids like oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) have more than one ionizable proton per molecule of the acid. Such acids are known as polybasic or polyprotic acids. The ionization reactions of a *dibasic acid* H_2A are represented by the equations:

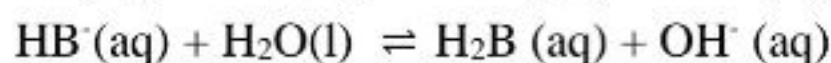
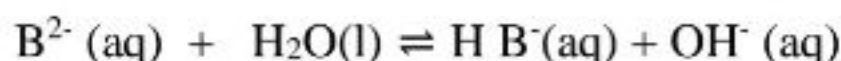


And the corresponding equilibrium constants (*acid ionization constants*) are given below:

$$K_{a_1} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{HA}^-(\text{aq})]}{[\text{H}_2\text{A}(\text{aq})]}$$

$$K_{a_2} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^{2-}(\text{aq})]}{[\text{HA}^-(\text{aq})]}$$

Likewise, the ionization reactions of a *diacidic base* B^{2-} are represented by the equations:



And the corresponding equilibrium constants (*base ionization constants*) are given below:

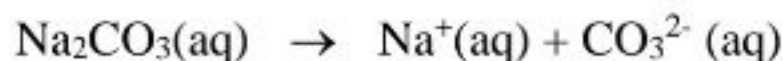
$$K_{b_1} = \frac{[\text{HB}^-(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{B}^{2-}(\text{aq})]}$$

$$K_{b_2} = \frac{[\text{H}_2\text{B}(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{HB}^-(\text{aq})]}$$

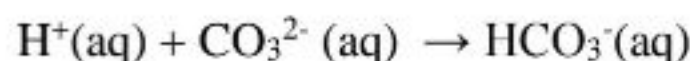
Polyacidic base titrations

The pH curve for the titration of hydrochloric acid with sodium hydroxide has only one equivalence (end) point (Figure 2.17), but the pH curve for the addition of $\text{HCl}(\text{aq})$ (titrant) to $\text{Na}_2\text{CO}_3(\text{aq})$ (Figure 2.22) displays two equivalence points, i.e. two rapid change in pH. Here, for example, two successive reactions occur. The two end points in Figure 2.22 can be explained by two different proton transfer equations.

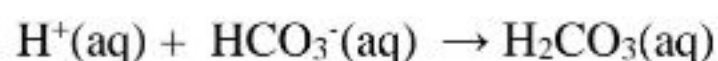
Sodium carbonate is a strong electrolyte and so fully dissociates into $\text{Na}^+(\text{aq})$ and $\text{CO}_3^{2-}(\text{aq})$ ions.



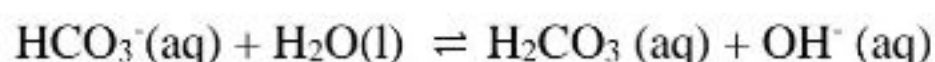
Therefore, the major entities in the mixture are $\text{Na}^+(\text{aq})$, $\text{CO}_3^{2-}(\text{aq})$ and $\text{H}_2\text{O}(\text{l})$. At the beginning of the titration, $\text{H}^+(\text{aq})$ ions from $\text{HCl}(\text{aq})$ react with $\text{CO}_3^{2-}(\text{aq})$ ions since carbonate ions are the strongest bases present in the initial mixture.



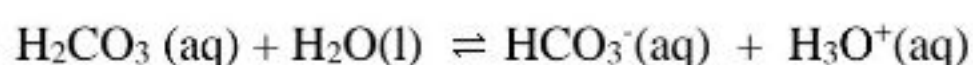
Then, in a second reaction, protons from HCl(aq) react with the hydrogen carbonate ions formed in the first reaction.



It is clear that at the first equivalence point, following equilibrium exists in the mixture and therefore the pH is determined by the hydrolysis of $\text{HCO}_3^-(\text{aq})$ ions.



At the second equivalence point following equilibrium exists in the mixture and therefore the pH is determined by the hydrolysis (first ionization) of $\text{H}_2\text{CO}_3(\text{aq})$ acid.



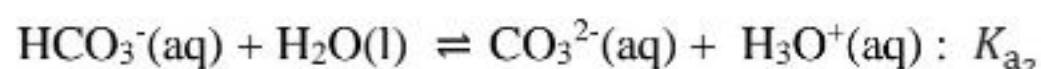
By looking at the above two reactions one may note that; at the first equivalence point mixture is basic while it becomes acidic at the second equivalence point.

Example:

Let's consider a titration of 25.00 cm^3 of $0.10 \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3(\text{aq})$ solution with $0.10 \text{ mol dm}^{-3} \text{ HCl(aq)}$ acid. Acid dissociation constants for the carbonic acid, H_2CO_3 are $K_{a_1} = 4.3 \times 10^{-7} \text{ mol dm}^{-3}$ and $K_{a_2} = 4.7 \times 10^{-11} \text{ mol dm}^{-3}$.

From the molarities of the solutions, one can note that the first equivalence point occurs at 25.00 cm^3 and the second equivalence point occurs at the 50.00 cm^3 of HCl .

When we consider the dissociation of H_2CO_3 acid:



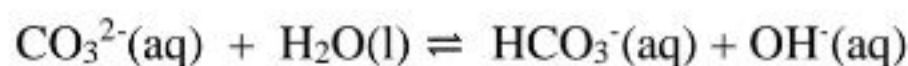
Therefore,

$$K_{a_1} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{HCO}_3^-(\text{aq})]}{[\text{H}_2\text{CO}_3(\text{aq})]} = 4.3 \times 10^{-7} \text{ mol dm}^{-3}$$

$$K_{a_2} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CO}_3^{2-}(\text{aq})]}{[\text{HCO}_3^-(\text{aq})]} = 4.7 \times 10^{-11} \text{ mol dm}^{-3}$$

Initial pH (at 0.00 cm^3 of HCl):

At this point as no acid has been added, and only $0.10 \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3(\text{aq})$ sodium carbonate solution is present. The pH is determined by the extent of carbonate ion reaction with water to give $\text{HCO}_3^-(\text{aq})$ and $\text{OH}^-(\text{aq})$.



Here water acts as an acid, providing a proton to carbonate ion, the base. The equilibrium constant for this reaction can be written as;

$$K' = \frac{[\text{HCO}_3^-(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{CO}_3^{2-}(\text{aq})]}$$

$$\text{Consider; } \frac{K_w}{K_{a2}} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]}{\frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CO}_3^{2-}(\text{aq})]}{[\text{HCO}_3^-(\text{aq})]}} = \frac{[\text{HCO}_3^-(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{CO}_3^{2-}(\text{aq})]} = K' = K_{b1}$$

$$\therefore K_{b1} = \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{4.7 \times 10^{-11} \text{ mol dm}^{-3}} = 2.13 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\therefore K_{b1} = \frac{[\text{OH}^-(\text{aq})]^2}{[\text{CO}_3^{2-}(\text{aq})]} \quad (\text{as } [\text{HCO}_3^-(\text{aq})] = [\text{OH}^-(\text{aq})])$$

$$[\text{OH}^-(\text{aq})]^2 = K_{b1} [\text{CO}_3^{2-}(\text{aq})] = 2.13 \times 10^{-4} \text{ mol dm}^{-3} \times 0.10 \text{ mol dm}^{-3} \\ = 2.13 \times 10^{-5} \text{ mol dm}^{-3}$$

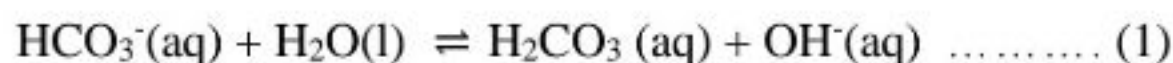
$$\therefore [\text{OH}^-(\text{aq})] = 4.61 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = 2.2 \times 10^{-12} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = 11.71$$

First equivalence point S (at 25.00 cm³ of HCl):

As previously explained, at the first equivalence point equilibrium existing is;



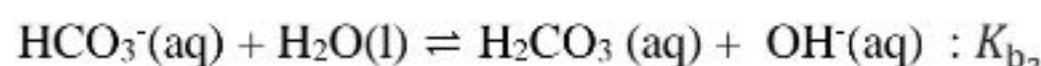
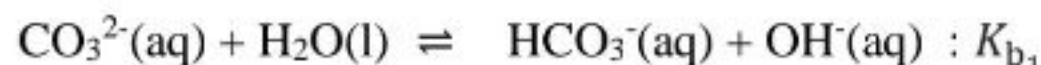
For the above equilibrium we can write,

$$K = \frac{[\text{H}_2\text{CO}_3(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{HCO}_3^-(\text{aq})]}$$

This K has a direct relationship with the K_{a1} of carbonic acid as,

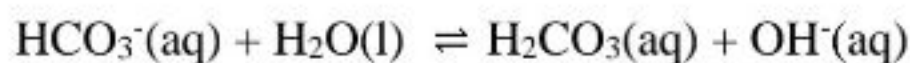
$$K = \frac{K_w}{K_{a1}} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{OH}^-(\text{aq})]}{\frac{[\text{H}_3\text{O}^+(\text{aq})][\text{HCO}_3^-(\text{aq})]}{[\text{H}_2\text{CO}_3(\text{aq})]}} = \frac{[\text{H}_2\text{CO}_3(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{HCO}_3^-(\text{aq})]} = K_{b2}$$

K_{b2} is the second ionization constant of $\text{CO}_3^{2-}(\text{aq})$ as we can write,



$$\therefore K_{b_2} = \frac{[\text{H}_2\text{CO}_3(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{HCO}_3^-(\text{aq})]} = \frac{1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{4.3 \times 10^{-7} \text{ mol dm}^{-3}} = 2.33 \times 10^{-8} \text{ mol dm}^{-3}$$

For the reaction (1),



$$K_{b_2} = \frac{[\text{H}_2\text{CO}_3(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{HCO}_3^-(\text{aq})]}$$

At equilibrium:

$$K_{b_2} = \frac{[\text{OH}^-(\text{aq})]^2}{[\text{HCO}_3^-(\text{aq})]} \quad (\text{as } [\text{H}_2\text{CO}_3(\text{aq})] = [\text{OH}^-(\text{aq})])$$

As the first equivalence point occurs at 25.00 cm³ of HCl;

$$[\text{HCO}_3^-(\text{aq})] = \frac{0.10 \text{ mol dm}^{-3} \times 25.00 \times 10^{-3} \text{ dm}^3}{50.00 \times 10^{-3} \text{ dm}^3} = 0.05 \text{ mol dm}^{-3}$$

$$\therefore [\text{OH}^-(\text{aq})]^2 = K_{b_2} [\text{HCO}_3^-(\text{aq})] = 2.33 \times 10^{-8} \text{ mol dm}^{-3} \times 0.05 \text{ mol dm}^{-3}$$

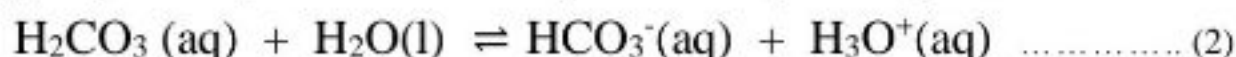
$$\therefore [\text{OH}^-(\text{aq})] = 3.4 \times 10^{-5} \text{ mol dm}^{-3}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = 2.9 \times 10^{-10} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = 9.47$$

Second equivalence point (at 50.00 cm³ of HCl):

As previously explained, at the second equivalence point equilibrium exist is;



For the above equilibrium we can write;

$$K' = \frac{[\text{HCO}_3^-(\text{aq})][\text{H}_3\text{O}^+(\text{aq})]}{[\text{H}_2\text{CO}_3(\text{aq})]} = K_{a_1} = \frac{[\text{H}_3\text{O}^+(\text{aq})]^2}{[\text{H}_2\text{CO}_3(\text{aq})]}$$

(as $[\text{H}_2\text{CO}_3(\text{aq})] = [\text{H}_3\text{O}^+(\text{aq})]$)

To reach the second equivalence point after the first equivalence point another 25.00 cm³ of HCl is needed. Therefore, $[\text{H}_2\text{CO}_3(\text{aq})]$ at the second equivalence point can be calculated as follows.

$$[\text{H}_2\text{CO}_3(\text{aq})] = \frac{0.10 \text{ mol dm}^{-3} \times 25.00 \times 10^{-3} \text{ dm}^3}{75.00 \times 10^{-3} \text{ dm}^3} = 0.03 \text{ mol dm}^{-3}$$

$$[\text{H}_3\text{O}^+(\text{aq})]^2 = K_{a_1} [\text{H}_2\text{CO}_3(\text{aq})]$$

$$[\text{H}_3\text{O}^+(\text{aq})]^2 = 4.3 \times 10^{-7} \text{ mol dm}^{-3} \times 0.03 \text{ mol dm}^{-3} = 1.3 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = 1.14 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = 3.94$$

According to above findings the pH at the first equivalence point is 9.4 and that at the second equivalence point it is ~ 4.0 . Therefore, it is clear that in an experiment, the first equivalence point can be detected by phenolphthalein indicator while methyl orange is suitable to detect the second equivalence point. Figure 2.22 shows the variation of pH during the titration.

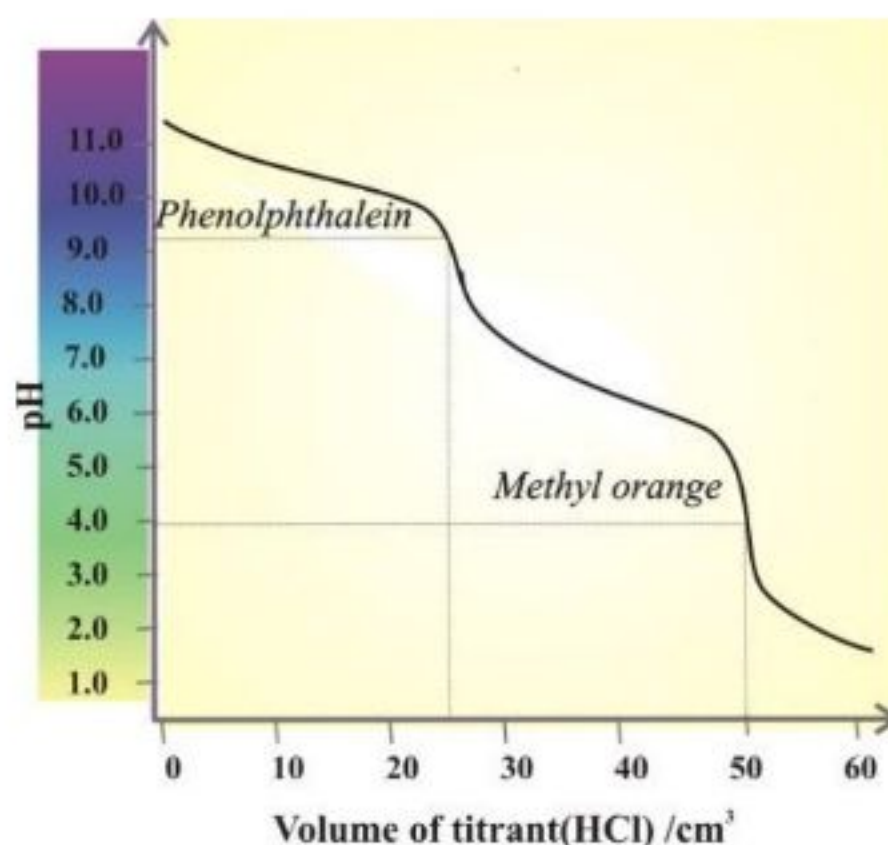


Figure 2.22 Titration curve for the titration of 25.00 cm^3 of $0.100 \text{ mol dm}^{-3} \text{ Na}_2\text{CO}_3$ with $0.100 \text{ mol dm}^{-3} \text{ HCl}$. There are two equivalence points: first is due to the reaction of CO_3^{2-} with HCl to form HCO_3^- and the second one is due to the conversion of HCO_3^- to H_2CO_3 .

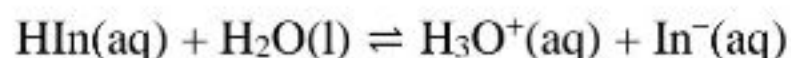
2.2.13 Acid-base indicators

In the previous section, we discussed the equivalence point of a titration of an acid and a base, as the point at which the number of moles of OH^- ions added to a solution is equal to the number of moles of H^+ ions originally present. To determine the equivalence point in a titration, then, we must know exactly what volume of a solution of a base has to be added from a burette to an acid in a flask. One way to achieve this goal is to add a few drops of a foreign substance called an acid-base indicator to the acid solution at the start of the titration.

Finding the end point with an indicator

One interesting group of these indicators is weak acids and bases which are derivatives of organic dyes. Because such compounds have at least one conjugate acid–base species that is highly coloured, their use in a titration results in a change in colour with the change in pH. This change in colour can serve as a useful means for determining the **end point** of a titration, provided that it occurs at the titration's equivalence point. Indicator has distinctly different colours in its non-ionized and ionized forms. These two forms are related to the pH of the solution in which the indicator is dissolved. The pH at which an

acid–base indicator changes colour is determined by its acid dissociation constant. For an indicator that is a monoprotic weak acid, HIn , the following dissociation reaction occurs.



for which the equilibrium constant is,

$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{In}^-(\text{aq})]}{[\text{HIn(aq)}]}$$

Taking the negative log of each side of equation and rearranging to solve for pH gives a familiar equation.

$$\begin{aligned} -\log[\text{H}_3\text{O}^+(\text{aq})] &= -\log K_{\text{In}} + \log \frac{[\text{In}^-(\text{aq})]}{[\text{HIn(aq)}]} \\ \text{pH} &= \text{p}K_{\text{In}} + \log \frac{[\text{In}^-(\text{aq})]}{[\text{HIn(aq)}]} \end{aligned}$$

The two forms of the indicator, HIn and In^- , have different colours. The colour of a solution containing an indicator, therefore, continuously changes as the concentration of HIn decreases and the concentration of In^- increases. If we assume that both HIn and In^- can be detected with equal ease, then the transition between the two colours reaches its midpoint when their concentrations are identical or when the **pH** is equal to the indicator's **pK_{In}**. The equivalence point and the end point coincide, therefore, if an indicator is selected whose **pK_{In}** is equal to the pH at the equivalence point, and the titration is continued until the indicator's colour is exactly halfway between that for HIn and In^- .

Unfortunately, the exact pH at the equivalence point is rarely known. In addition, detecting the point where the concentrations of HIn and In^- are equal may be difficult if the change in colour is subtle. We can establish a range of **pHs** within which we can observe a change in colour of the indicator if we assume that a solution of the indicator is the colour of HIn whenever its concentration is ten times more than that of In^- , and the colour of In^- whenever the concentration of HIn is ten times less than that of In^- .

i.e. If the indicator is in a sufficiently acidic medium, the equilibrium, according to Le Chatelier's principle, shifts to the left and the predominant colour of the indicator is that of the nonionized form (HIn). On the other hand, in a basic medium the equilibrium shifts to the right and the colour of the solution will be due mainly to that of the conjugate base (In^-). Therefore, we can use the following concentration ratios to predict the perceived colour of the indicator:

When,

$$\frac{[\text{HIn(aq)}]}{[\text{In}^-(\text{aq})]} \geq 10$$

$$\text{pH} = \text{p}K_{\text{In}} + \log \frac{1}{10}$$

$$\text{pH} = \text{p}K_{\text{In}} - 1$$

\therefore color of HIn acid predominates

When,

$$\frac{[\text{In}^-(\text{aq})]}{[\text{HIn}(\text{aq})]} \geq 10$$

$$\text{pH} = \text{p}K_{\text{In}} + \log \frac{10}{1}$$

$$\text{pH} = \text{p}K_{\text{In}} + 1$$

color of In^- conjugate base predominates

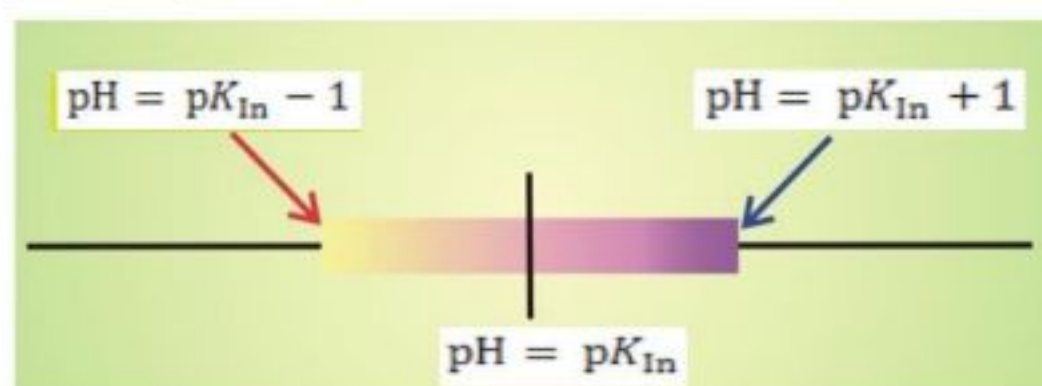
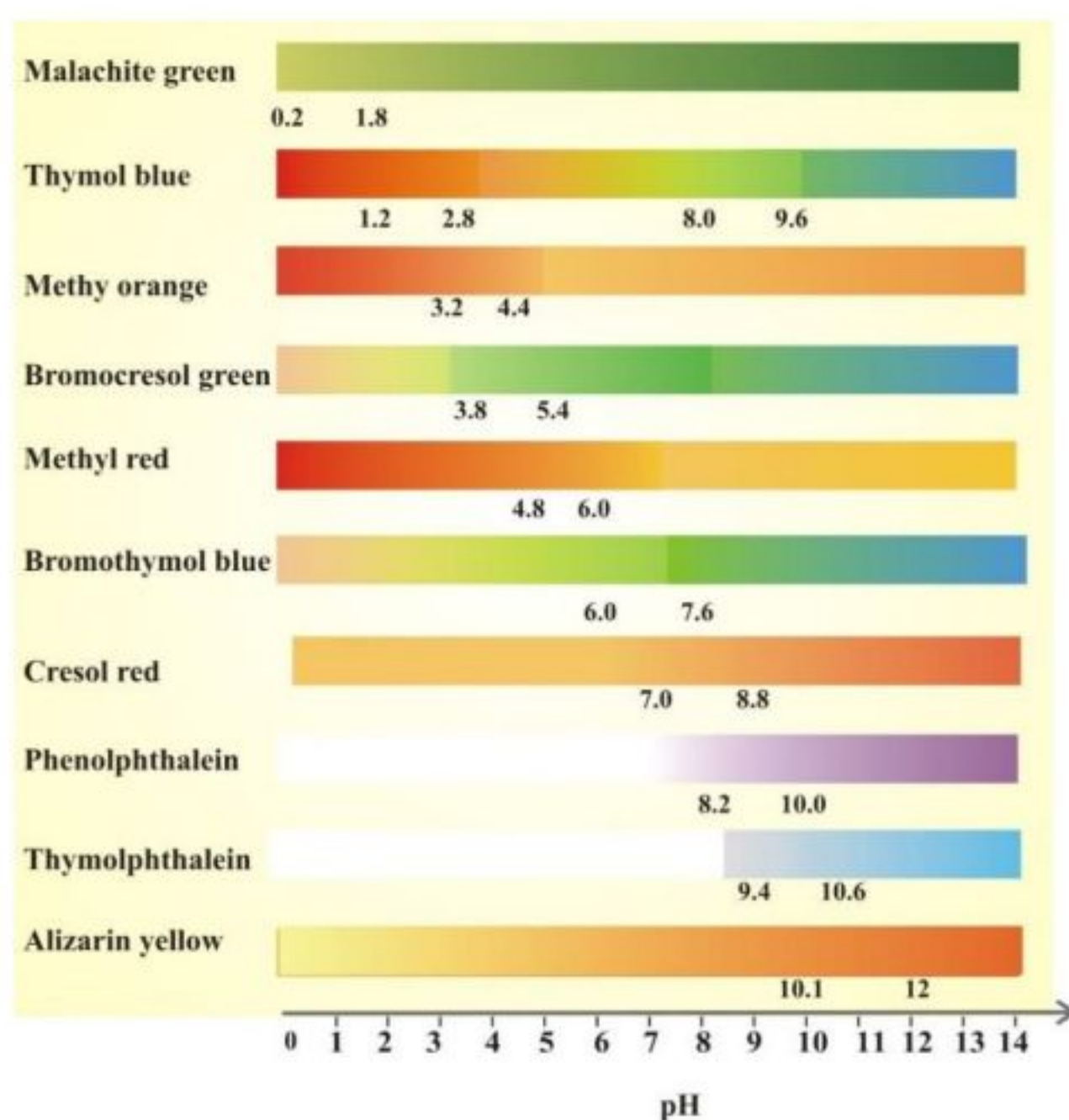


Figure 2.23 Behaviour of an indicator: $\text{HIn}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{In}^-(\text{aq})$

The end point of an indicator does not occur at a specific pH; rather, there is a range of pH within which the end point will occur. In practice, we choose an indicator whose end point lies on the steep part of the titration curve. Because the equivalence point also lies on the steep part of the curve, this choice ensures that the pH at the equivalence point will fall within the range over which the indicator changes colour. For example, phenolphthalein is a suitable indicator for the titration of NaOH and HCl. Phenolphthalein is colourless in acidic and neutral solutions, but reddish pink in basic solutions. Measurements show that at $\text{pH} = 8.3$ the indicator is colourless but that it begins to turn reddish pink when the pH exceeds 8.3. As shown in Figure 2.22, the steepness of the pH curve near the equivalence point means that the addition of a very small quantity of NaOH ($\sim 0.05 \text{ cm}^3$) brings about a large rise in the pH of the solution. What is important, however, is the fact that the steep portion of the pH profile includes the range over which phenolphthalein changes from colourless to reddish pink. Whenever such a correspondence occurs, the indicator can be used to locate the equivalence point of the titration.

Table 2.4 Some common acid-base indicators

Indicator	Colour in acid	Colour in base	pH range	pK _{In}
Thymol blue	Red	Yellow	1.2–2.8	1.7
Bromophenol blue	Yellow	Purple	3.0–4.6	4.1
Methyl orange	Orange	Yellow	3.1–4.4	3.7
Methyl red	Red	Yellow	4.2– 6.3	5.0
Chlorophenol red	Yellow	Red	5.2– 6.8	6.0
Bromothymol blue	Yellow	Blue	6.0 –7.6	7.1
Cresol red	Yellow	Red	7.2– 8.8	8.2
Phenolphthalein	Colorless	Reddish pink	8.3–10.0	9.6

**Figure 2.24** Colour changing pH ranges for some indicators**Selection of an indicator for a titration**

The relatively broad range of pHs over which any indicator changes colour places additional limitations on the feasibility of a titration. To minimize a titration error or to conduct the titration with acceptable high accuracy, an indicator's entire colour transition must lie within the sharp transition in pH occurring near the equivalence point. Thus, in Figure 2.25 (a) we see that phenolphthalein is an appropriate indicator for the titration of 0.1 mol dm^{-3} acetic acid with 0.1 mol dm^{-3} NaOH. Methyl red, on the other hand, is an

inappropriate indicator since its change in colour begins before the initial sharp rise in pH and, as a result, spans a relatively large range of volumes. The early change in color increases the probability of obtaining inaccurate results, and the range of possible end point volumes increases the probability of obtaining imprecise results. Figure 2.25 (b) shows that for a titration of 0.1 mol dm^{-3} HCl acid with 0.1 mol dm^{-3} NaOH i.e. strong acid vs strong base titration, both phenolphthalein and methyl red can be used as the indicator.

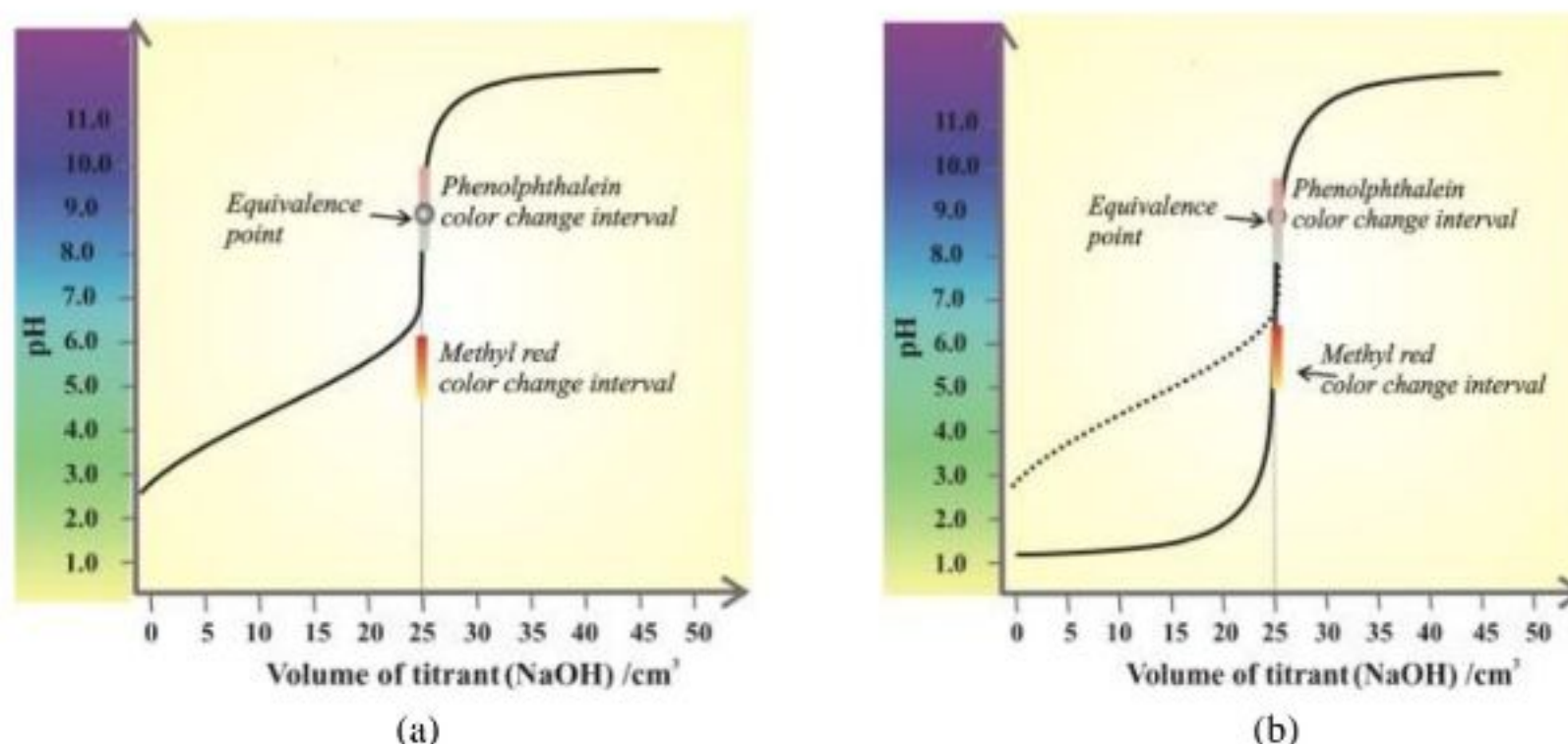


Figure 2.25 Selection of an appropriate indicator for a given titration. In the case of weak acid-strong base titration phenolphthalein is a suitable indicator. Methyl orange indicator has no colour changing pH range in the equivalence point pH changing range as shown in (a). As shown in (b) both the indicators can be used for the titration between a strong acid and a strong base.

2.3 Buffer solutions

From a simple experiment we can observe that adding as little as 0.10 cm^3 of concentrated HCl to a 1.0 dm^3 of H_2O shifts the pH from 7.0 to 3.0. Also the addition of about 0.10 cm^3 of concentrated NaOH to a 1.0 dm^3 of H_2O shifts the pH from 7.0 to 11.0. However, the same addition of either HCl or NaOH to a solution that is 0.10 mol dm^{-3} in both a weak acid and its conjugate weak base, results in only a negligible change in pH. Such solutions are called **buffers**, and their buffering action is a consequence of the relationship between pH and the relative concentrations of the conjugate weak acid/weak base pair.

i.e. A **buffer solution** is a solution of a weak acid or a weak base and its salt. The solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base.

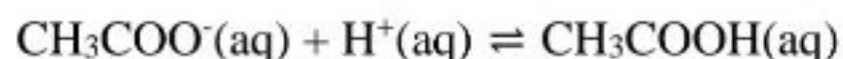
Or

A buffer solution is a solution containing a conjugate weak acid/weak base pair that is resistant to a change in pH when small volumes of a strong acid or a strong base are added.

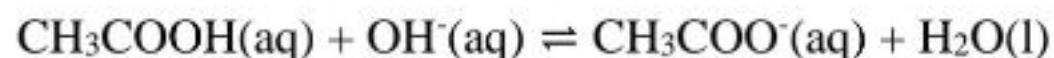
According to above definition, a buffer solution must contain a relatively large concentration of acid to react with any OH^- ions that are added to it, and it must contain a similar concentration of base to react with any added H^+ ions. The acid and the base components of the buffer must not consume each other in a neutralization reaction. These requirements are satisfied by an acid-base conjugate pair, for example, a weak acid and its conjugate base (supplied by a salt) or a weak base and its conjugate acid (supplied by a salt). Buffer solutions of known pH can be prepared from the knowledge of $\text{p}K_{\text{a}}$ of the acid or $\text{p}K_{\text{b}}$ of base and by controlling the ratio of the salt and acid or salt and base. A mixture of acetic acid and sodium acetate acts as buffer solution around pH 4.75 and a mixture of ammonium chloride and ammonium hydroxide act as a buffer around pH 9.25. Let us consider a buffer solution prepared by adding comparable amounts of acetic acid (CH_3COOH) and its salt sodium acetate (CH_3COONa) to water. The equilibrium concentrations of both the acid and the conjugate base (from CH_3COONa) are assumed to be the same as the starting concentrations as the presence of a common ion suppresses the dissociation of a weak acid/base. A solution containing these two substances has the ability to neutralize either added acid or added base. In the solution CH_3COONa , a strong electrolyte, dissociates completely in water:



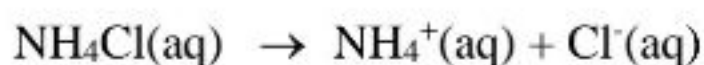
If an acid is added, the H^+ ions will be consumed by the conjugate base in the buffer, CH_3COO^- , according to the equation:



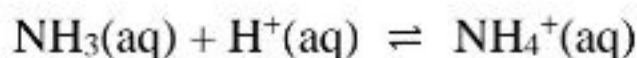
If a base is added to the buffer system, the OH^- ions will be neutralized by the acid in the buffer:



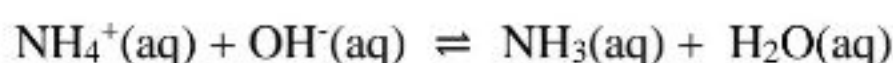
Similarly let us consider a buffer solution prepared by adding comparable amounts of ammonia (NH_3) and its salt ammonium chloride (NH_4Cl) to water. The equilibrium concentrations of both the base and the conjugate acid (from NH_4Cl) are assumed to be the same as the starting concentrations as the presence of a common ion suppresses the dissociation of a weak base NH_3 . A solution containing these two substances has the ability to neutralize either added acid or added base. In the solution NH_4Cl , a strong electrolyte, dissociates completely in water:



If an acid is added, the H^+ ions will be consumed by the base in the buffer, NH_3 , according to the equation:

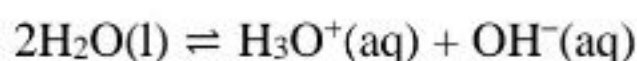
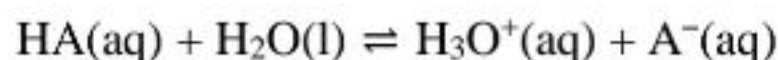
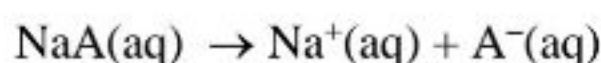


If a base is added, the OH^- ions will be consumed by the conjugate acid in the buffer, NH_4^+ , according to the equation:



Common expression for the pH of buffer solutions

A general buffer equation can be derived by considering the following reactions for a weak acid, HA, and the salt of its conjugate weak base, NaA in an aqueous solution. Following reactions are the reactions involved with the species present in a solution.



Here we can take $[\text{A}^-(\text{aq})]$ as the concentration of $\text{A}^-(\text{aq})$ from NaA and assume that the dissociation of HA is suppressed due to the presence of $\text{A}^-(\text{aq})$ as the common ion. Substituting these terms in the K_a expression of a weak acid we have,

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

We can also neglect the concentrations of H_3O^+ and OH^- from water as these values are much smaller compared to the initial concentrations of HA and NaA. Hence,

$$[\text{H}_3\text{O}^+(\text{aq})] = K_a \frac{[\text{HA}(\text{aq})]}{[\text{A}^-(\text{aq})]}$$

and finally we get the equation,

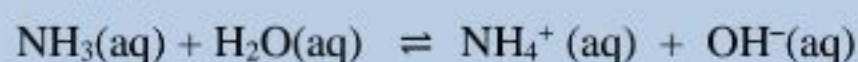
$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{[\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} \\ &\text{or} \\ \text{pH} &= \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]} \end{aligned}$$

i.e. the **Henderson-Hasselbalch equation**.

This Henderson–Hasselbalch equation provides a simple way to calculate the pH of a buffer and to determine the change in pH upon adding a strong acid or strong base.

Example 2.22

How many moles of NH_4Cl are necessary to be added to 1.0 dm^3 of 0.10 mol dm^{-3} NH_3 solution to prepare a buffer solution with pH 9.0. $K_b(\text{NH}_3) = 1.8 \times 10^{-5}$.

Answer

First, we need to estimate the $[\text{NH}_4^+(\text{aq})]$

$$K_b = \frac{[\text{NH}_4^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_3(\text{aq})]} = 1.8 \times 10^{-5}$$

As we know the pH of the solution, $[\text{OH}^-(\text{aq})]$ can be calculated.

$$\text{pOH} = 14 - \text{pH} = 5.0 \text{ and hence } [\text{OH}^-(\text{aq})] = 1.0 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\begin{aligned} [\text{NH}_4^+(\text{aq})] &= K_b \frac{[\text{NH}_3(\text{aq})]}{[\text{OH}^-(\text{aq})]} \\ &= 1.8 \times 10^{-5} \text{ mol dm}^{-3} \times \frac{0.10 \text{ mol dm}^{-3}}{1.0 \times 10^{-5} \text{ mol dm}^{-3}} \\ &= 0.18 \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} \therefore \text{Number of moles of } \text{NH}_4^+ &= 0.18 \text{ mol dm}^{-3} \times 1.0 \text{ dm}^3 \\ &= 0.18 \text{ mol} \end{aligned}$$

Example 2.23

Calculate the pH of a buffer system containing 1.0 mol dm^{-3} CH_3COOH and 2.0 mol dm^{-3} CH_3COONa . What is the pH of the buffer system after the addition of 0.10 mole of HCl to 1.0 dm^3 of the solution? Assume that the volume of the solution does not change when the HCl is added.

$$K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5} \text{ mol dm}^{-3}$$

Answer

Due to the presence of common ion of CH_3COO^- from $\text{CH}_3\text{COONa(aq)}$, we can neglect the ionization of CH_3COOH and hydrolysis of the CH_3COO^- ion. Therefore, $[\text{CH}_3\text{COOH(aq)}] = 1.0 \text{ mol dm}^{-3}$ and $[\text{CH}_3\text{COO}^-(\text{aq})] = 2.0 \text{ mol dm}^{-3}$

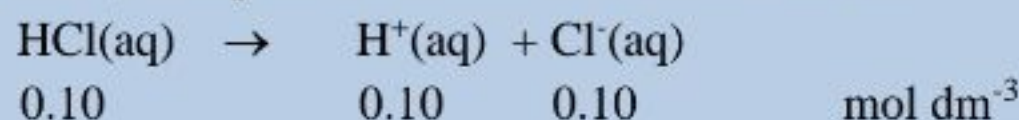
$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH(aq)}]} = 1.8 \times 10^{-5}$$

$$[\text{H}_3\text{O}^+(\text{aq})] = \frac{[1.0]}{[2.0]} \times 1.8 \times 10^{-5}$$

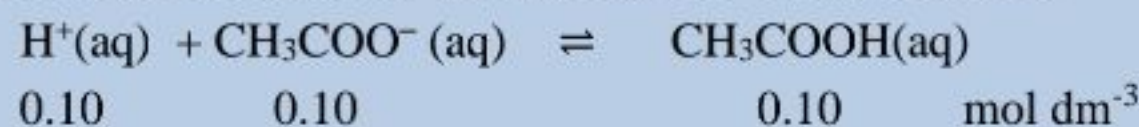
$$[\text{H}_3\text{O}^+(\text{aq})] = 9.0 \times 10^{-6}$$

$$\text{pH} = 5.05$$

After the addition of 0.2 mol of HCl to 1.0 dm^3 of the buffer solution (i.e. $[\text{H}^+(\text{aq})] = 0.10 \text{ mol dm}^{-3}$), complete ionization of HCl acid occurs:



Then the H^+ from HCl is neutralized by the 2.0 mol dm^{-3} CH_3COONa as



(Equilibrium constant for the reaction is very large and therefore we can assume that the reaction goes to completion giving 0.10 mol dm^{-3} of CH_3COOH)

\therefore The number of moles of acetic acid and the number of moles of acetate ions present in 1.0 dm^3 solution are,

$$\text{CH}_3\text{COOH(aq)} = 1.10 \text{ mol} \text{ or } [\text{CH}_3\text{COOH(aq)}] = 1.10 \text{ mol dm}^{-3}$$

$$\text{CH}_3\text{COO}^-(\text{aq}) = 1.90 \text{ mol} \text{ or } [\text{CH}_3\text{COO}^-(\text{aq})] = 1.90 \text{ mol dm}^{-3}$$

Substituting these values in K_a expression,

$$\begin{aligned} [\text{H}_3\text{O}^+(\text{aq})] &= \frac{1.1}{1.9} \times 1.8 \times 10^{-5} \\ [\text{H}_3\text{O}^+(\text{aq})] &= 1.04 \times 10^{-5} \text{ mol dm}^{-3} \\ \text{pH} &= 4.98 \end{aligned}$$

Note: if the initial concentrations of the acid and the salt in the buffer solution are the same, for example, 1.0 mol dm^{-3} , without adding any acid or base, we get

$$\begin{aligned} [\text{H}_3\text{O}^+(\text{aq})] &= \frac{1.0}{1.0} \times 1.8 \times 10^{-5} \\ [\text{H}_3\text{O}^+(\text{aq})] &= 1.8 \times 10^{-5} \\ \text{pH} &= 4.74 \end{aligned}$$

i.e. $\text{pH} = \text{pK}_a$

This can be easily understood by, applying the equation,

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log \frac{[\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]} \\ \text{pH} &= \text{pK}_a + \log \frac{1.0}{1.0} \\ \therefore \text{pH} &= \text{pK}_a \end{aligned}$$

Example 2.24

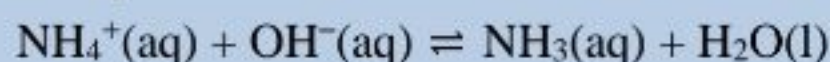
Calculate the pH of a buffer that is $0.020 \text{ mol dm}^{-3}$ in NH_3 and $0.030 \text{ mol dm}^{-3}$ in NH_4Cl . What is the pH after adding 1.00 cm^3 of 0.10 mol dm^{-3} NaOH to 0.10 dm^3 of this buffer? The acid dissociation constant for NH_4^+ is $5.70 \times 10^{-10} \text{ mol dm}^{-3}$

Answer

We can directly use,

$$\begin{aligned} \text{pH} &= \text{pK}_a + \log \frac{[\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]} \\ \text{pH} &= 9.24 + \log \frac{(0.02)}{(0.03)} \\ \text{pH} &= 9.06 \end{aligned}$$

Adding NaOH converts a portion of the NH_4^+ to NH_3 due to the following reaction



Since the equilibrium constant for this reaction is large, we may treat the reaction as if it went to completion. The new concentrations of NH_4^+ and NH_3 are therefore

$$[\text{NH}_4^+(\text{aq})] = \frac{\text{moles of initial } \text{NH}_4^+ - \text{moles of } \text{OH}^- \text{ added}}{\text{total volume}}$$

$$[\text{NH}_4^+(\text{aq})] = \frac{(0.03) \times (0.1) - (0.1) \times (1.0 \times 10^{-3})}{(0.101)} = 0.029 \text{ mol dm}^{-3}$$

and

$$[\text{NH}_3(\text{aq})] = \frac{\text{moles of initial NH}_3 + \text{moles of OH}^- \text{ added}}{\text{total volume}}$$

$$[\text{NH}_3(\text{aq})] = \frac{(0.02) \times (0.1) + (0.1) \times (1.0 \times 10^{-3})}{(0.101)} = 0.021 \text{ mol dm}^{-3}$$

Substituting these in the equation, we get

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3(\text{aq})]}{[\text{NH}_4^+(\text{aq})]}$$

$$\text{pH} = 9.24 + \log \frac{(0.021)}{(0.029)}$$

$$\text{pH} = 9.10$$

From the above examples we can see that the addition of a little amount of acid or base does not affect the pH of the buffer solutions significantly. This nature is explained in Figure 2.26 in which the addition of either an acid or a base to the buffer solutions are compared with the addition of an acid or a base to water and buffer solutions with different concentrations of acid-base pairs. Figure 2.27 also explains the events happening in buffer solutions when an acid or a base is added. Finally, the following can be considered the basic characteristics of buffer solutions.

- (i) Contain relatively large concentrations of a weak acid (base) and its conjugate base (acid).
- (ii) When acid is added, it reacts with the conjugate base.
- (iii) When base is added, it reacts with the conjugate acid.
- (iv) pH is determined by the ratio of the base and acid.

These characteristics are depicted in Figure 2.26 and Figure 2.27.

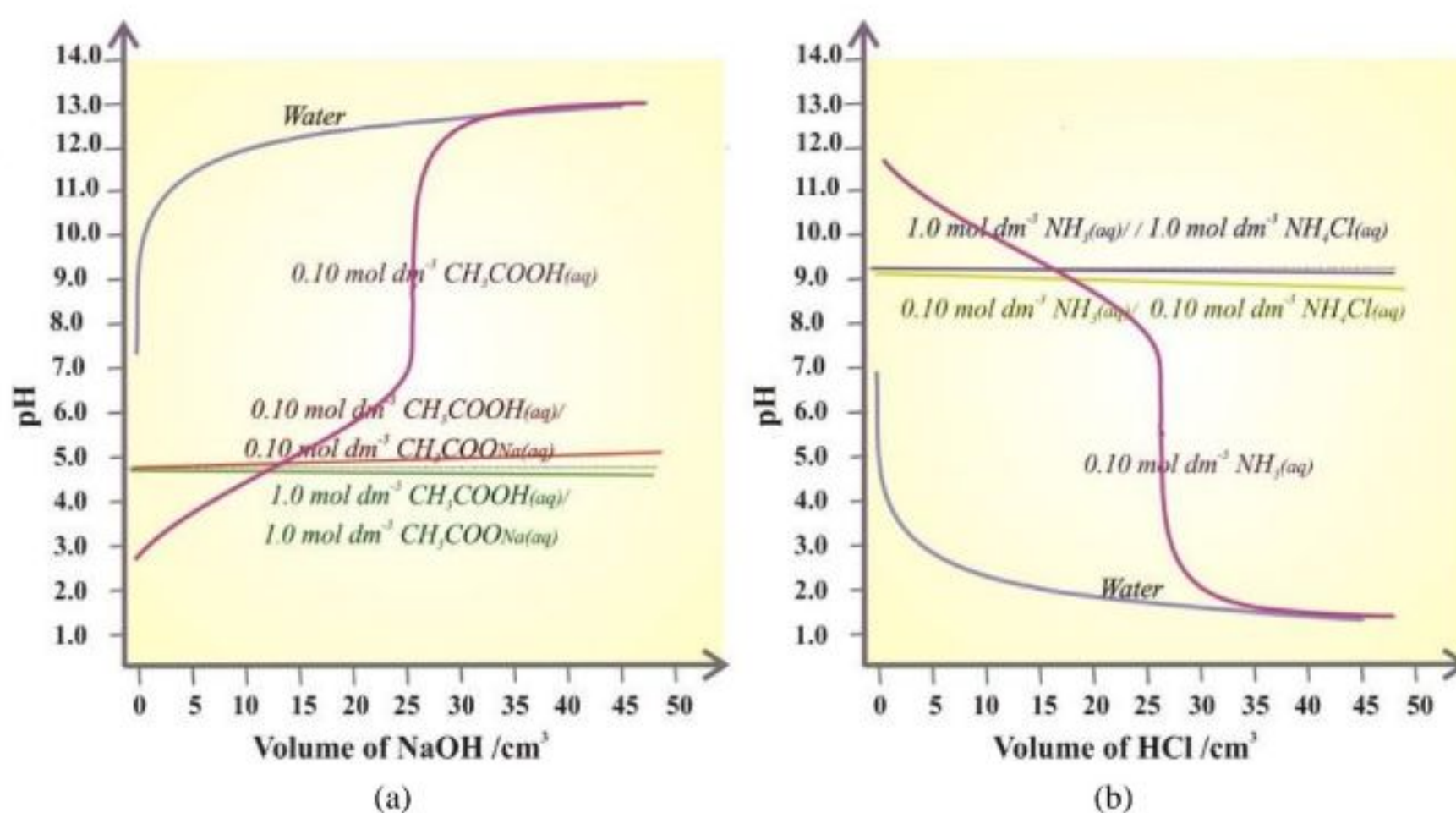


Figure 2.26 Comparison of buffer action for acidic- and basic- buffers is given in (a) and (b) sides respectively. When the strength of the acid and salt (conjugate base) of the buffer is high the variation in pH with the addition of either an acid or a base is minimal. The variation in pH upon the addition of either an acid or a base to water and acid alone (or base alone) are also shown for comparison.

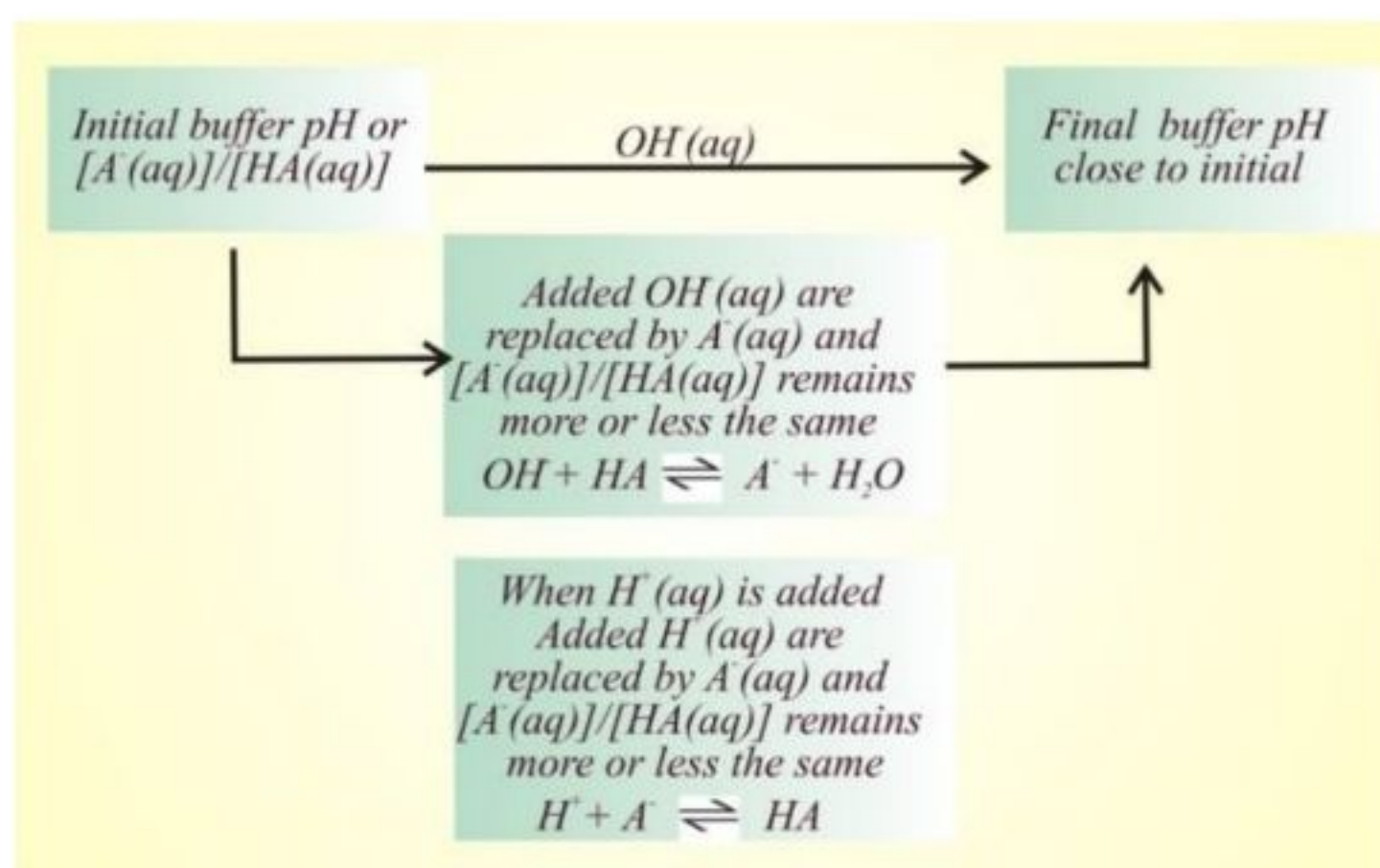


Figure 2.27 Summary of buffer action

For convenience, we will assume that an acid–base buffer exists when the concentration ratio of weak base to weak acid is between 0.1 and 10. Applying the Henderson–Hasselbalch equation:

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{1}{10} = \text{p}K_a - 1 \\ &\text{and} \\ \text{pH} &= \text{p}K_a + \log \frac{10}{1} = \text{p}K_a + 1 \end{aligned}$$

Thus it is seen that acid–base buffer exists within the range of $\text{pH} = \text{p}K_a \pm 1$

2.4 Solubility equilibria

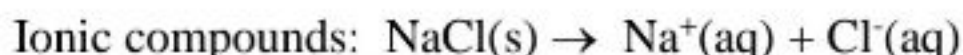
Solubility of ionic solids in water varies a great deal. Some of these (like calcium chloride, sodium chloride) are so soluble that they are hygroscopic in nature and even absorb water vapour from the atmosphere. Others (such as lithium fluoride) have so little solubility that they are commonly termed insoluble. The solubility depends on a number of factors amongst which are the lattice enthalpy of the salt and the solvation enthalpy of the ions in a solution. For a salt to dissolve in a solvent, the strong forces of attraction between its ions (lattice enthalpy) must be overcome by the ion-solvent interactions. The solvation enthalpy of ions is referred to in terms of solvation which is always negative i.e. energy is released in the process of solvation. The amount of solvation enthalpy depends on the nature of the solvent. In case of a non-polar (covalent) solvent, solvation enthalpy is small and hence, not sufficient to overcome lattice enthalpy of the salt. Consequently, the salt does not dissolve in non-polar solvent. As a general rule, for a salt to be able to dissolve in a particular solvent, its solvation enthalpy must be greater than its lattice enthalpy so that the latter may be overcome by the former. With this fact we can start to understand the term solubility in the following way: First see the solubility of ionic salts and then understand the solubility of molecular compounds/ covalent compounds and then see the difference with sparingly soluble salts in a saturated solution.

2.4.1 Ionic and covalent solutions

Solutions are made up of two components, the solute and the solvent. There are many examples for different types of solutions such as solid-solid (metal alloys), solid-liquid (salt-water), liquid-liquid (alcohol-water), liquid-gas (soft drinks like soda water) and gas- gas (air) in which we see that the two components are distributed homogeneously to making the system appear to be in one phase. In this section we mainly deal with the solid-liquid systems where the solvent is water or in other words we deal with “*ionic equilibria*”.

We know that an ionic or covalent solution is a *homogeneous mixture* consisting of one phase when the concentration of the solute is small or the solution is very dilute. In an ionic solution like the salt solution, NaCl is dissolved (or dissociated) in water to produce ions of $\text{Na}^+(\text{aq})$ and $\text{Cl}^-(\text{aq})$ while in a covalent solution, a covalent substance like sugar is

dissolved in water. That is, ionic compounds dissolve by separating into respective ions and covalent substances dissolve as the entire molecule. Therefore, we can simply distinguish these two compounds by the following equations.



This in turn helps us to understand that ionic solutions as electrolytes which show conductivity while covalent or molecular solutions are non-electrolytes which do not show conductivity.

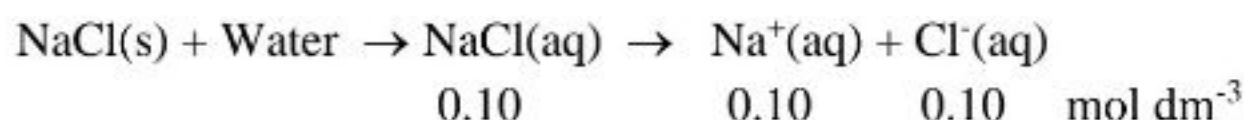
When we consider ionic salts, each salt has its characteristic solubility which depends on the temperature. It is possible to classify salts on the basis of their solubility in the following three categories.

Category I : Soluble - Solubility $> 0.10 \text{ mol dm}^{-3}$

Category II : Slightly soluble - $0.01 \text{ mol dm}^{-3} < \text{Solubility} < 0.10 \text{ mol dm}^{-3}$

Category III : Sparingly soluble - Solubility $< 0.01 \text{ mol dm}^{-3}$

Usually we know that when 0.10 mol of solid NaCl is dissolved in 1.00 dm^3 of water, i.e. the concentration of solution is 0.10 mol dm^{-3} , it produces $0.10 \text{ mol dm}^{-3} \text{Na}^{\text{+}}(\text{aq})$ and $0.10 \text{ mol dm}^{-3} \text{Cl}^{\text{-}}(\text{aq})$ ions showing complete dissociation.



A set of conditions need to be considered to understand the solubility. First, a *saturated* solution is needed in which the maximum amount of solute is dissolved and in the case of sparingly soluble salts some amount of the solid has to remain still.

Under this condition, we can understand that there is a heterogeneous equilibrium in the system as the rate of dissolution equals the rate of precipitation or crystallization - or in other words the system is in dynamic equilibrium. Simply, the following equation explains this situation.



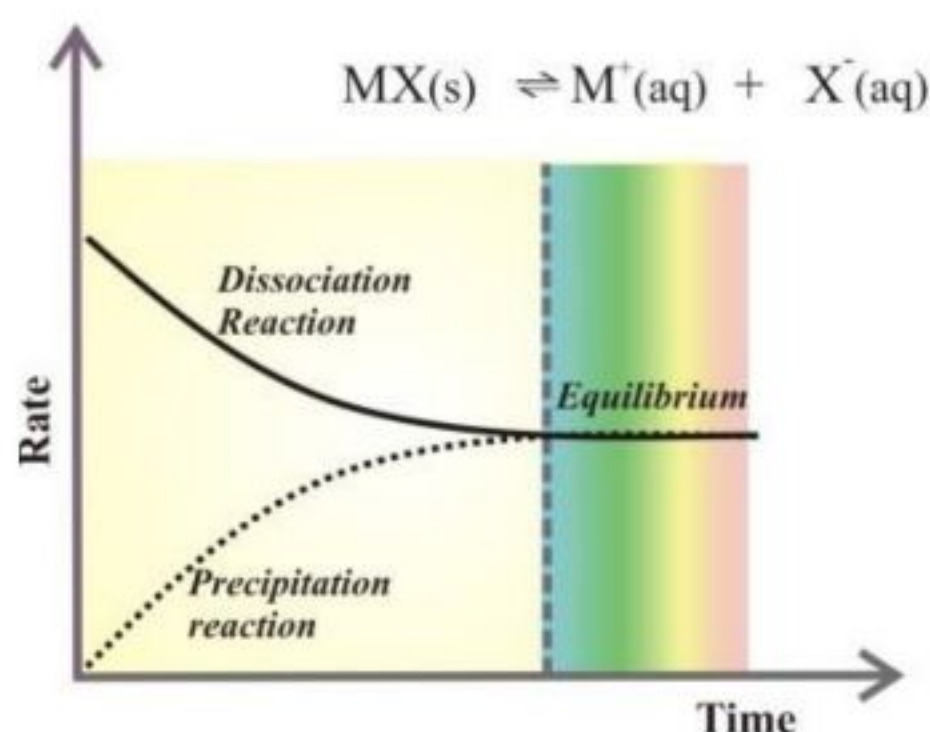


Figure 2.28 In saturated solutions dynamic equilibrium exists between undissolved solids and ionic species in the solution. Hence solid continues to dissolve and ion-pairs continue to form the solid and the rate of dissolution is equal to the rate of precipitation.

Solubility of a substance: **Equilibrium concentration** of a substance in a saturated solution at a given temperature or solubility is a measure of how much of a solute (maximum amount) can dissolve in a solvent at a given temperature. Therefore it is a quantitative value and is expressed mainly as molar solubility (mol dm^{-3}). Other units used to express solubility are g dm^{-3} , g cm^{-3} etc. i.e to find solubility experimentally, it is necessary to find the amount (mass) of solute required to make a known volume of a saturated solution.

Note: There are two ways by which a saturated aqueous solution of a salt MX can be made.

- (i) *Direct method:* Add solid MX salt to water with vigorous stirring until excess MX salt remains on the bottom of the beaker.
- (ii) *Indirect method:* Mix two solutions together, one containing M^+ and the other containing X^- and at a certain point a saturated solution of MX will be formed.

Example 2.25

1.00 dm³ of a saturated AgCl solution was prepared by dissolving 1.8×10^{-3} g of AgCl completely. What is the molar solubility of AgCl? (AgCl : 143.4 g mol⁻¹)

Answer

Amount of moles of AgCl = $1.8 \times 10^{-3} \text{ g} / 143.4 \text{ g mol}^{-1} = 1.26 \times 10^{-5} \text{ mol}$

Since molar solubility is expressed in units of mol dm⁻³:

Molar solubility = $1.26 \times 10^{-5} \text{ mol} / 1.00 \text{ dm}^3 = 1.26 \times 10^{-5} \text{ mol dm}^{-3}$

We can express solubility in other units as $1.8 \times 10^{-3} \text{ g dm}^{-3}$

2.4.2 Solubility product (solubility product constant)

Let us now consider a solid MX in contact with its **saturated** aqueous solution. The equilibrium between the undissolved solid and the ions in a saturated solution is represented by the equation:



The equilibrium constant K is given by the equation:

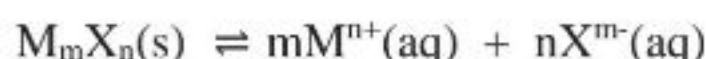
$$K = \frac{[\text{M}^+(\text{aq})][\text{X}^-(\text{aq})]}{[\text{MX(s)}]}$$

For a pure solid substance the concentration remains constant and we can write;

$$K [\text{MX(s)}] = [\text{M}^+(\text{aq})][\text{X}^-(\text{aq})]$$

$$\therefore K_{\text{sp}} = [\text{M}^+(\text{aq})][\text{X}^-(\text{aq})]$$

In general, if we have an equilibrium;



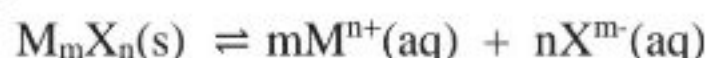
Solubility product,

$$K_{\text{sp}} = [\text{M}^{n+}(\text{aq})]^m [\text{X}^{m-}(\text{aq})]^n$$

K_{sp} is called as the *solubility product constant* or simply the *solubility product* and its expression does not have a denominator because the reactant is a solid. It has to be noted that the solubility product is defined only for saturated solutions. Large values for K_{sp} indicate that the products are favored; therefore, the *larger the value of K_{sp} , the greater the number of ions and hence the greater the solubility of the compound*. Usually, it has no units as we described in equilibrium constant when the concentrations are measured with respect to standard concentration of 1.0 mol dm⁻³. Unless a mention is made about the standard conditions, we include the respective units for the concentrations appearing in

the solubility product expression. The units for solubility products differ depending on the solubility product expression.

In general, if we have an equilibrium;



Solubility product,

$$K_{sp} = [M^{n+}(aq)]^m [X^{m-}(aq)]^n$$

Units:

$$\frac{(\text{mol}^m \text{dm}^{-3m}) (\text{mol}^n \text{dm}^{-3n})}{\text{mol}^{(m+n)} \text{dm}^{-3(m+n)}}$$

Simply for the equilibrium: $MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$

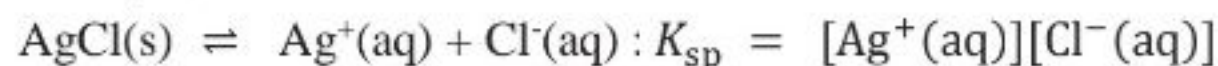
$$K_{sp} = [M^+(aq)][X^-(aq)] \text{ mol}^2 \text{ dm}^{-6}$$

2.4.3 Solubility and solubility product calculations

Calculations involving K_{sp} are simpler than for previous equilibrium calculations because the reactant is a solid and therefore omitted from the equilibrium expression. There are only two types of problems that need to be solved:

- (a) Calculating K_{sp} from solubility data or
- (b) Calculating solubility from K_{sp} .

Consider the example,



$$\text{At } 298 \text{ K, } K_{sp} = 1.60 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

When we consider the above equilibrium, concentrations of the two ions will be equal to the molar solubility of silver chloride. If molar solubility is s , then



At the equilibrium: $s \qquad s \quad \text{mol dm}^{-3}$

$$\text{At } 298 \text{ K, } K_{sp} = 1.60 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6} = s \times s = s^2$$

$$\therefore s = 1.26 \times 10^{-5} \text{ mol dm}^{-3}$$

Thus, at 298 K, molar solubility of silver chloride will be equal to $1.26 \times 10^{-5} \text{ mol dm}^{-3}$.

A solid salt of the general formula



Molar solubility S in equilibrium $mS \qquad nS$

$$K_{sp} = [M^{n+}(aq)]^m [X^{m-}(aq)]^n$$

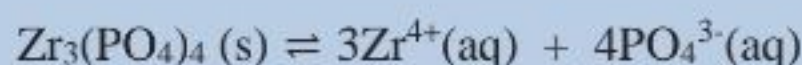
$$K_{sp} = (m s)^m (n s)^n = m^m n^n s^{(m+n)}$$

$$s^{(m+n)} = \frac{K_{sp}}{m^m n^n}$$

$$s = \left[\frac{K_{sp}}{m^m n^n} \right]^{1/(m+n)}$$

Example 2.26

Derive an expression for the solubility (s) of aqueous saturated solution $Zr_3(PO_4)_4(s)$ at 298 K.

Answer

At equilibrium: $3s$ $4s$

$$K_{sp} = [Zr^{4+}(aq)]^3 [PO_4^{3-}(aq)]^4 = (3s)^3 (4s)^4 = 6912 (s)^7$$

$$\therefore s = \left[\frac{K_{sp}}{6912} \right]^{1/7}$$

In this example we can notice that $K_{sp} = [Zr^{4+}(aq)]^3 [PO_4^{3-}(aq)]^4$ has units $(\text{mol dm}^{-3})^7$.

And the units of s is $[(\text{mol dm}^{-3})^7]^{1/7} = \text{mol dm}^{-3}$

That is the units of molar solubility.

Example 2.27

At 298 K, 100.00 cm^3 of a saturated PbI_2 solution was prepared by dissolving $5.60 \times 10^{-2} \text{ g PbI}_2(s)$. Calculate K_{sp} .

Answer

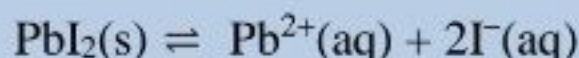
First we need the molar solubility of PbI_2 :

$$\text{Moles of PbI}_2 = 5.60 \times 10^{-2} \text{ g} / 461 \text{ g mol}^{-1} = 1.21 \times 10^{-4} \text{ mol}$$

$$\text{Molar solubility of PbI}_2 = 1.21 \times 10^{-4} \text{ mol} / 0.100 \text{ dm}^3$$

$$= 1.21 \times 10^{-3} \text{ mol dm}^{-3}$$

Next calculate the concentration of the ions and substitute in the K_{sp} expression:



At equilibrium : $[Pb^{2+}(aq)] = 1.21 \times 10^{-3} \text{ mol dm}^{-3}$ and

$$[I^{-}(aq)] = 2 \times 1.21 \times 10^{-3} \text{ mol dm}^{-3} = 2.42 \times 10^{-3} \text{ mol dm}^{-3}$$

$$K_{sp} = [Pb^{2+}(aq)] [I^{-}(aq)]^2$$

$$K_{sp} = (1.21 \times 10^{-3} \text{ mol dm}^{-3}) \times (2.42 \times 10^{-3} \text{ mol dm}^{-3})^2$$

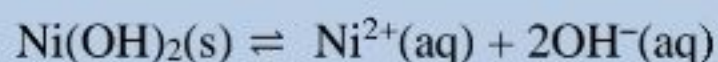
$$K_{sp} = 7.1 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$$

Example 2.28

At 298 K, the values of K_{sp} of two sparingly soluble compounds Ni(OH)_2 and AgCN are $2.0 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$ and $6 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$ respectively. Which salt is more soluble?

Answer

Consider the equilibrium,



If the solubility is x ,

At equilibrium :

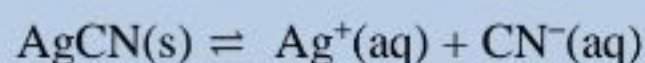
$x \qquad 2x$

$$K_{sp} = [\text{Ni}^{2+}(\text{aq})] [\text{OH}^{-}(\text{aq})]^2 = 4x^3$$

$$4x^3 = 2.0 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$$

$$x = 7.94 \times 10^{-5} \text{ mol dm}^{-3}$$

Similarly,



If the solubility is y ,

At equilibrium :

$y \qquad y$

$$K_{sp} = [\text{Ag}^{+}(\text{aq})] [\text{CN}^{-}(\text{aq})] = y^2$$

$$y^2 = 6 \times 10^{-17} \text{ mol}^2 \text{ dm}^{-6}$$

$$y = 7.8 \times 10^{-9} \text{ mol dm}^{-3}$$

we can notice that; $x > y$

Therefore, $\text{Ni(OH)}_2(\text{s})$ is more soluble than $\text{AgCN}(\text{s})$.

(It is also possible to predict this comparing K_{sp} values; Since $K_{sp} (\text{Ni(OH)}_2(\text{s})) > K_{sp} (\text{AgCN}(\text{s}))$, solubility of $\text{Ni(OH)}_2(\text{s})$ is higher than that of $\text{AgCN}(\text{s})$).

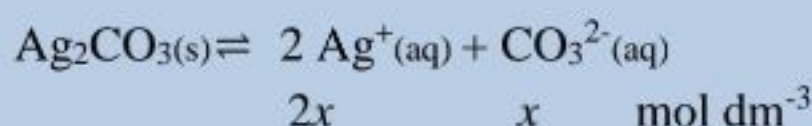
Calculating ion concentrations from K_{sp} **Example 2.29**

Estimate the $[Ag^+(aq)]$ in a saturated solution of Ag_2CO_3 at 298 K.

$$K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$$

Answer

First, consider the equilibrium, and if x is the molar solubility, we can write



At equilibrium:

$$K_{sp} = [Ag^+_{(aq)}]^2 [CO_3^{2-}_{(aq)}]$$

$$= (2x)^2(x) = 4x^3$$

$$\therefore 4x^3 = 8.1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$$

We get

$$x = (8.1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9})^{1/3}$$

$$x = 1.26 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\therefore [Ag^+_{(aq)}] = 2x = 2 \times 1.26 \times 10^{-4} \text{ mol dm}^{-3} = 2.53 \times 10^{-4} \text{ mol dm}^{-3}$$

Example 2.30

Which of the saturated solutions $AgCl$ and Ag_2CO_3 will have a higher $[Ag^+(aq)]$ at 298 K? $K_{sp}(AgCl) = 1.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ and $K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12} \text{ mol}^3 \text{ dm}^{-9}$

Answer

One can note that this problem is similar to the Example 12.29. However, we were asked to estimate $[Ag^+(aq)]$. Also one has to note that we cannot compare the values of K_{sp} as the two constants have different units. Therefore, it is necessary to estimate the $Ag^+_{(aq)}$ concentrations in cases.

	AgCl	Ag ₂ CO ₃
From previous examples:		
$[Ag^+_{(aq)}]$	$1.34 \times 10^{-5} \text{ mol dm}^{-3}$	$2.53 \times 10^{-4} \text{ mol dm}^{-3}$

Now we can see that the saturated Ag_2CO_3 solution has higher $[Ag^+(aq)]$ though the $K_{sp}(Ag_2CO_3) < K_{sp}(AgCl)$.

2.4.4 Predicting the formation of a precipitate

Whenever two solutions containing ions are mixed, there is a possibility that a precipitate may form. If the concentrations of the ions is 0.10 mol dm^{-3} or higher any compound having low solubility will precipitate. However, if the concentrations of the ions is less than 0.10 mol dm^{-3} , a calculation must be performed to predict the formation of the precipitate.

For example, if we mix equal volumes of 0.20 mol dm^{-3} AgNO_3 and NaCl solutions, a precipitate of AgCl(s) will form with NO_3^- and Na^+ ions as spectators. In this case as AgNO_3 and NaCl are strong electrolytes there is a precipitate of AgCl formed with 0.10 mol dm^{-3} concentrations.

However, the situation with very dilute solutions (concentrations $< 0.10 \text{ mol dm}^{-3}$) is different: When two soluble salt solutions are mixed, a cation from one solution is introduced to an anion from another solution, and *vice versa*.

One or both of the new ion combinations (cation and anion) could have low solubility. If this is the case, and there are too many of the low solubility ions present (more than what is necessary for a saturated solution), a precipitate will result.

If there is not enough of the low solubility ions present to reach the saturation concentration, a precipitate will not form and the ions will stay dissolved in solution.

In such situations **Ion-product (IP)** calculation is required to predict the formation of a precipitate.

Ion-product can be calculated for these mixtures to deduce whether a precipitate will form or not when the two solutions are mixed and the following conditions are defined.

*If the **Ion-product** is larger than the actual K_{sp} , the concentration of low solubility ions is greater than saturation, so a precipitate will form.*

*If the **Ion-product** is smaller than the actual K_{sp} , the concentrations of low solubility ions have not yet reached saturation, a precipitate will not form.*

We can summarize the above as;

$IP > K_{sp}$ then precipitate forms

$IP = K_{sp}$ then solution is saturated, no precipitate

$IP < K_{sp}$ then solution is not saturated, no precipitate

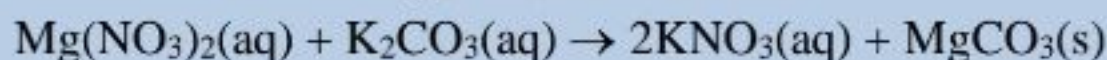
Example 2.31

Will a precipitate form if the solutions 50.00 cm^3 of $5.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ Mg(NO}_3)_2$ and 50.00 cm^3 of $1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ K}_2\text{CO}_3$ are mixed?

$$K_{\text{sp}}(\text{MgCO}_3) = 3.5 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$

Answer

First write the reaction between $\text{Mg(NO}_3)_2$ and K_2CO_3



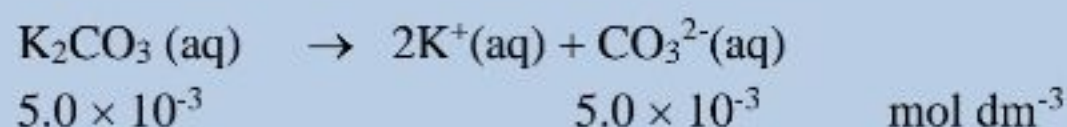
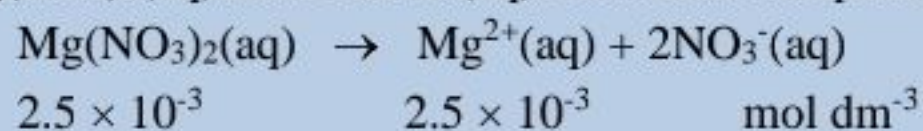
As two solutions are being mixed, dilution occurs.

Therefore the concentrations of the solutions are different when mixed.

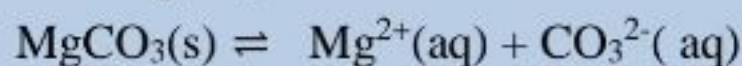
$$\begin{aligned} [\text{Mg(NO}_3)_2(\text{aq})] &= (5.0 \times 10^{-3} \text{ mol dm}^{-3} \times 50 \times 10^{-3} \text{ dm}^3) / 100 \times 10^{-3} \text{ dm}^3 \\ &= 2.5 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} [\text{K}_2\text{CO}_3(\text{aq})] &= (1.0 \times 10^{-2} \text{ mol dm}^{-3} \times 50 \times 10^{-3} \text{ dm}^3) / 100 \times 10^{-3} \text{ dm}^3 \\ &= 5.0 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

As $\text{Mg(NO}_3)_2(\text{aq})$ and $\text{K}_2\text{CO}_3(\text{aq})$ dissociate completely, we can write:



As the precipitate formed is MgCO_3 :



$$K_{\text{sp}} = [\text{Mg}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})]$$

$$\begin{aligned} \text{Ion Product} &= [\text{Mg}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})] = (2.5 \times 10^{-3})(5.0 \times 10^{-3}) \text{ mol}^2 \text{ dm}^{-6} \\ &= 12.5 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

$$IP (12.5 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}) > K_{\text{sp}}(\text{MgCO}_3) (3.5 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6})$$

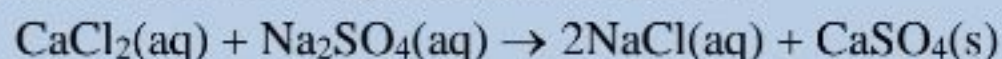
Therefore a precipitate of MgCO_3 will form.

Example 2.32

Will a precipitate form if 50.00 cm^3 of $1.0 \times 10^{-3} \text{ mol dm}^{-3} \text{ CaCl}_2$ solution is added to 50.00 cm^3 of $1.0 \times 10^{-2} \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution? $K_{\text{sp}}(\text{CaSO}_4) = 2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$

Answer

First write the reaction between $\text{Mg}(\text{NO}_3)_2$ and K_2CO_3 .

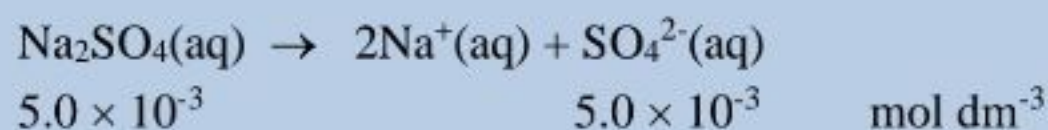
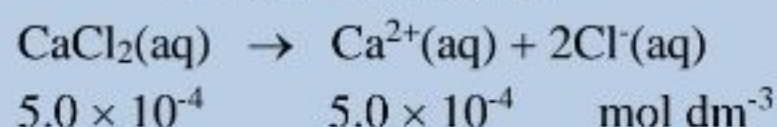


As two solutions are mixed, dilution occurs

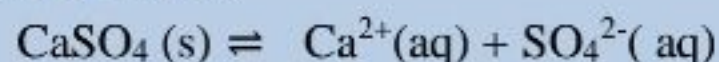
Therefore the concentrations of the solutions are different when mixed.

$$\begin{aligned} [\text{CaCl}_2(\text{aq})] &= (1.0 \times 10^{-3} \text{ mol dm}^{-3} \times 50 \times 10^{-3} \text{ dm}^3) / 100 \times 10^{-3} \text{ dm}^3 \\ &= 5.0 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

$$\begin{aligned} [\text{Na}_2\text{SO}_4(\text{aq})] &= (1.0 \times 10^{-2} \text{ mol dm}^{-3} \times 50 \times 10^{-3} \text{ dm}^3) / 100 \times 10^{-3} \text{ dm}^3 \\ &= 5.0 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$



As the precipitate formed is CaSO_4 :



$$K_{\text{sp}} = [\text{Ca}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})]$$

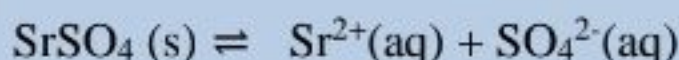
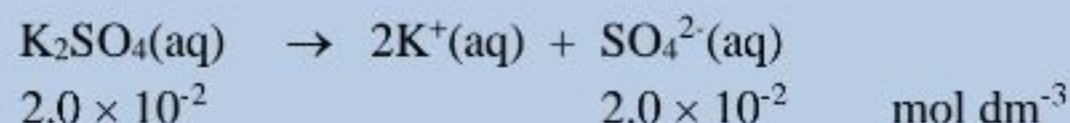
$$\begin{aligned} \text{Ion Product} &= [\text{Ca}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})] = (5.0 \times 10^{-4})(5.0 \times 10^{-3}) \text{ mol}^2 \text{ dm}^{-6} \\ &= 2.5 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6} \end{aligned}$$

$$IP (2.5 \times 10^{-6} \text{ mol}^2 \text{ dm}^{-6}) < K_{\text{sp}}(\text{CaSO}_4) = 2.4 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$

Therefore a precipitate of CaSO_4 will not be formed.

Example 2.33

What is the maximum $[\text{Sr}^{2+}(\text{aq})]$ that can exist in a $0.020 \text{ mol dm}^{-3}$ solution of K_2SO_4 without forming a precipitate of SrSO_4 ? $K_{\text{sp}}(\text{SrSO}_4) = 3.2 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$

Answer

$$K_{\text{sp}} = [\text{Sr}^{2+}(\text{aq})][\text{SO}_4^{2-}(\text{aq})]$$

$$\therefore 3.2 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6} = [\text{Sr}^{2+}(\text{aq})](2.0 \times 10^{-2} \text{ mol dm}^{-3})$$

$$[\text{Sr}^{2+}(\text{aq})] = 1.6 \times 10^{-5} \text{ mol dm}^{-3}$$

Example 2.34

$\text{XA}(\text{s})$ and $\text{YA}(\text{s})$ are two sparingly water soluble salts.

At 298 K, $K_{\text{sp}}(\text{XA}) = 1.80 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$ and $K_{\text{sp}}(\text{YA}) = 1.80 \times 10^{-7} \text{ mol}^2 \text{ dm}^{-6}$.

A completely water soluble salt of NaA is added slowly to a 1.00 dm^3 solution containing 0.100 moles of $\text{X}^+(\text{aq})$ and $\text{Y}^+(\text{aq})$.

- Predict which of the salts precipitates first.
- Calculate also the cation concentration that remains in the solution of the salt that precipitates first when the second salt begins to precipitate.

Answer

(i) For XA

$$K_{\text{sp}} = [\text{X}^+(\text{aq})][\text{A}^-(\text{aq})]$$

$$[\text{A}^-(\text{aq})] = K_{\text{sp}} / [\text{X}^+(\text{aq})] = (1.80 \times 10^{-10} / 0.100) \text{ mol dm}^{-3} = 1.80 \times 10^{-9} \text{ mol dm}^{-3}$$

For YA

$$K_{\text{sp}} = [\text{Y}^+(\text{aq})][\text{A}^-(\text{aq})]$$

$$[\text{A}^-(\text{aq})] = K_{\text{sp}} / [\text{Y}^+(\text{aq})] = (1.80 \times 10^{-7} / 0.100) \text{ mol dm}^{-3} = 1.80 \times 10^{-6} \text{ mol dm}^{-3}$$

$[\text{A}^-(\text{aq})]$ necessary to precipitate XA is less than that needed to precipitate YA.

\therefore XA precipitates first.

(ii) $K_{\text{sp}}(\text{XA}) = [\text{X}^+(\text{aq})][\text{A}^-(\text{aq})]$

at this stage $[\text{A}^-(\text{aq})]$ is the $[\text{A}^-(\text{aq})]$ needed to start precipitation of YA.

$$\begin{aligned} [\text{X}^+(\text{aq})] \text{ left in the solution} &= (1.80 \times 10^{-10} / 1.80 \times 10^{-6}) \text{ mol dm}^{-3} \\ &= 1.0 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

Example 2.35

Consider a solution of $0.10 \text{ mol dm}^{-3} \text{ A}^{2+}(\text{aq})$ and $0.20 \text{ mol dm}^{-3} \text{ B}^{3+}(\text{aq})$.

$$K_{\text{sp}}(\text{AI}_2) = 9.0 \times 10^{-9} \text{ and } K_{\text{sp}}(\text{BI}_3) = 1.6 \times 10^{-18}$$

- What are the minimum concentration of $\text{I}^{-}(\text{aq})$ needed to start precipitation of the $\text{A}^{2+}(\text{aq})$ and $\text{B}^{3+}(\text{aq})$?
- What range of concentrations of $\text{I}^{-}(\text{aq})$ can be used to precipitate only $\text{B}^{3+}(\text{aq})$?

Answer

(i) For AI_2

$$K_{\text{sp}} = [\text{A}^{2+}(\text{aq})] [\text{I}^{-}(\text{aq})]^2$$

$$\begin{aligned} [\text{I}^{-}(\text{aq})] &= \sqrt{\frac{K_{\text{sp}}}{[\text{A}^{2+}(\text{aq})]}} \\ &= \sqrt{\frac{9.0 \times 10^{-9}}{0.10}} \\ &= 3.0 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

For BI_3

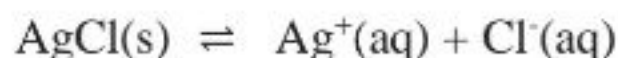
$$K_{\text{sp}} = [\text{B}^{3+}(\text{aq})] [\text{I}^{-}(\text{aq})]^3$$

$$\begin{aligned} [\text{I}^{-}(\text{aq})] &= \sqrt[3]{\frac{K_{\text{sp}}}{[\text{B}^{3+}(\text{aq})]}} \\ &= \sqrt[3]{\frac{1.6 \times 10^{-18}}{0.20}} \\ &= 2.0 \times 10^{-6} \text{ mol dm}^{-3} \end{aligned}$$

(ii) $2.0 \times 10^{-6} \text{ mol dm}^{-3} < [\text{I}^{-}(\text{aq})] < 3.0 \times 10^{-4} \text{ mol dm}^{-3}$

2.4.5 Factors affecting solubility**Common-ion effect**

Consider the following equilibrium in a saturated solution of AgCl at 298 K.



If $[\text{Ag}^{+}(\text{aq})]$ is increased, according to Le Chatelier principle the equilibrium will shift to left to keep the value of equilibrium constant, i. e. K_{sp} constant. This increase of $[\text{Ag}^{+}(\text{aq})]$ can be achieved by adding a soluble salt like AgNO_3 to the initial equilibrium. Because of this shift, more AgCl(s) is produced and hence the solubility of AgCl is decreased. This is called the “**common-ion effect**” because an ion that is already a part of the equilibrium (common to the equilibrium) is being added.

This can be stated as follows too.

*If we cause the equilibrium to **shift to the left** then the rate of crystallization is increased more than the rate of dissolving. More Ag^{+} ions and Cl^{-} ions will combine to form solid AgCl and its **solubility decreases**.*

According to Le Chatelier’s principle, the opposite is also true: if we can cause the equilibrium to shift to the right, then the rate of dissolution is increased more than the rate of crystallization and more solid AgCl will dissolve and its solubility increases.

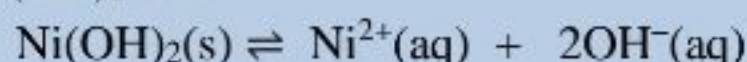
Example 2.36

Calculate the molar solubility of Ni(OH)_2 in $0.10 \text{ mol dm}^{-3} \text{ NaOH}$.

$$K_{\text{sp}}(\text{Ni(OH)}_2) = 2.0 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9}$$

Answer

Let the solubility of Ni(OH)_2 as s .



$$\text{At equilibrium :} \quad \quad \quad s \quad \quad \quad 2s + 0.10$$

$$K_{\text{sp}} = [\text{Ni}^{2+}(\text{aq})] [\text{OH}^{-}(\text{aq})]^2$$

$$= s (2s + 0.10)^2$$

As K_{sp} is small, $(2s \ll 0.10)$

$$\therefore (2s + 0.10) \approx 0.10$$

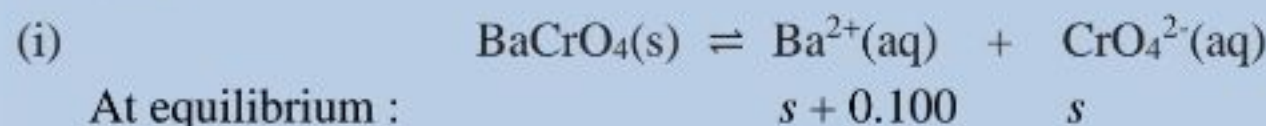
$$2.0 \times 10^{-15} \text{ mol}^3 \text{ dm}^{-9} = s (0.10)^2$$

$$s = 2.0 \times 10^{-13} \text{ mol dm}^{-3}$$

If we do not have a common ion solubility is $7.94 \times 10^{-6} \text{ mol dm}^{-3}$.

Example 2.37

Calculate the molar solubility of BaCrO_4 in (i) $0.100 \text{ mol dm}^{-3}$ and (ii) $1.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ BaCl}_2$ solutions at 298 K. $K_{\text{sp}}(\text{BaCrO}_4) = 1.2 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$.

Answer

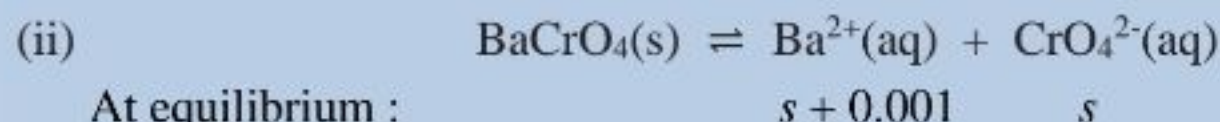
$$K_{\text{sp}} = [\text{Ba}^{2+}(\text{aq})] [\text{CrO}_4^{2-}(\text{aq})] = (s + 0.10) s$$

As K_{sp} is small, $(s \ll 0.100)$

$$\therefore (s + 0.100) \approx 0.100$$

$$1.2 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6} = s (0.100)$$

$$s = 1.2 \times 10^{-9} \text{ mol dm}^{-3}$$



$$K_{\text{sp}} = [\text{Ba}^{2+}(\text{aq})] [\text{CrO}_4^{2-}(\text{aq})] = (s + 0.001) s$$

As K_{sp} is small, $(s \ll 0.001)$

$$\therefore (s + 0.001) \approx 0.001$$

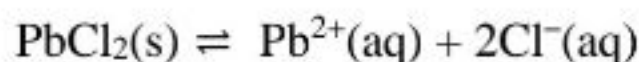
$$1.2 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6} = s (0.001)$$

$$s = 1.2 \times 10^{-7} \text{ mol dm}^{-3}$$

These results indicate that the solubility of $\text{BaCrO}_4(\text{s})$ is comparatively high in dilute solutions of BaCl_2 .

As we know that according to Le Chatelier's principle, if we can cause the equilibrium to shift to the right then the rate of dissolution is increased more than the rate of crystallization.

Consider the following equilibrium:



The solubility of the $\text{PbCl}_2(\text{s})$ can be increased by decreasing either $[\text{Pb}^{2+}(\text{aq})]$ or $[\text{Cl}^{-}(\text{aq})]$.

The $[\text{Pb}^{2+}(\text{aq})]$ can be decreased by adding some ion which precipitates the Pb^{2+} . Any of the following ions: Br^{-} , I^{-} , SO_4^{2-} , S^{2-} , OH^{-} , PO_4^{3-} , CO_3^{2-} , SO_3^{2-} , will precipitate Pb^{2+} . Even though there is a possibility to add any of the above anions, all of them may not decrease the $[\text{Pb}^{2+}(\text{aq})]$.

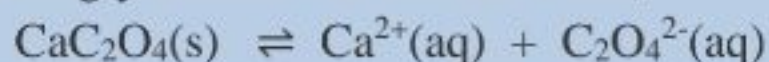
A new precipitate formed must have a lower solubility than that of the PbCl_2 . Therefore, for example, we can choose a soluble salt containing I^{-} ions like KI because K_{sp} of PbI_2 is $1.4 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}$ while K_{sp} of PbCl_2 is $1.8 \times 10^{-5} \text{ mol}^3 \text{ dm}^{-9}$. Similarly, AgNO_3 can be added to decrease the $[\text{Cl}^{-}(\text{aq})]$ which precipitates as AgCl .

Example 2.38

Compare the relative solubility of $\text{CaC}_2\text{O}_4(\text{s})$ in 0.10 mol dm^{-3} solutions of (i) NaOH , (ii) KCl and (iii) $\text{Ca}(\text{NO}_3)_2$

Answer

As $\text{CaC}_2\text{O}_4(\text{s})$ is a sparingly soluble salt we can write,



(i) In $\text{NaOH}(\text{aq})$: $\text{NaOH}(\text{aq}) \rightarrow \text{Na}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq})$

$\text{OH}^{-}(\text{aq})$ will precipitate $\text{Ca}^{2+}(\text{aq})$ as $\text{Ca}(\text{OH})_2(\text{s})$

Thus, $[\text{Ca}^{2+}(\text{aq})]$ decreases, causing a shift to right, so the solubility of $\text{CaC}_2\text{O}_4(\text{s})$ increases.

(ii) In $\text{KCl}(\text{aq})$: $\text{KCl}(\text{aq}) \rightarrow \text{K}^{+}(\text{aq}) + \text{Cl}^{-}(\text{aq})$

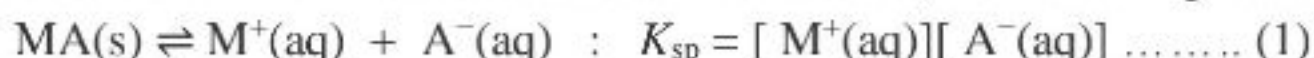
$\text{K}^{+}(\text{aq})$ and $\text{Cl}^{-}(\text{aq})$ will not affect the equilibrium.

(iii) In $\text{Ca}(\text{NO}_3)_2(\text{aq})$: $\text{Ca}(\text{NO}_3)_2(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{NO}_3^{-}(\text{aq})$

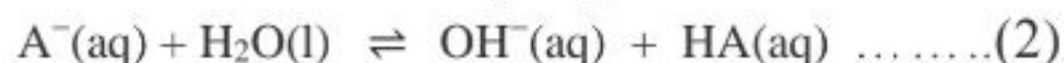
$\text{Ca}^{2+}(\text{aq})$ is a common ion, so $[\text{Ca}^{2+}(\text{aq})]$ increases, causing a shift to left, forming more $\text{CaC}_2\text{O}_4(\text{s})$. Therefore the solubility of CaC_2O_4 decreases.

2.4.6 pH effect

The solubility of many compounds depends strongly on the pH of the solution. For example, the anion in many sparingly soluble salts is the conjugate base of a weak acid that may become protonated in solution. In addition, the solubility of simple binary compounds such as oxides and sulfides, both strong bases, is often dependent on pH. For example consider the effect of pH on the solubility of a salt, MA where A^- is the conjugate base of the weak acid HA. When the salt dissolves in water, the following reaction occurs:

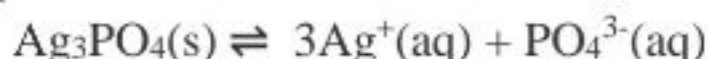


The anion can also react with water in a hydrolysis reaction:

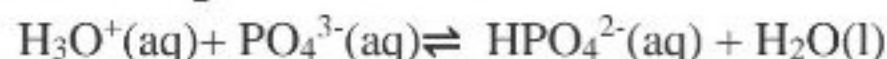


Because of the reaction described above, solubility of salt MA increases as the $A^-(aq)$ produced in (1) is removed by reaction (2). For example predicted solubility of a sparingly soluble salt that has a basic anion such as S^{2-} , PO_4^{3-} , or CO_3^{2-} is increased. If instead a strong acid is added to the solution, the added H^+ will react almost completely with A^- to form HA. This reaction decreases $[A^-(aq)]$, which decreases the magnitude of the ionic product ($IP = [M^+(aq)][A^-(aq)]$). According to Le Chatelier's principle, more MA will dissolve until $IP = K_{sp}$. Hence *an acidic pH dramatically increases the solubility of virtually all sparingly soluble salts whose anion is the conjugate base of a weak acid.*

Consider the following equilibrium:

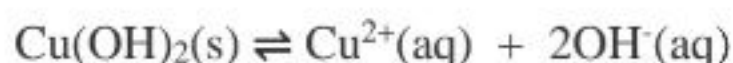


If HNO_3 is added, the following reaction occurs:



This reaction reduces PO_4^{3-} in solution, causing more solid Ag_3PO_4 to dissolve (NO_3^- ions remain in the solution as spectators without participating in any events).

Consider the following equilibrium:



- Increasing the pH means increasing $[OH^-]$ and equilibrium will shift to the left, causing some of $Cu(OH)_2$ to precipitate out or decrease the solubility.
- If the pH is lowered, $[OH^-]$ decreases and equilibrium shifts to the right, causing solid $Cu(OH)_2$ to dissolve or increase the solubility.
- The solubility of compounds of the type $M(OH)_n$ decreases as pH is increased, and increases as pH is decreased.

Thus, insoluble basic salts tend to dissolve in acidic solutions. Similarly, insoluble acidic solutions tend to dissolve in basic solutions.

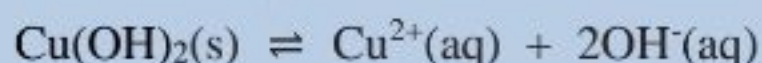
Example 2.39

Calculate the $\text{Cu}^{2+}(\text{aq})$ concentration in a saturated solution of $\text{Cu}(\text{OH})_2$ at 298 K, (i) when $\text{pH} = 10.0$ and (ii) when $\text{pH} = 5.0$. $K_{\text{sp}}(\text{Cu}(\text{OH})_2) = 2.2 \times 10^{-20} \text{ mol}^3 \text{dm}^{-9}$.

Answer

(i) when $\text{pH} = 10.00$

$$[\text{H}^+(\text{aq})] = 1.0 \times 10^{-10} \text{ and } [\text{OH}^-(\text{aq})] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$$



$$\text{At equilibrium:} \quad \quad \quad x \quad \quad \quad 1.0 \times 10^{-4} \text{ mol dm}^{-3}$$

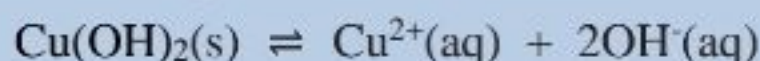
$$K_{\text{sp}} = [\text{Cu}^{2+}(\text{aq})] [\text{OH}^-(\text{aq})]^2 = 2.2 \times 10^{-20} \text{ mol}^3 \text{dm}^{-9}$$

$$x (1.0 \times 10^{-4} \text{ mol dm}^{-3})^2 = 2.2 \times 10^{-20}$$

$$\therefore x = [\text{Cu}^{2+}(\text{aq})] = 2.2 \times 10^{-12} \text{ mol dm}^{-3}$$

(ii) when $\text{pH} = 5.00$

$$[\text{H}^+(\text{aq})] = 1.0 \times 10^{-5} \text{ and } [\text{OH}^-(\text{aq})] = 1.0 \times 10^{-9} \text{ mol dm}^{-3}$$



$$\text{At equilibrium:} \quad \quad \quad x \quad \quad \quad 1.0 \times 10^{-9}$$

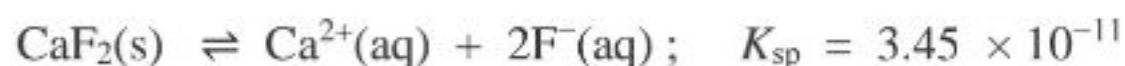
$$K_{\text{sp}} = [\text{Cu}^{2+}(\text{aq})] [\text{OH}^-(\text{aq})]^2 = 2.2 \times 10^{-20}$$

$$x (1.0 \times 10^{-9} \text{ mol dm}^{-3})^2 = 2.2 \times 10^{-20} \text{ mol}^3 \text{dm}^{-9}$$

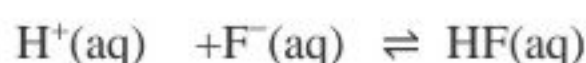
$$\therefore x = [\text{Cu}^{2+}(\text{aq})] = 2.2 \times 10^{-2} \text{ mol dm}^{-3}$$

We can note that decreasing pH increases the solubility of such metal hydroxides.

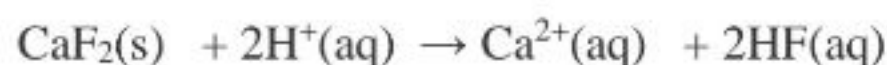
In the above example, the anion $\text{OH}^-(\text{aq})$ is derived from water and thus we could consider the effect of $\text{H}^+(\text{aq})$ in the medium. Such pH-dependent solubility is not restricted to salts that contain anions derived from water (metal hydroxides). For example, CaF_2 is a sparingly soluble salt containing a basic anion: consider the equilibrium below at 298 K.



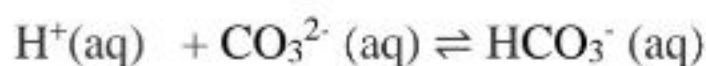
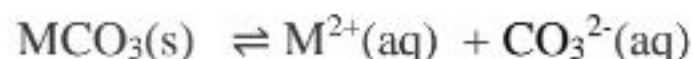
When strong acid is added to a saturated solution of CaF_2 , the following reaction occurs.



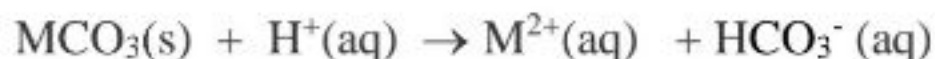
Because the forward reaction decreases the fluoride ion concentration, more CaF_2 dissolves to relieve the stress on the system and the net reaction of CaF_2 with strong acid is thus



In another case of metal carbonates: $\text{MCO}_3(\text{s})$



The overall reaction is thus,



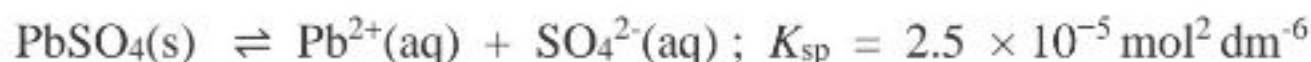
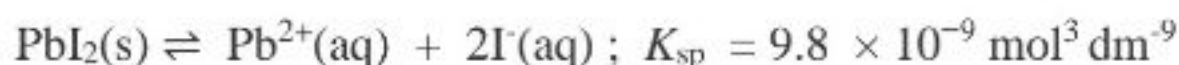
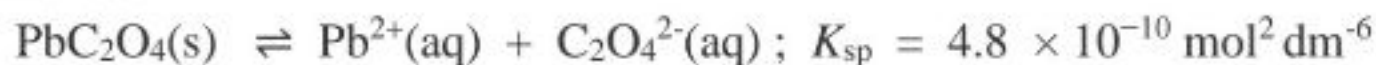
i.e. More $\text{MCO}_3(\text{s})$ dissolves to relieve the stress on the system which means that the increase in pH decreases the solubility while decrease in pH increases the solubility.

From the above, we can note that sparingly soluble salts derived from weak acids such as fluorides, oxalates, carbonates, phosphates, etc. tend to be more soluble in an acidic solution.

Consider the following example.

PbC_2O_4 , PbI_2 and PbSO_4 are sparingly soluble salts with K_{sp} values of $4.8 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$, $9.8 \times 10^{-9} \text{ mol}^3 \text{ dm}^{-9}$ and $2.5 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$, respectively at 298 K. Compare their relative solubilities when a strong acid is added to saturated solutions of them.

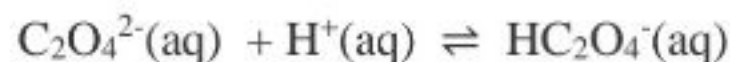
We can write:



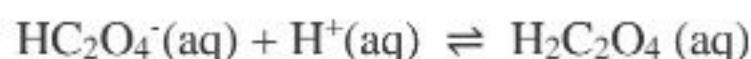
The anions $\text{C}_2\text{O}_4^{2-}$, I^- , and SO_4^{2-} formed in the above equilibria are all conjugate bases of acids $\text{H}_2\text{C}_2\text{O}_4$, HI , and H_2SO_4 . Because the strongest conjugate base will be most affected by the addition of a strong acid, we can then relate the relative solubilities to their relative basicities.

Because HI is a strong acid, we predict that adding a strong acid to a saturated solution of PbI_2 will not greatly affect its solubility; the acid will simply dissociate to form $\text{H}^+(\text{aq})$ and the corresponding anion.

$\text{C}_2\text{O}_4^{2-}(\text{aq})$ has high affinity for one proton and low affinity for a second proton. Therefore, addition of a strong acid to a saturated solution of $\text{PbC}_2\text{O}_4(\text{s})$ will result in the following reactions:

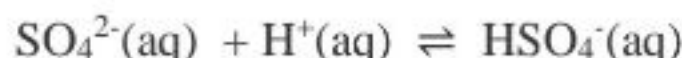


and



These reactions will decrease $[\text{C}_2\text{O}_4^{2-}(\text{aq})]$, causing more lead oxalate to dissolve to relieve the stress on the system.

Adding a strong acid to a saturated solution of PbSO_4 will result in the following reaction.



The $\text{p}K_{\text{a}}$ of $\text{HSO}_4^-(\text{aq})$ (1.99) \ll $\text{p}K_{\text{a}2}$ of oxalic acid, so the reverse reaction in the above equilibrium is largely favored. In other words, basicity of oxalic acid \gggg basicity of sulfuric acid. Therefore, the effect of the strong acid added is significantly less on the solubility of PbSO_4 than on PbC_2O_4 .

From this example we can also note that the solubilities of salts containing anions (such as Cl^- , Br^- , I^-) that do not hydrolyze are unaffected by pH.

Example 2.40

A sample has $3.0 \times 10^{-6} \text{ mol dm}^{-3}$ of $\text{M}^{3+}(\text{aq})$ in an acidic solution. To what pH must the solution be adjusted to begin precipitation of M^{3+} as $\text{M}(\text{OH})_3$?

$$K_{\text{sp}} = 2.4 \times 10^{-20} \text{ mol}^4 \text{ dm}^{-12}$$

Answer

$$K_{\text{sp}} = [\text{M}^{3+}(\text{aq})] [\text{OH}^-(\text{aq})]^3 = 2.4 \times 10^{-20} \text{ mol}^4 \text{ dm}^{-12}$$

$$[\text{OH}^-(\text{aq})] = \sqrt[3]{\frac{2.4 \times 10^{-20}}{3.0 \times 10^{-6}}} = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\therefore \text{pOH} = 4.7$$

$$\text{pH} = 9.3$$

Thus, the solution will not begin to precipitate until enough base is added to adjust the pH to 9.3.

2.4.7 Application of solubility product in qualitative (cation) analysis

It is useful to know how to detect the presence of specific ions in an aqueous solution and the procedure used here comes under *qualitative analysis*, which addresses the question "What is in a sample?" The basis of qualitative analysis is the fact that ions will undergo specific chemical reactions with certain reagents to yield observable products. For example, silver ion can be precipitated with hydrochloric acid to yield insoluble solid silver chloride. Because many cations will not react with hydrochloric acid in this way, this simple reaction can be used to separate ions that form insoluble chlorides from those that do not. In fact, the qualitative detection of ions in a mixture is commonly accomplished by a systematic analysis in which precipitation reactions play a major role.

The various salts of the cations have varying solubilities in water. The differences in solubilities of these salts can be exploited in such a way as to allow for separation of the ions. For example, the addition of an appropriate chemical reagent to an aqueous mixture of cations can selectively cause one or more of the cations to form a precipitate while one or more of the cations will remain dissolved in water.

We know that cations can be separated into five major groups according to the solubilities of their compounds:

Group I (Ag^+ , Pb^{2+} , Hg_2^{2+}) cations produce insoluble chlorides so they can be precipitated with dilute HCl, while all other cations remain in solution.

Group II (Cu^{2+} , Bi^{3+} , Cd^{2+} , Hg^{2+} , As^{3+} , Sb^{3+} , $\text{Sn}^{4+}/\text{Sn}^{2+}$) cations produce very insoluble sulfides (K_{sp} values less than 10^{-25}) so they can be precipitated by low amounts of sulfide ion; this can be achieved by adding H_2S to an acidic solution of metal ions.

Group III (Al^{3+} , Cr^{3+} , Fe^{2+} , Fe^{3+}) cations produce very insoluble hydroxides and they can be precipitated by adding relatively low amount of hydroxyl ions.

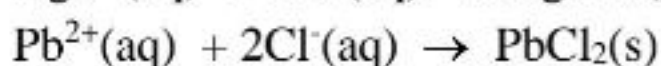
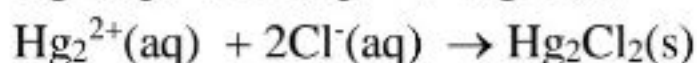
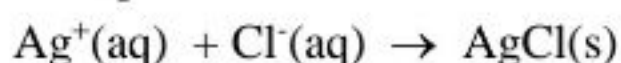
Group IV (Zn^{2+} , Ni^{2+} , Co^{2+} , Mn^{2+}) cations produce slightly soluble sulfides (K_{sp} values more than 10^{-20}) so they can be precipitated by relatively high amounts of sulfide ion; this can be achieved by adding H_2S to a basic solution of metal ions.

Group V (Ca^{2+} , Sr^{2+} , Ba^{2+}) cations, as well as all of the above groups, produce insoluble carbonates so they can be precipitated by the addition of carbonate once the ions of the first four groups have been removed.

(Mg^{2+} , Na^+ , K^+ , NH_4^+) cations do not precipitate with any of the above reagents.

The chemistry of the precipitation of the Group I cations

The precipitating reagent of Group I is a dilute solution of hydrochloric acid (6 M), and the ions precipitated are those of silver, Ag^+ , mercury (I), Hg_2^{2+} , and lead (II), Pb^{2+} . The net ionic equations are:

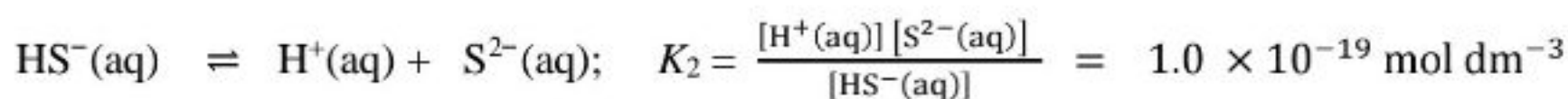
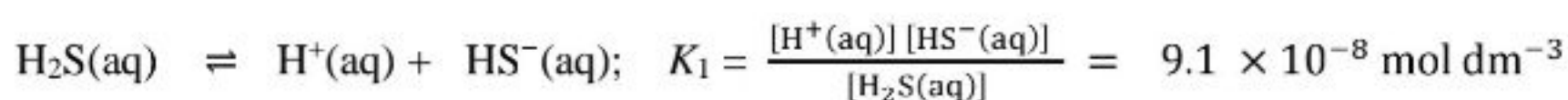
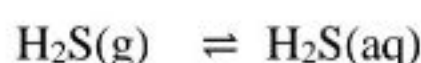


A slight excess of chloride ion is used to reduce the solubility of the precipitates in accordance with the common ion effect. Even so the solubility of lead chloride is sufficiently high for an appreciable concentration of lead ion to remain in solution. Most of this is precipitated with the Group II reagent.

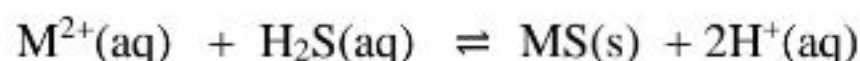
The chemistry of the precipitation of the Group II cations

The ions of Group II (and Group IV) are separated by precipitation as their insoluble sulfides. The sulfide ion is furnished by the weak electrolyte of gaseous hydrogen sulfide, which is only sparingly soluble in water. At 25 °C and 1 atmosphere pressure, a saturated aqueous solution contains about 0.1 mol in a litre). The dissolved molecular hydrogen sulfide dissociates into hydrogen ions, hydrogen sulfide ions, $\text{HS}^-(\text{aq})$, and sulfide ions, $\text{S}^{2-}(\text{aq})$ and we can consider the following equilibria.

Three equilibria are involved:

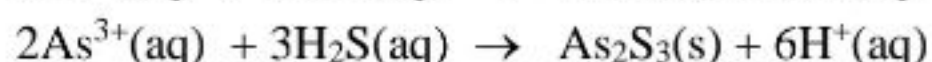
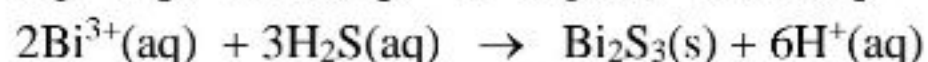
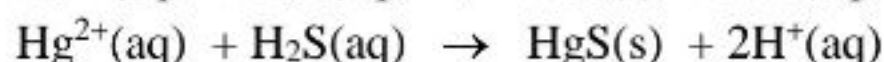


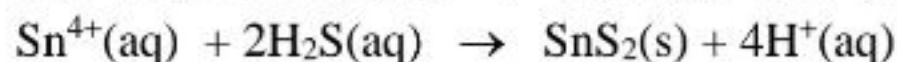
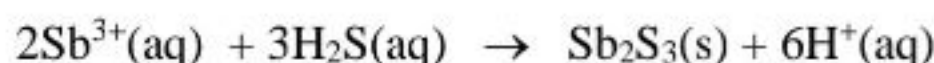
The low value of K_2 suggests that there is very little free S^{2-} in aqueous solutions unless they are extremely basic. Therefore, the precipitation of metal sulfides is best written as:



As with any equilibrium, the extent of reaction depends on the relative concentrations of products and reactants. In this case, making the solution acidic will tend to prevent precipitation of metal sulfides. Adding an acid shifts the above equilibrium to left. As The K_{sp} values of group II metal ions is very low. Therefore sulfides of the metal ions with very low solubility will precipitate from acidic hydrogen sulfide solutions, while sulfides of greater solubility (Group IV) will remain in solution. Controlling the concentration of $\text{H}^+(\text{aq})$, therefore, can be used to separate ions on this basis of differences in the solubility of their sulfides. Group II is often called the acid hydrogen sulfide group in which the hydrogen ion concentration is maintained in the range of 0.1 mol dm^{-3} - 0.3 mol dm^{-3} ($\text{pH} = 0.5 - 1.0$). By this the concentration of sulfide ions is so adjusted that only ionic products of the sulphides of group II exceed their solubility products and, therefore, get precipitated, but not the ions of group IV of which the sulfides are more soluble. These conditions can be achieved by passing $\text{H}_2\text{S}(\text{g})$ into the filtrate from group I separation.

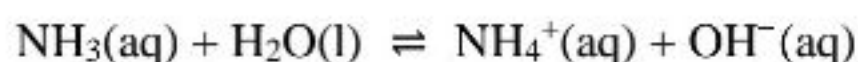
The reactions involved in the precipitation of Group II cations are as follows.





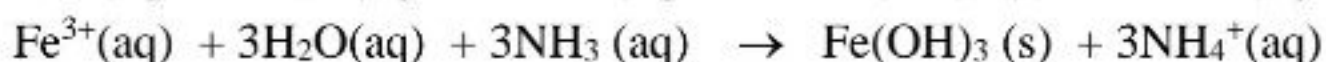
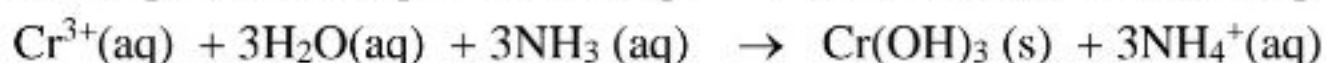
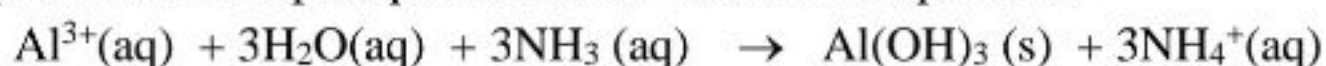
The chemistry of the precipitation of the Group III cations

K_{sp} values of the hydroxides of group III cations are very low and hence they can be precipitated as hydroxide by controlling the concentration of hydroxide ions very low. In this separation care must be taken not to have the solution of hydrogen sulfide too basic. If the concentration of hydroxide ion is sufficiently high, unwanted precipitation of magnesium hydroxide will take place. To achieve a hydroxide ion concentration of the necessary concentration (about $1 \times 10^{-5} \text{ mol dm}^{-3}$) an ammonia-ammonium chloride ($\text{NH}_3 / \text{NH}_4\text{Cl}$) buffer is used. In the ammonia solution the following ionization equilibrium prevails:

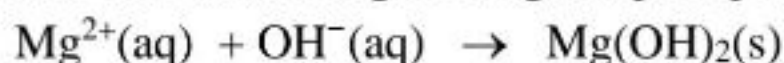


If $0.10 \text{ mol dm}^{-3} \text{ NH}_3$ solution is used, the hydroxide ion concentration will be $1.3 \times 10^{-3} \text{ mol dm}^{-3}$ which is sufficiently high to precipitate magnesium hydroxide. The presence of the added ammonium ion concentration from the ammonium chloride displaces the ammonia equilibrium to the left (common ion effect) reducing the hydroxide ion concentration. A $[\text{OH}^-(\text{aq})]$ of about $1 \times 10^{-5} \text{ mol dm}^{-3}$ is sufficient to precipitate the slightly soluble aluminum and chromium hydroxides but not the more soluble magnesium hydroxide. We can understand this by comparing their K_{sp} values : $K_{\text{sp}}(\text{Al}(\text{OH})_3) = 1.8 \times 10^{-33} \text{ mol}^4 \text{ dm}^{-12}$, $K_{\text{sp}}(\text{Cr}(\text{OH})_3) = 3.0 \times 10^{-29} \text{ mol}^4 \text{ dm}^{-12}$, $K_{\text{sp}}(\text{Fe}(\text{OH})_3) = 1.4 \times 10^{-28} \text{ mol}^4 \text{ dm}^{-12}$ and $K_{\text{sp}}(\text{Mg}(\text{OH})_2) = 1.8 \times 10^{-11} \text{ mol}^3 \text{ dm}^{-9}$.

The equations for the precipitation of the ions of Group III are:



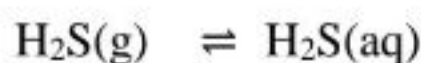
At this stage, if the $[\text{OH}^-(\text{aq})]$ is high enough to precipitate $\text{Mg}(\text{OH})_2$



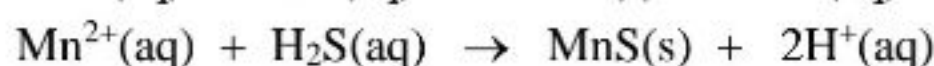
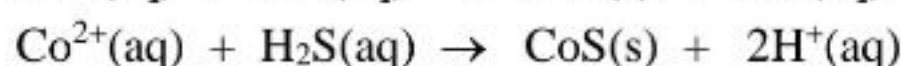
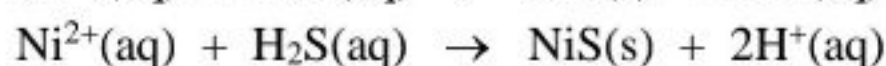
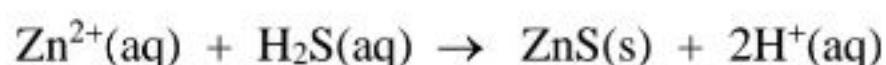
Therefore, control of OH^- concentration is a must in the separation of Al^{3+} , Cr^{3+} and Fe^{3+} without the precipitation of Mg^{2+} ions.

The chemistry of the precipitation of the Group IV cations

The ions of Group IV are precipitated as their sulfides, from a basic solution of hydrogen sulfide. In a basic solution, more of the ionization of H_2S occurs and, thus, concentration of S^{2-} ions increases. It becomes so high that ionic products of the sulphides of group IV exceed their solubility products and they get precipitated.

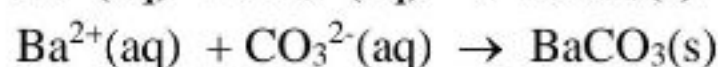
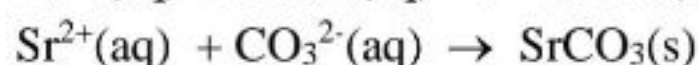
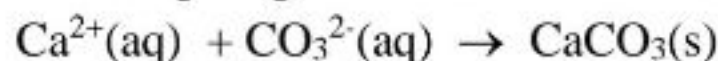


In the presence of $\text{OH}^-(\text{aq})$ ions, the $\text{H}^+(\text{aq})$ ions are neutralized and therefore the solution contains fairly high concentration of $\text{S}^{2-}(\text{aq})$ ions enough to precipitate group IV cations as their sulfides. The sulfides of the ions of group IV are not sufficiently insoluble to be precipitated in the acidic solution of hydrogen sulfide of Group II but will be precipitated by basic solutions of hydrogen sulfide. The equations for the precipitation of the ions of Group IV are:



The chemistry of the precipitation of the Group V cations

The ions of Group V are precipitated as their carbonates in basic solution. This condition is achieved by removing $\text{H}_2\text{S(aq)}$ in filtrate from group IV by boiling and adding $\text{NH}_4\text{Cl}/\text{NH}_4\text{OH}$ in excess. Adding $(\text{NH}_4)_2\text{CO}_3$ solution will enable the precipitation of group V cations. The equations for the precipitation of the ions of Group V are:



The chemistry of the precipitation of the Group VI cations

Magnesium : If only Mg^{2+} ions present in a solution it is easy to identify by simple tests. However, in a mixture of cations, it is difficult to identify and therefore, a specific test with 8-hydroxyquinoline is carried out to identify Mg^{2+} by precipitation which forms a yellow-green precipitate or complex.

Na^+ , K^+ , NH_4^+ cations do not precipitate with any of the above reagents and usually identified by the flame test by the observation of their characteristic colors in the flame.

The following example explains the importance of pH in selective precipitation.

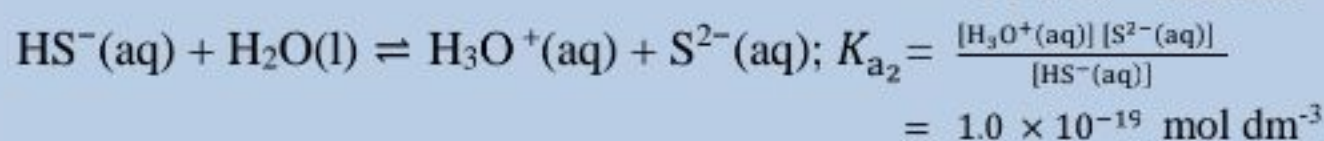
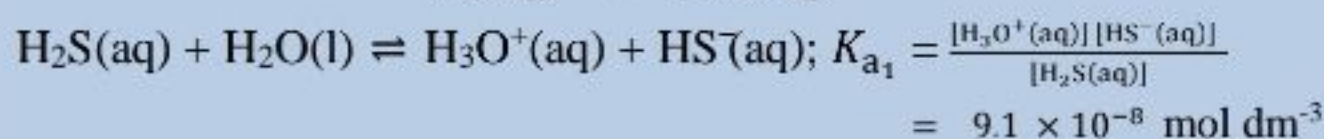
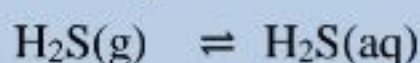
Example 2.41

A solution contains $0.1 \text{ mol dm}^{-3} \text{ Zn}^{2+}$ and $0.1 \text{ mol dm}^{-3} \text{ Fe}^{2+}$ ions. What should be the pH of the solution, if they are to be separated by passing H_2S gas through the solution?

Given that K_{sp} for $\text{ZnS} = 1.6 \times 10^{-24} \text{ mol}^2 \text{ dm}^{-6}$ and K_{sp} for $\text{FeS} = 6.3 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6}$. In a solution $\text{H}_2\text{S(aq)}$ has a concentration of 0.10 mol dm^{-3} .

Answer

When $\text{H}_2\text{S(g)}$ is passed through a solution following equilibria exist.



From these two equations we can write

$$K_{a_1} K_{a_2} [\text{H}_2\text{S(aq)}] = [\text{H}_3\text{O}^+(\text{aq})]^2 [\text{S}^{2-}(\text{aq})]$$

Substituting the given, we get,

$$[\text{H}_3\text{O}^+(\text{aq})]^2 [\text{S}^{2-}(\text{aq})] = (9.1 \times 10^{-8}) (1.0 \times 10^{-19}) (0.1) \text{ mol}^3 \text{ dm}^{-9}$$

$$= 9.1 \times 10^{-28} \text{ mol}^3 \text{ dm}^{-9}$$

From the given data, we have,

$$K_{sp}(\text{ZnS}) = [\text{Zn}^{2+}(\text{aq})][\text{S}^{2-}(\text{aq})] = 1.6 \times 10^{-24} \text{ mol}^2 \text{ dm}^{-6} \text{ and}$$

$$K_{sp}(\text{FeS}) = [\text{Fe}^{2+}(\text{aq})][\text{S}^{2-}(\text{aq})] = 6.3 \times 10^{-18} \text{ mol}^2 \text{ dm}^{-6}$$

In case when $[\text{Zn}^{2+}(\text{aq})] = 0.1 \text{ mol dm}^{-3}$, minimum $[\text{S}^{2-}(\text{aq})]$ required for precipitating ZnS can be calculated as,

$$[\text{S}^{2-}(\text{aq})] = \frac{1.6 \times 10^{-24}}{0.1} = 1.6 \times 10^{-23} \text{ mol dm}^{-3}$$

Corresponding to this minimum concentration of S^{2-} ions we can calculate the maximum H_3O^+ concentration by using the following equation

$$[\text{H}_3\text{O}^+(\text{aq})]^2 [\text{S}^{2-}(\text{aq})] = 9.1 \times 10^{-28} \text{ mol}^3 \text{ dm}^{-9}$$

$$\therefore [\text{H}_3\text{O}^+(\text{aq})]^2 = \frac{9.1 \times 10^{-28}}{1.6 \times 10^{-23}} = 5.7 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6}$$

$$\therefore [\text{H}_3\text{O}^+(\text{aq})] = 7.6 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log[\text{H}_3\text{O}^+(\text{aq})] = 2.1$$

\therefore The minimum pH required for precipitation of ZnS = 2.1

Likewise in case when $[\text{Fe}^{2+}(\text{aq})] = 0.1 \text{ mol dm}^{-3}$

Minimum $[\text{S}^{2-}(\text{aq})]$ required for precipitating FeS is,

$$[\text{S}^{2-}(\text{aq})] = \frac{6.3 \times 10^{-18}}{0.1} = 6.3 \times 10^{-17} \text{ mol dm}^{-3}$$

And the maximum $[\text{H}_3\text{O}^+(\text{aq})]$ required is given by,

$$\therefore [\text{H}_3\text{O}^+(\text{aq})]^2 = \frac{9.1 \times 10^{-28}}{6.3 \times 10^{-17}} = 1.4 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$$

$$\therefore [\text{H}_3\text{O}^+(\text{aq})] = 3.7 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log[\text{H}_3\text{O}^+(\text{aq})] = 5.4$$

Therefore, the minimum pH at which FeS precipitates = 5.4

It is seen that if the H_3O^+ ion concentration is higher than $10^{-5.4} \text{ mol dm}^{-3}$ ($3.7 \times 10^{-6} \text{ mol dm}^{-3}$), Fe^{2+} will not be precipitated whereas Zn^{2+} will get precipitated.

The pH of the solution to separate the two ions should be between 2.1 and 5.4.

2.5 Equilibria in different phases

As we already have an idea that the matter exists in three phases solid, liquid and gas and when the matter undergoes phase changes (transformations) from one phase to another macroscopic properties of the system remain unchanged while microscopic properties change. Usually, phase changes occur when the temperature or pressure of the system is changed and the phase changes are physical changes characterized by changes in molecular order; molecules in the solid phase have the greatest order, and those in the gas phase have the greatest randomness. In this section, we deal with systems having liquid – vapour equilibrium.

Liquid- vapour equilibrium

Molecules in a liquid are not arranged tidily as those in a solid and therefore they have lesser freedom than those of gaseous molecules, though they are in constant motion. Because liquids have higher intermolecular attractions than gases, the collision rate among molecules is much higher in the liquid phase than in the gas phase. The *average* energy of the particles in a liquid is governed by the temperature as shown in Figure 2.29. When the molecules in a liquid have sufficient energy to escape from the surface a phase change occurs. **Evaporation**, or **vapourization**, is the process in which a liquid is transformed into a gas.

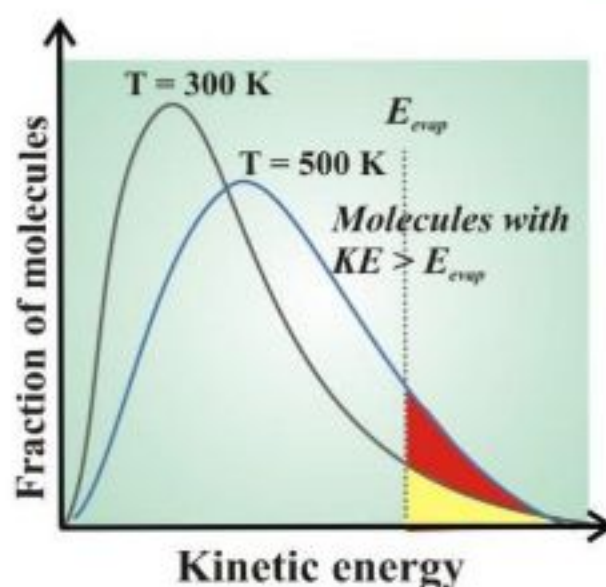


Figure 2.29 The distribution of the kinetic energies of the molecules of a liquid at two temperatures of 300 K and 400 K. Increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_{evap} can escape from the liquid to enter the vapour phase, and the proportion of molecules with $KE > E_{\text{evap}}$ is greater at the higher temperature.

For example, when we consider a liquid (water or alcohol) in an open container, at any given instant a small fraction of the molecules in the liquid phase will be moving quite fast. If one of these is close to the surface and is travelling upward, it can escape from the attraction with its fellow molecules entirely and pass into the gas phase. As the higher energy molecules depart, the average energy of the molecules in the liquid decreases and the temperature of the liquid falls due to the absorption of energy in the form of heat by the surroundings, an effect which you can feel if you let water or alcohol to evaporate from your skin. Absorption of heat maintains the average molecular speed in the liquid, so that, given enough time, all the liquid can evaporate. *The heat absorbed during the entire process corresponds to the enthalpy of vapourization.* The evaporation only takes place on the surface of the liquid. If we look at water which is just evaporating in the sun, we don't see any bubbles. Water molecules are simply breaking away from the surface layer and the process is different from boiling where we observe bubbling. This is illustrated in Figure 2.30.

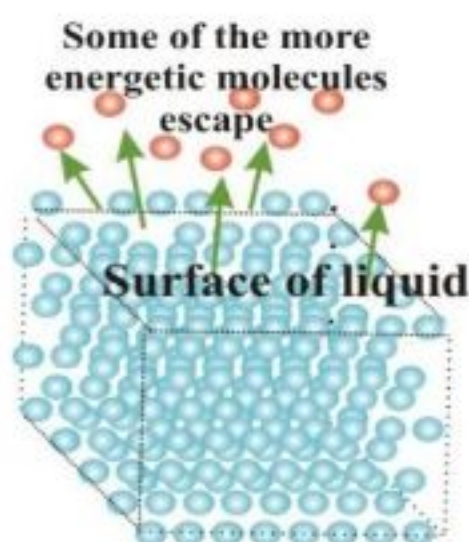


Figure 2.30 Pattern of evaporation of a liquid in an open container at a given temperature. Most of the molecules with high energy that escape into the vapour phase will not collide with the surface of the liquid again and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container.

2.5.1 Evaporation of a liquid in a closed container

If the liquid is in a closed container, at the first look it doesn't seem to evaporate and also it doesn't disappear over time. But there is constant evaporation from the surface. Particles continue to break away from the surface of the liquid but this time they are trapped in the space above the liquid.

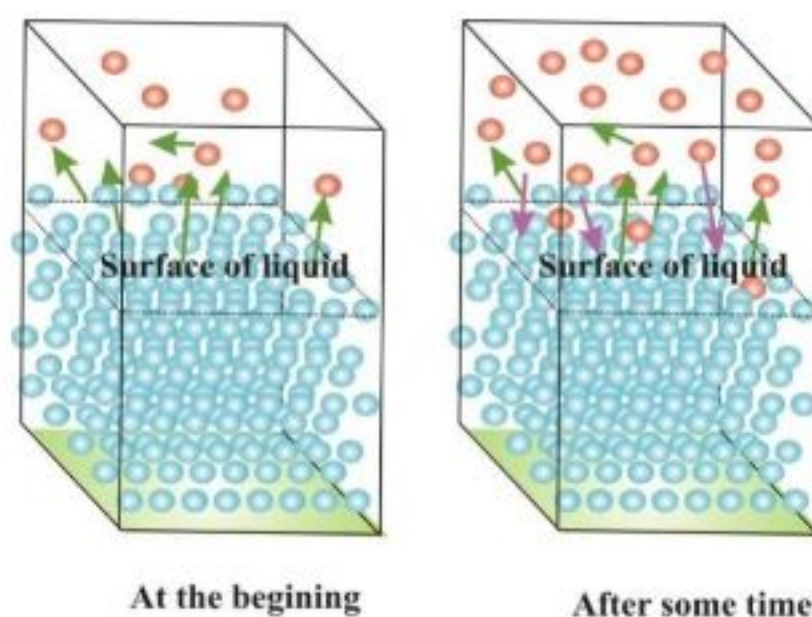


Figure 2.31 Macroscopic view of the molecular interpretation of vapour pressure. When a liquid is placed in a closed container at a given temperature, few molecules start to evaporate at the beginning and none of them can come back and re-enter into the liquid. After some time the density of the molecules in the vapour phase becomes high and some of the molecules start to condense.

On the microscopic level, though molecules are still escaping from the liquid surface into the vapour above, the vapour remains inside the container. Molecules of the vapour behave like any other gas: they bounce around colliding with each other and the walls of the container and hence producing a pressure above the liquid surface. In this case one of these “walls” is the surface of the liquid. Once a molecule collides with the liquid surface there is a tendency that the molecule will re-enter into the liquid.

When the liquid is first introduced into the container, there are very few molecules of vapour and the rate of recapture/ condensation will be quite low, but as more and more molecules evaporate, the chances of a recapture will become proportionately larger. Eventually the vapour pressure will be attained, and the rate of recapture will exactly balance the rate of escape. There will then be no net evaporation of liquid or condensation of gas. i.e. the amount of vapour remains the same only because molecules are reentering the liquid just as fast as they are escaping from it.

Once the vapour-liquid system has attained this state, the macroscopic properties such as the amount, the volume, the pressure, the temperature, the density, etc., of both liquid and gas will all remain constant with time and therefore the system has attained an *equilibrium*. As there is no change in the macroscopic level of the system, the two opposing microscopic processes of *vaporization* and *condensation* occur with equal rates.

Since both microscopic processes are still in operation, the system is in **dynamic equilibrium**. When these particles hit the walls of the container, they exert a pressure. *The pressure exerted by a vapour in dynamic equilibrium with a liquid is defined as the **equilibrium vapor pressure** of the liquid (sometimes called the **saturated vapour pressure** of the liquid).* This process is shown in Figure 2.32 where we have to note that the evaporation rate is constant over the time and the rate of condensation increases with time and reaches the equilibrium.

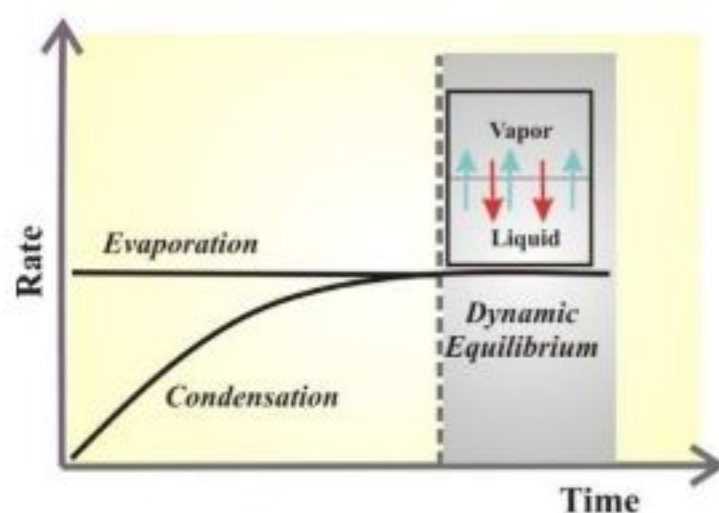


Figure 2.32 Variation of the rates of evaporation and condensation over the time for a liquid in a closed container at a given temperature. Rate of evaporations remains a constant while the rate of condensation increases as the number of molecules in the vapour phase increases till the two rates become equal. At this point the system reaches a state of dynamic equilibrium having the equilibrium vapour pressure of the liquid at a constant temperature.

The magnitude of the vapour pressure of a liquid depends mainly on two factors: the strength of the forces holding the molecules together and the temperature. It is easy to see that if the intermolecular forces are weak, the vapour pressure will be high and vice versa. Weak intermolecular forces will permit molecules to escape relatively easily from the liquid. The rate at which molecules escape will thus be high. Quite a large concentration of molecules will have to build up in the gas phase before the rate of re-entry can balance the escape rate. Consequently the vapour pressure will be large.

2.5.2 Measuring the equilibrium (saturated) vapour pressure

The equilibrium vapour pressure can be measured with a simple mercury - barometer as described below. At the atmosphere pressure the height of the mercury column will be 760 mm. [100 kPa = 760 mmHg ("millimetres of mercury")]. This is illustrated in Figure 2.33 (a). When a few drops of liquid is added into the tube, it will rise to form a thin layer floating on top of the mercury. Some of the liquid will vapourize and the equilibrium is attained. At this point some liquid will remain on top of the mercury. The vapour pressure of the liquid forces the mercury level down a bit. The drop in the mercury level gives a value for the saturated vapour pressure of the liquid at this temperature.

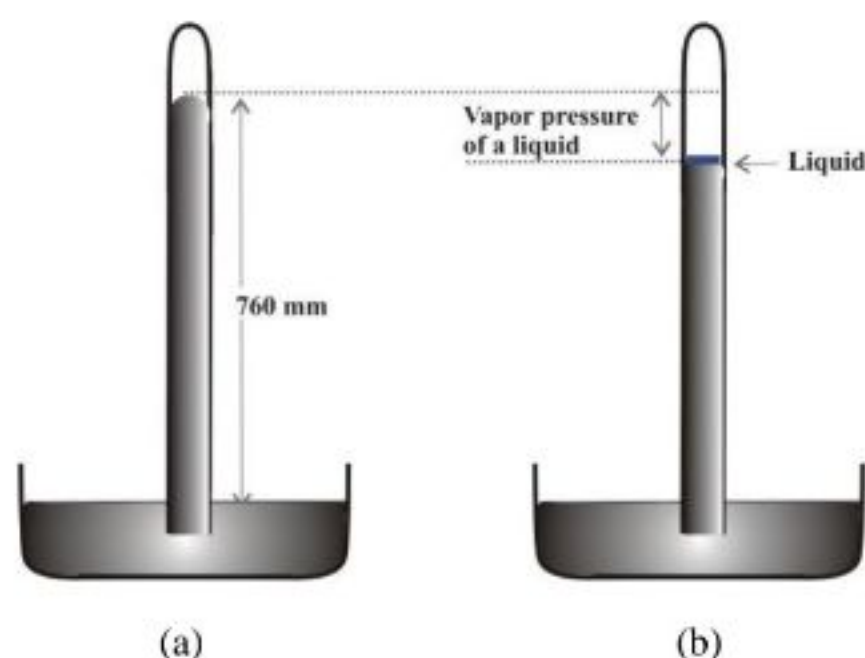


Figure 2.33 Measuring the saturated vapour pressure. (a) when a mercury barometer is just in air, the reading is 760 mmHg. (b) when a liquid is introduced into the tube, it goes on to the top of the mercury in a barometer and the level of Hg falls down. The difference is the saturated vapour pressure of the liquid.

2.5.3 The variation of saturated vapour pressure with temperature

Increase in the temperature increases the average energy of the molecules present. That means, more of them are likely to have enough energy to escape from the surface of the liquid. That will tend to increase the saturated vapour pressure.

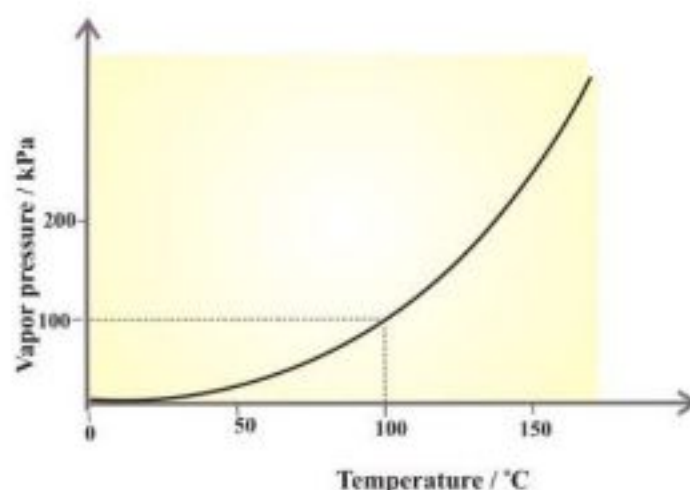


Figure 2.34 Variation of the saturated vapour pressure of water with temperature.

For example, any size sample of water held at 25 °C will produce a vapour pressure of 23.8 mmHg (3.168 kPa) in any closed container, provided all the water does not evaporate.

If a liquid is in an *open* container, however, most of the molecules that escape into the vapour phase will *not* collide with the surface of the liquid and return to the liquid phase. Instead, they will diffuse through the gas phase away from the container, and the equilibrium will never be established. Under these conditions, the liquid will continue to evaporate until it “disappears”. The speed with which this occurs depends on the vapour pressure of the liquid and the temperature. Volatile liquids have relatively high vapour pressures and tend to evaporate readily; nonvolatile liquids have low vapor pressures and

evaporate slowly. As a general guideline, we consider that substances with vapour pressures greater than that of water (3.168 kPa) are relatively volatile, whereas those with vapour pressures less than that of water are relatively nonvolatile. Thus diethyl ether, acetone, and gasoline are volatile, but mercury, ethylene glycol, etc. are non-volatile. The equilibrium vapour pressure of a substance at a particular temperature is a characteristic of the material, like its molecular mass, melting point, and boiling point. It does *not* depend on the amount of liquid as long as at least a tiny amount of liquid is present in equilibrium with the vapor. The equilibrium vapour pressure does, however, depend very strongly on the temperature and the intermolecular forces present, as shown for several substances in Figure 2.35. Molecules that can have hydrogen bonds, such as ethylene glycol, have a much lower equilibrium vapour pressure than those that cannot make hydrogen bonds, such as octane. The non-linear increase in vapour pressure with increasing temperature is *much* steeper than the increase in pressure expected for an ideal gas over the corresponding temperature range. This is mainly due to the dependence of vapour pressure on the fraction of molecules that have a kinetic energy greater than that needed to escape from the liquid phase, and this fraction increases exponentially with temperature.

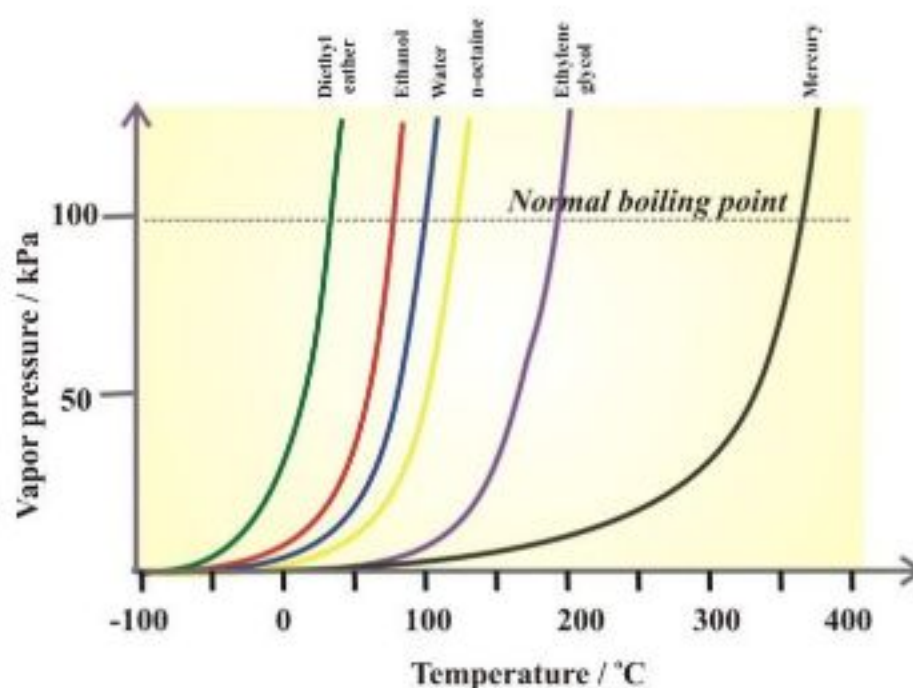


Figure 2.35 The vapour pressures of several liquids as a function of temperature. The point at which the vapour pressure curve crosses the $P = 100$ kPa line (dotted) is the normal boiling point of the liquid.

2.5.4 Boiling point

As the temperature of a liquid increases, the vapour pressure of the liquid increases until it equals the external pressure, or the atmospheric pressure in the case of an open container. Bubbles of vapour begin to form throughout the liquid, and the liquid begins to boil. The temperature at which a liquid boils at exactly 100 kPa (1 atm) pressure is the **normal boiling point** of the liquid. For water, the normal boiling point is exactly 100 °C at the sea level. The normal boiling points of the other liquids in Figure 2.35 are represented by the points at which the vapour pressure curves cross the line corresponding to a pressure of 1 atm.

Although we usually cite the normal boiling point of a liquid, the *actual* boiling point depends on the pressure. At a pressure greater than 100 kPa (1 atm), water boils at a temperature greater than 100 °C because the increased pressure forces vapour molecules above the surface to condense. Hence the molecules must have greater kinetic energy to escape from the surface. Conversely, at pressures less than 100 kPa (1 atm), water boils below 100 °C. Typical variations in atmospheric pressure at sea level are relatively small, causing only minor changes in the boiling point of water. At high altitudes, on the other hand, the dependence of the boiling point of water on pressure becomes significant. At an elevation of Mount Everest, for example, the boiling point of water is about 70 °C. However, in the case of pressure cookers, which have a seal that allows the pressure inside them to exceed 100 kPa (upto around 200 kPa /2 atm), are used to cook food more rapidly by raising the boiling point of water to around 120 °C and thus the temperature at which the food is being cooked.

As pressure increases, the boiling point of a liquid increases and vice versa. Volatile substances have low boiling points and relatively weak intermolecular interactions; non-volatile substances have high boiling points and relatively strong intermolecular interactions.

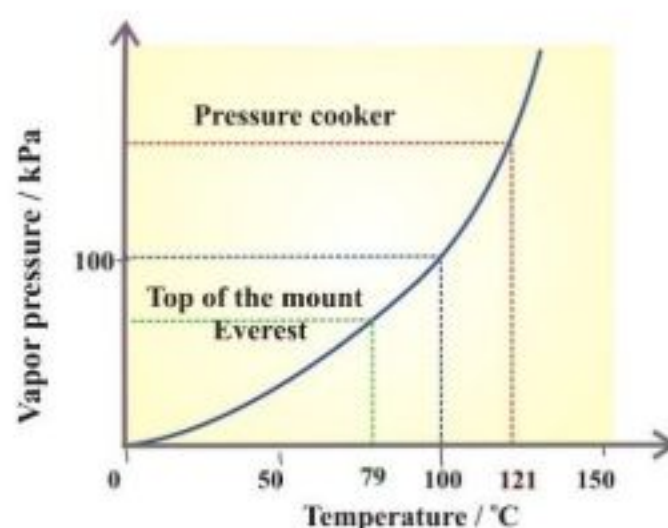


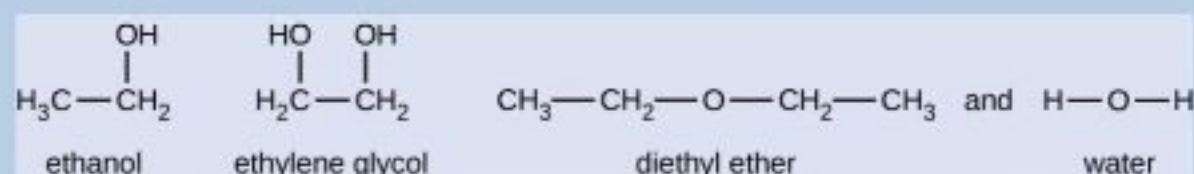
Figure 2.36 Change in boiling point of water with the pressure: water boils at normal boiling point of 100 °C at atmospheric pressure of 100 kPa, boiling of water occurs at around 79 °C at mountain top and the boiling temperature increases to around 121 °C when it boils inside a pressure cooker.

Example 2.42

Compare the variation in relative vapour pressures of ethanol, ethylene glycol, diethyl ether and water at 100 kPa pressure and room temperature.

Answer

First, we have to know the structures of these compounds and we have,



Diethyl ether: is the largest, however, it has a very small dipole and its intermolecular attractions are London forces. As a result, its molecules most readily escape from the liquid. It also has the highest vapour pressure.

Ethanol: Due to its smaller size, ethanol exhibits weaker dispersion forces than diethyl ether. It has a capability to form hydrogen bonds. Therefore it exhibits stronger overall intermolecular forces, which means that fewer molecules escape from the liquid at any given temperature, so ethanol has a lower vapour pressure than diethyl ether.

Water: is much smaller than either of the previous substances and exhibits weaker dispersion forces, but its extensive hydrogen bonding provides stronger intermolecular attractions, fewer molecules escaping the liquid, and a lower vapour pressure than in either diethyl ether or ethanol.

Ethylene glycol: has two $-\text{OH}$ groups like water and therefore, it exhibits extensive hydrogen bonding. It is much larger than water and thus experiences larger London forces. Its overall intermolecular forces are the largest of these four substances, which means its vapourization rate will be the slowest and, consequently, its vapour pressure being the lowest.

Therefore, the variation in vapour pressure is in the order,
diethyl ether > ethanol > water > ethylene glycol

Example 2.43

At 20 °C, the vapour pressures of methanol, ethanol, propanol and butanol are 12.0 kPa, 6.0 kPa, 2.7 kPa and 0.60 kPa, respectively. Explain this variation.

Answer

All of these are alcohols and exhibit hydrogen bonding. As the size of molecule increases from methanol to butanol, dispersion forces increase, which means that the vapor pressures decrease as observed.

$$P_{\text{methanol}} > P_{\text{ethanol}} > P_{\text{propanol}} > P_{\text{butanol}}$$

2.5.5 Enthalpy of vapourization

Vapourization is an endothermic process. This can be understood with a simple phenomenon of our own. When water on the skin evaporates, it removes heat from the body and causes to feel cold. The energy change associated with the vapourization process is the enthalpy of vapourization, ΔH_{vap} . For example, the vapourization of water at standard temperature is represented by:



As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

**Example 2.44**

At normal body temperature, how much heat is required when 1.5 dm³ of water (as sweat) is evaporated from the body? $\Delta H_{\text{vap}} = 43.46 \text{ kJ mol}^{-1}$ at 37 °C.

Answer

Weight of 1.5 dm³ of water = $1.5 \text{ dm}^3 \times 1000 \text{ g dm}^{-3} = 1.5 \times 10^3 \text{ g}$

\therefore Amount of moles of water evaporated = $1.5 \times 10^3 \text{ g} / (18 \text{ g mol}^{-1}) = 83.333 \text{ mol}$

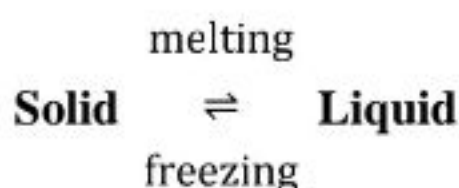
\therefore Heat required = $43.46 \text{ kJ mol}^{-1} \times 83.333 \text{ mol} = 3621 \text{ kJ}$

In the sequel other phase changes of a single component system are also described as they are essential in understanding the behaviour of them in the light of getting knowledge of energy/ enthalpy changes during such events in chemical processes.

Melting and Freezing

When a crystalline solid is heated, the average energy of its atoms is increased and molecules or ions and the solid get some kinetic energy. At some point, when the added energy/ heat becomes large enough to partially overcome the forces holding the molecules or ions together, the solid starts the process of transition to the liquid state, or melting. At this point, despite the continuous heating the temperature remains constant until the entire solid is melted. After all of the solid has melted the temperature of the liquid then increases if the heating is continued.

For example, if we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container, the solid and liquid phases remain in equilibrium. This can be observed experimentally when a mixture of ice and water is kept in a thermos flask and we can observe that the mixture of solid ice and liquid water remains for hours. At this point the mixture of solid and liquid is at equilibrium and the reciprocal processes of melting of ice and freezing of water occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the *melting point of the solid or the freezing point of the liquid*. This equilibrium is expressed as:



The amount of heat required to change one mole of a substance from the solid state to the liquid state is the *enthalpy of fusion*, ΔH_{fus} of the substance. The enthalpy of fusion (melting) of ice is 6.0 kJ mol^{-1} at 0°C and is an endothermic process:



The opposite process, freezing, is an exothermic process whose enthalpy change is -6.0 kJ mol^{-1} at 0°C :



The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the repeating units present in the crystal. Molecules with weak attractive forces form crystals with low melting points while crystals consisting of particles with stronger attractive forces melt at higher temperatures.

Sublimation and deposition

Some solids can undergo transition directly into the gaseous state, bypassing the liquid state, via a process known as *sublimation*. For example, at room temperature and standard pressure, a piece of dry ice (solid CO_2) used in fire extinguishers sublimates (disappears) without ever forming any liquid. Snow and ice sublime at temperatures below the melting

point of water. When solid iodine is warmed, the solid sublimes and a vivid purple vapor forms. The reverse of sublimation is called *deposition*, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.

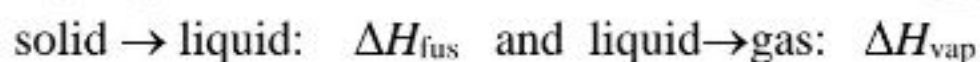
Like vapourization, the sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub} , is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:



Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:



Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vapourization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vapourization for which Hess Law can be applied.



Therefore by applying Hess's law we can write,



Viewed in this manner, the enthalpy of sublimation for a substance may be approximated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 2.37.

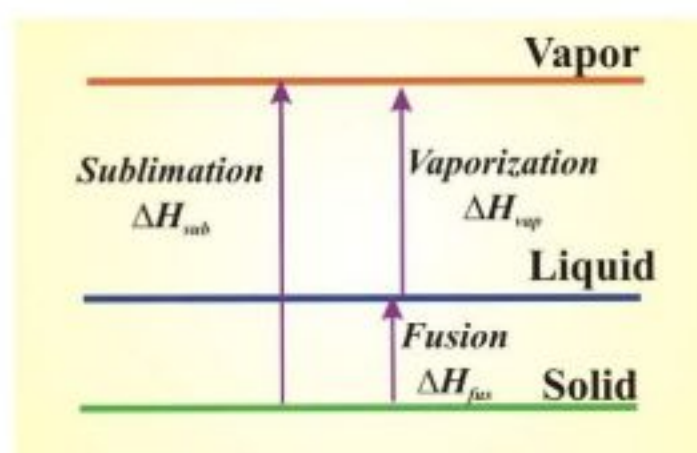


Figure 2.37 For a given substance, the sum of its enthalpy of fusion and enthalpy of vapourization is approximately equal to its enthalpy of sublimation.

The processes of phase transitions described above can be experimentally observed by constructing either heating or cooling curves. When a substance for example ice ($\text{H}_2\text{O}(\text{s})$)

being heated or cooled reaches a temperature corresponding to one of its phase transitions (melting/fusion) and further heating results in vapourization. The heating curve of this process is depicted in the Figure 2.38.

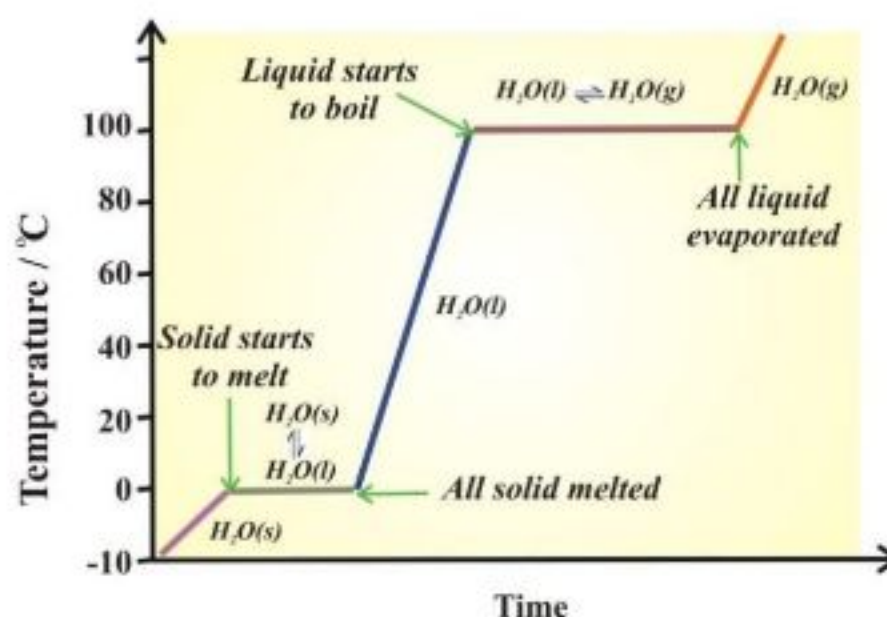


Figure 2.38 A typical heating curve for water depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the water undergoes phase transitions. Longer plateau for the equilibrium of $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ compared to that of $\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$ is due to $\Delta H_{\text{fus}} < \Delta H_{\text{vap}}$.

Example 2.45

How much heat is required to convert 180 g of ice at -15°C into liquid water at 0°C ?

Answer

First, 180 g (10 moles) of ice at -15°C has to be converted into ice at 0°C . The heat required for this can be calculated by using $q_1 = ms(\Delta t)$, where, s is the specific heat capacity of ice: $2.09 \text{ J g}^{-1}^\circ\text{C}^{-1}$

$$\therefore q_1 = ms(\Delta t) = 180 \text{ g} \times 2.09 \text{ J g}^{-1}^\circ\text{C}^{-1} \times 15^\circ\text{C} = 5643 \text{ J} = 5.6 \text{ kJ}$$

Then, the heat needed to induce a phase change of ice to liquid water is a given $q_2 = n \times \Delta H_{\text{fus}}$.

$$\therefore q_2 = 10 \text{ mol} \times 6.0 \text{ kJ mol}^{-1} = 60 \text{ kJ}$$

$$\therefore \text{Total heat required} = q_1 + q_2 = 65.6 \text{ kJ}$$

2.5.6 Phase diagrams of pure substances

As we know, a phase is simply a physical state of a substance present under given conditions such as at a given temperature and pressure. That is, a phase is another meaning for solid, liquid or gas. If we consider some ice floating in water, there are two phases of a solid present and a liquid. If there is air above the mixture, then that is another phase.

We can further understand this by considering the system where oil floats on water. This consists two phases of liquids, oil and water. If the oil and water are contained in a beaker, then beaker is yet another phase. From this we can recognise the presence of the different phases and they are separated by a boundary between them.

Phase diagrams

A phase diagram depicts exactly what phases are present at any given temperature and pressure and they are separated by lines which are called boundaries between them. The line between two phases gives the temperature and pressure at which two phase are in equilibrium. For simplicity of understanding first we will consider phase diagrams of pure substances or we define these as phase diagrams of one-component systems. For example, Figure 2.39 shows a skeletal phase diagram of a one component system.

In the diagram we can see that there are three lines, three areas marked "solid", "liquid" and "vapour", and two special points marked "C" and "T". This indicates that we have a pure substance at three different sets of conditions of ranges of temperature and pressure corresponding to solid, liquid and vapour phases.

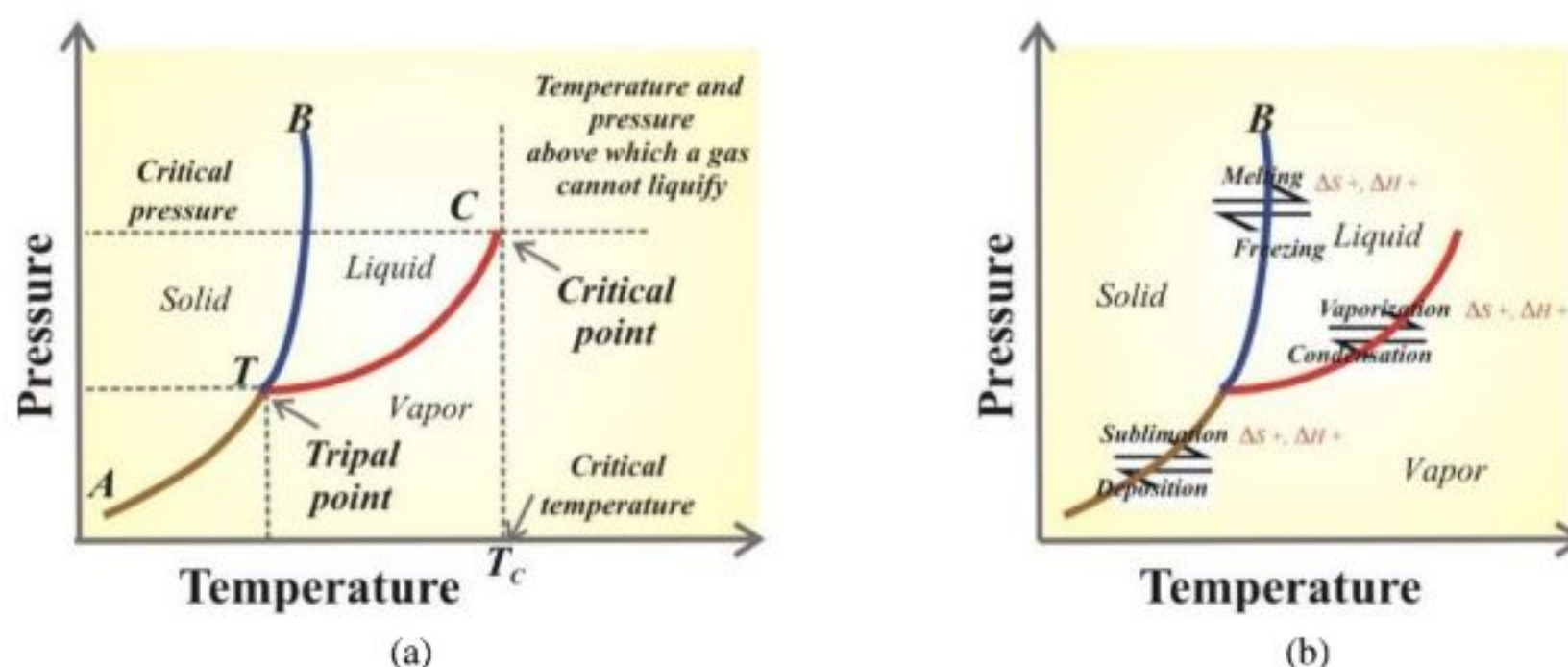


Figure 2.39 Phase diagrams of one component system. In (a) curve TB represents the equilibrium that can exist between the molecules of a given solid and those of the same compound in its liquid state. This situation is only found at the melting point of the compound concerned. Line TB is therefore represents the melting point at various pressures. The line TC represents the equilibrium that exists between molecules in the vapour phase and those in the liquid state, i.e. the equilibrium that is found at the boiling point of the compound concerned. The line TC then shows the variation of boiling point with pressure. AT represents the sublimation curve showing the relationship that exists between the sublimation temperature and the pressure – an equilibrium which is only possible if the external pressure is below that at T, the triple point of the compound. (b) shows the equilibria existing in those regions and the signs of ΔS and ΔH .

Point T: The triple point

In the phase diagram shown in Figure 2.39, the three curves representing solid-vapour equilibrium (curve AT), solid-liquid equilibrium (curve TB) and liquid-vapour equilibrium (curve TC) meet at the point T.

Where all three curves meet, there is a *unique combination of temperature and pressure* where all three phases are in equilibrium together and that point is called the *triple point*. If the conditions of temperature and pressure are controlled in order to reach this point, there would be an equilibrium which involves the solid melting and subliming, and the boiling liquid in contact with its vapour.

Point C : Critical point

In the phase diagram illustrated in Figure 2.39, the liquid-vapour equilibrium curve (TC) has a top limit labelled C. This is known as the **critical point**. The temperature and pressure corresponding to this are known as the **critical temperature (T_c)** and **critical pressure**.

If the pressure of a gas is increased at a temperature lower than the critical temperature, the system will cross the liquid-vapour equilibrium line and the vapour will condense to give a liquid. However, when the temperature is *above* the critical temperature, there is no line to cross. That is because, above the critical temperature, it is impossible to condense/liquify a gas into a liquid just by increasing the pressure. What we get only is a highly compressed gas.

For example, if the gaseous molecules are compressed together by a high external pressure, but with a temperature high enough not to allow condensation to occur, we will have properties pertaining to both the liquid as well as the gaseous states. The density will be that of a liquid but in this state called the **super critical fluid state**, the compound behaves like a gas also.

The critical temperature obviously varies from substance to substance and depends on the strength of the attractions among molecules. “*The stronger the intermolecular attractions, the higher the critical temperature.*”

Understanding of the behaviour of the substance undergoing phase changes can be interpreted as follows with the help of Figure 2.40.

Point P: Solid phase

In the Figure 2.40 (a), we can see that at the point I with temperature (T_1) and pressure (P_1) water exists as a solid. Assume that the temperature of the system is slowly increased to (T_2) while keeping the pressure constant (P_1), *i.e. temperature moves along the line PQ*. It crosses the curve TB at the point X at which there is equilibrium between solid and

liquid (*Anywhere on this line, there is an equilibrium between solid and liquid.*) and then turn to a pure liquid at the temperature T_2 (point Q) or in other words, it melts.

If we repeat this at a higher fixed pressure (P_2), the melting temperature is higher (T_2). See the point I' as illustrated in Figure 2.40 (a). From this we can understand that the curve TB which separate solid and liquid phases simply illustrates the *effect of pressure on melting point of a solid*.

Further understanding of this behaviour of change in melting point can be treated as follows: As now you have knowledge on Le Chatelier's principle, increase in the pressure leads the equilibrium to move in such a way as to counter the change. As we are having $\text{solid} \rightleftharpoons \text{liquid}$ equilibrium, increasing the pressure on the equilibrium mixture of solid and liquid at its original melting point will convert the mixture back into the solid again. In other words, it will no longer melt at this temperature. Therefore, to make it melt at this higher pressure (P_2), increase in the temperature is needed. Thus, raising the pressure raises the melting point of most solids.

Point Q

If we continue heating at the same pressure (P_1), along line PR, the liquid will meet the TC curve at point Y at which there is equilibrium between liquid and vapour and then turns into a pure vapour at the temperature T_3 (point R). In other words, it vapourizes. i.e., the liquid will change into a vapour through boiling when it crosses the boundary line between the two phases (TC curve) shown in Figure 2.40 (b). *Therefore by varying the temperature at a constant pressure the boiling temperature can easily be read at that pressure from the phase diagram.* As we know, anywhere along this line, there will be an equilibrium between the liquid and the vapour.

Further, if the pressure of the system is decreased by keeping the temperature constant at T_2 , (downward arrow from "point Q"), we meet the TC curve and further decrease in pressure to P_2' will turn the liquid into vapour. Therefore, the curve TC illustrates the *effect of pressure on the boiling point of the liquid*. As the pressure increases, the boiling point increases and vice versa.

Point S: Moving from solid to vapour

Consider the point S labelled in the phase diagram in Figure 2.40 (c). Solid phase exists at that given temperature (T_4) and pressure (P_4). The curve AT represents the boundary between solid and vapour phases on which solid-vapour equilibrium exists. As we have discussed the points P and Q, the curve AT can be crossed by either increasing the temperature of the solid, or decreasing the pressure.

The arrow in the diagram shows the effect of increasing the temperature of a solid phase at a (probably very low) constant pressure. The pressure obviously has to be low enough that a liquid can't form - in other words, it has to happen below the point labelled T. Once

the line meets the curve AT, solid starts to sublime attaining equilibrium between solid and vapour phases. When the selected temperatures and pressures are below the temperature and pressure of the point T we can see that only the solid or vapour phase can exist in the system. Once the point T is passed, it can be seen that the vapour at a constant temperature can be converted into a liquid by increasing the pressure, where the phenomenon of liquifaction of gasses can be understood.

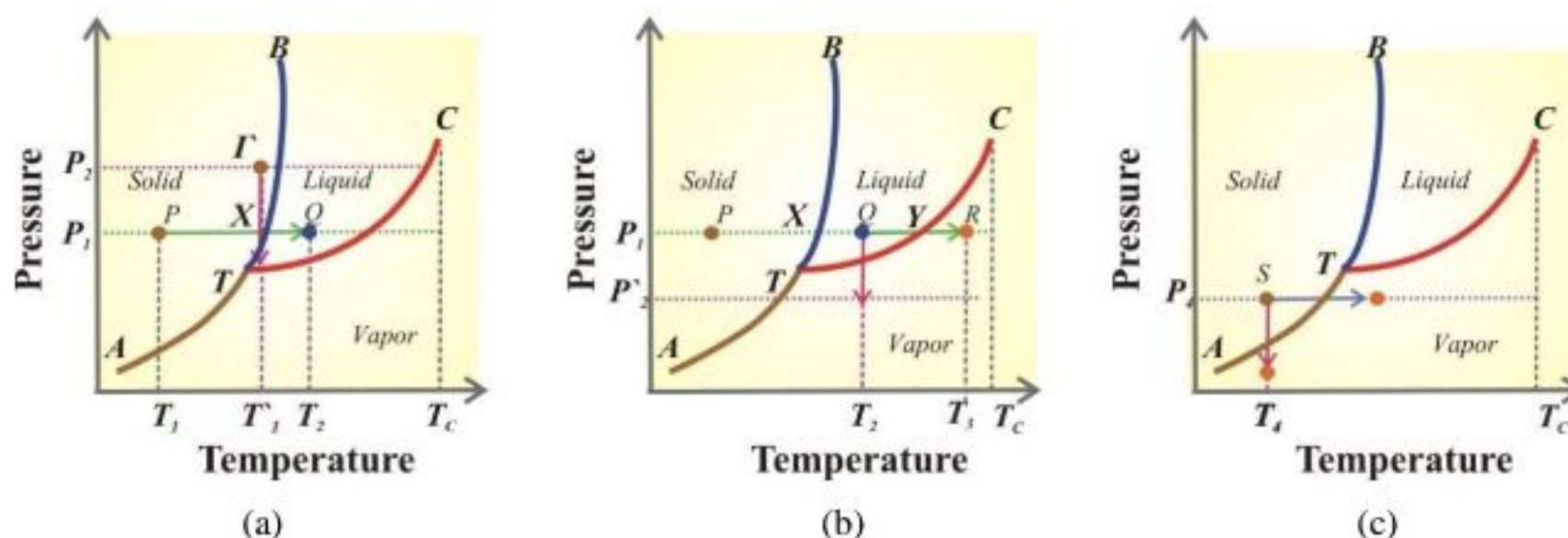


Figure 2.40 Behaviour of substance undergoing phase changes

Normal melting and boiling points

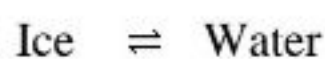
As the normal melting and boiling points are the temperatures when the pressure is 100 kPa, these can be found from the phase diagram by drawing a line across 100 kPa pressure.

Detailed phase diagram of water

Notice that the triple point for water occurs at a very low pressure of 611 Pa and at the temperature of 0.01 °C. Melting and boiling points are at 0.00 °C and 100 °C, respectively, where the pressure is 100 kPa. The critical temperature is 374 °C and the critical pressure is 201 kPa. The complete phase diagram of water is thus depicted in the Figure 2.41 with the inclusion of above information.

Note: In the case of water, “the melting point gets lower at higher pressures”.

For the melting, we have the equilibrium of;



Ice is less dense than water; therefore, water formed by melting of ice occupies a smaller volume. When the pressure is increased, according to Le Chatelier's Principle the equilibrium will move to reduce the pressure again. That means it will move to the side with the smaller volume. Liquid water is produced. Therefore, to make the liquid water freeze again at this higher pressure, temperature has to be reduced and hence higher pressures bring about lower melting (freezing) points. Thus, the slope of the line/curve for the equilibrium between solid and liquid phases of water has a negative gradient.

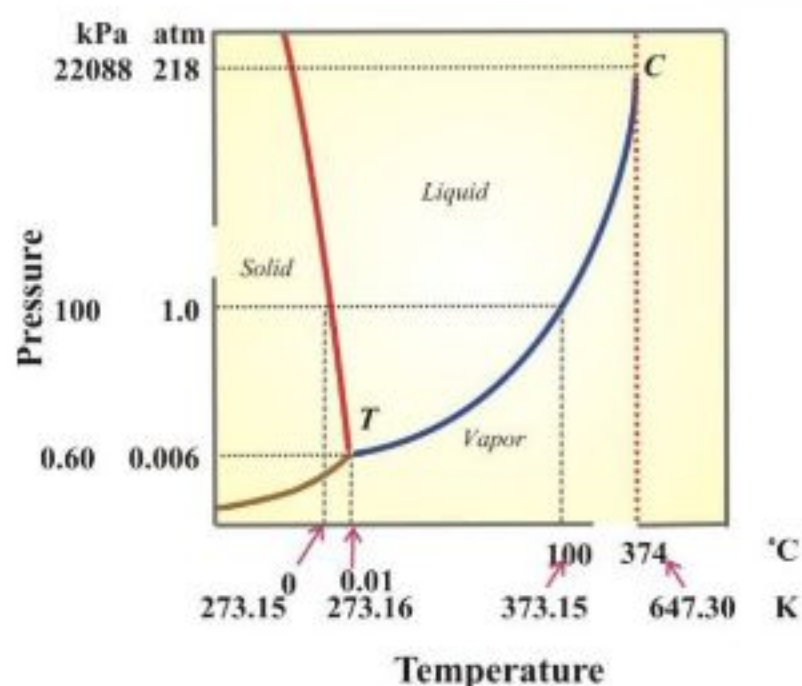


Figure 2.41 Phase diagram of water

When the different phases of water are considered there is a marked difference in the density near ambient conditions and at critical conditions. For example:

At 100 kPa (1 atm) and 0 ° C:

Density of liquid water = $1 \text{ g cm}^{-3} = 55.6 \text{ mol dm}^{-3}$

Density of gaseous water = $2.7 \times 10^{-4} \text{ mol dm}^{-3}$

At 218 atm and 374 ° C:

Density of gaseous water = Density of liquid water = 4.1 mol dm^{-3}

Phase diagram of CO₂ is shown in the Figure 2.42.

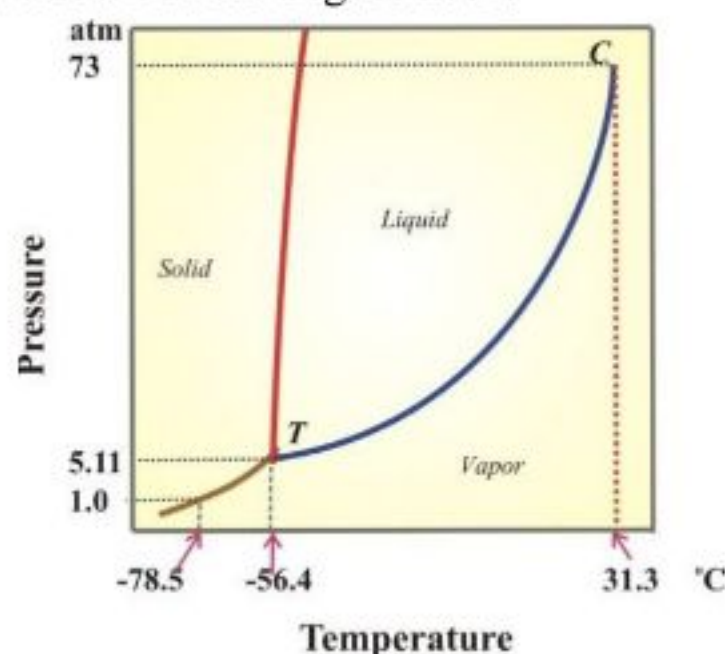


Figure 2.42 Phase diagram of CO₂

Compared to the phase diagram of water, the only thing special about the the phase diagram of CO₂ is the position of the triple point which is well above atmospheric pressure. Therefore, it is impossible to get any liquid carbon dioxide at pressures less than 5.11 atm. That is CO₂ does not display normal melting and boiling points. That means at 1 atm pressure, carbon dioxide can only sublime at a temperature of -78 °C. This is the reason why solid carbon dioxide is often known as "dry ice". You can't get liquid carbon dioxide under normal conditions - only the solid or the vapour.

2.6 Liquid - vapour equilibrium in binary liquid systems

In this section, characteristics of the mixtures of two volatile liquids will be discussed with the help of theoretical concepts first. In the first part the discussion is made on the cases where the two liquids are entirely miscible in all proportions to give a single liquid. To understand the behaviour of these solutions, a concept of an ideal mixture will be introduced and the characteristics of phase diagrams of such ideal mixtures. Are dealt with. Later on, a comparison between ideal and non-ideal mixtures will be made.

2.6.1 Characteristics of ideal mixtures

When a completely miscible liquid mixture is formed by mixing two very closely similar liquids, we assume that they get fairly close to being ideal. Some examples are *hexane and heptane*, *benzene and toluene*, *water and ethanol* etc.

Intermolecular forces

As we have discussed under the vapour pressure, in a pure liquid, some of the more energetic molecules have a tendency to escape from the liquid surface to form the vapour and in substances having smaller intermolecular forces, more molecules will be able to escape at any given temperature. For another liquid the same thing is true and this is illustrated in Figure 2.43.

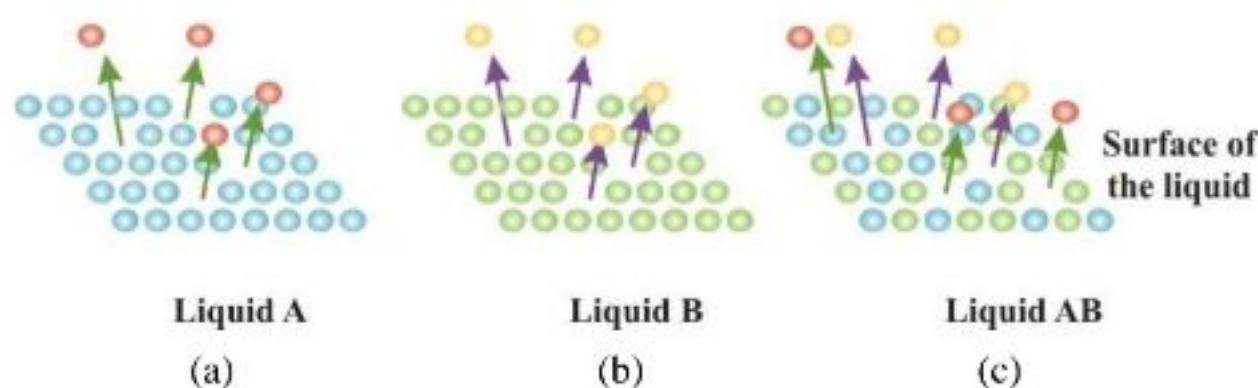


Figure 2.43 Formation of 1:1 ideal liquid mixture AB with the pure components of A and B

Once these two liquids are mixed assuming a complete miscibility the resultant mixture is said to be an ideal (*subjected to obey some rules*), and the tendency of the two different molecules of the liquids to escape is unchanged as described in Figure 2.43(c).

In the Figure 2.43(c) you can see that when the mixture is 1:1 of the two liquids and the proportion of each type of molecule escaping is the same. In other words, the number of molecules escape from each component of the mixture is the same.

If A and B molecules still have the same tendency to escape as before (when they exist alone), we can understand that the intermolecular forces between two A molecules must be exactly the same as the intermolecular forces between a A and a B molecule (If the forces were any different, the tendency to escape would change).

With this characteristic we can understand that the intermolecular interactions between A and B molecules also be exactly the same as the interactions between A-A and B-B molecules.

Enthalpy change of mixing

When a mixture of liquids is made, breaking of the existing intermolecular attractions and the remaking of new attractions occur. Energy is needed to break the interactions while energy is released during the formation of new attractions. If all these attractions are the same, there won't be any heat either evolved or absorbed. That means an ideal mixture of two liquids will have zero enthalpy change of mixing.

At a given temperature, when a binary completely miscible liquid mixture is formed by mixing liquid A and liquid B, with the intermolecular interactions between f_{A-A} , f_{B-B} and f_{A-B} are equal ($f_{A-A} = f_{B-B} = f_{A-B}$) and with no enthalpy change, such a solution is called an ideal solution.

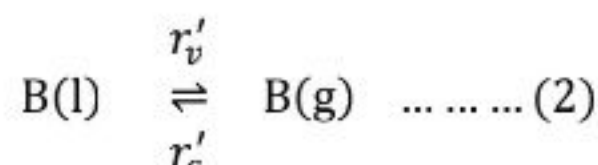
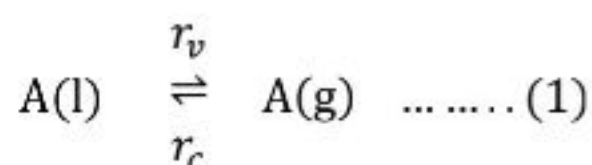
A mixture of hexane and heptane gets close to ideal behaviour because they are similar in size and so have equal van der Waals attractions between them.

Roult law

Consider an ideal binary liquid solution (mixture) made by mixing of liquids **A** and **B** in a closed container with a vacuum above at a given temperature. As we know, the molecules of **A** and **B** with sufficient energy will escape into the space above the surface of liquid and build up a pressure. Once the system reaches the dynamic equilibrium, rates of evaporation and condensation of **A** and **B** become equal. The dynamic equilibrium at this point can be testified with the consistency of the **total vapour pressure** and the **composition of the vapour phase** at a constant temperature. According to Dalton law, *total pressure is the sum of partial pressures of components in the system*. Composition of the vapour phase depends on the relative volatilities (boiling points) of **A** and **B** and the relative concentrations of **A** and **B** in the solution.

The component with high volatility (low boiling point) and higher concentration in solution tends to build up the higher partial pressure. That is, concentration of a component in the vapour phase is proportional to its partial pressure ($[A(g)] \propto p_A$) and in a mixture the concentration of a component is proportional to its mole fraction ($[A(l)] \propto x_A$).

Consider the vapor – liquid equilibrium of an ideal solution with components **A** and **B** described above. As the rate of evaporation equals the rate of condensation, we can write:



r_v and r_c are the rates of vapourization and condensation, respectively of the component A.

r'_v and r'_c are the rates of vapourization and condensation, respectively of the component B.

Considering (1), we can write;

$$r_v = k [A(l)] = k_1 x_A$$

x_A is the mole fraction of A in solution.

Likewise,

$$r'_v = k' [A(g)] = k_2 p_A$$

p_A is the partial pressure of A in vapour phase.

At equilibrium,

$$\begin{aligned} r_v &= r'_v \\ k_2 p_A &= k_1 x_A \\ \therefore p_A &= \frac{k_1}{k_2} x_A \text{ or } \therefore p_A = k x_A \\ \text{when } x_A &= 1, p_A = p_A^0 = \text{saturated vapor pressure of A} \\ \therefore k &= p_A^0 \\ \therefore p_A &= p_A^0 x_A \\ \text{and } p_B &= p_B^0 x_B \end{aligned}$$

Thus;

*In an ideal solution, the partial pressure of a given component is equal to the product of its saturated vapour pressure and the mole fraction of it in the liquid phase at a constant temperature. This relationship is called **Roult law**.*

It is clear that $\therefore p_A < p_A^0$ and $p_B < p_B^0$

Therefore, decrease or lowering in the vapor pressure of A

$$= p_A^0 - p_A = p_A^0 - p_A^0 x_A = p_A^0 (1 - x_A)$$

$$= p_A^0 x_B$$

$$\therefore \frac{p_A^0 - p_A}{p_A^0} = x_B \text{ and } \frac{p_B^0 - p_B}{p_B^0} = x_A$$

The above is an alternative form of Roults law.

Relative lowering of vapour pressure of a given component in the vapour phase is equal to the mole fraction of the other component in the solution.

Combining the Roults law with Dalton law of partial pressures, it is possible to determine the composition in the vapour phase. If p is the total vapour pressure and y_A and y_B are the mole fractions of A and B in the vapor phase, respectively, from Dalton law:

$$p_A = py_A = (p_A + p_B)y_A$$

$$p_A^0 x_A = (p_A^0 x_A + p_B^0 x_B)y_A$$

$$\therefore y_A = \frac{p_A^0 x_A}{(p_A^0 x_A + p_B^0 x_B)} \text{ and } y_B = \frac{p_B^0 x_B}{(p_A^0 x_A + p_B^0 x_B)}$$

Roults law is only applied for ideal mixtures or ideal mixtures follow Roults law.

Vapour pressure/ composition diagrams

In an ideal mixture of two liquids A and B, each of A and B is making its own contribution to the overall vapour pressure of the mixture at a constant temperature. When we consider the component A alone we have $p_A = p_A^0 x_A$; p_A^0 being a constant, results a straight line for the dependence of p_A on x_A as shown in Figure 2.44 (a). (if $x = 0$, $p_A = 0$. p_A increases proportionately with the increase in x_A : if you double the x_A , p_A will be doubled. Therefore, the straight line goes through the (0,0) point in the graph). Similar behaviour will be followed by the component B. If we assume that $p_A^0 > p_B^0$, i.e A is more volatile than B, Figure 2.44 (b) shows the line of variation of vapor pressure of B with its composition (x_B). The total vapour pressure of the mixture at each composition is therefore the sum of the vapour pressures of A and B at the point concerned. The complete graph of the ideal liquid mixture formed by mixing liquids A and B at a constant temperature is shown in Figure 2.44 (c). The line p_T (p_{AB}) shows the variation of total vapour pressure of the system with the composition of A and B.

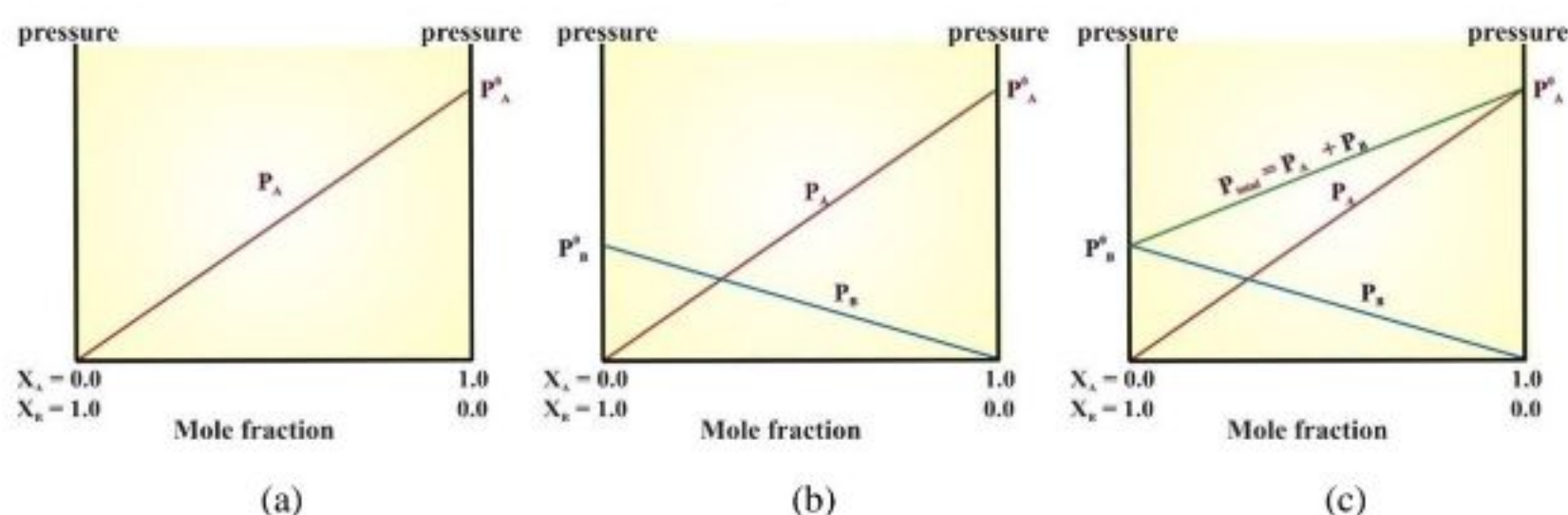


Figure 2.44 Vapour pressure – composition diagrams for an ideal mixture AB which obeys the Roults law at constant temperature. (a) Variation of vapour pressure of component A; (b) variation of vapour pressure of component B included and (c) variation in total vapour pressure of the mixture.

Temperature (Boiling point) - composition diagrams

As we have discussed before, if the molecules are escaping easily from the liquid surface at a constant pressure it means that the intermolecular forces are relatively weak and the liquid needs little energy to boil and vapourize.

Therefore, the liquid with the higher vapour pressure at a particular temperature has the lower boiling point.

Or we can understand the relation between vapour pressure and boiling point (temperature) as follows too.

Liquids boil when their vapour pressures become equal to the external atmospheric pressure. If a liquid has a high vapour pressure at a given temperature, little increase in the temperature is enough to bring the vapour pressure equal to the level of the external atmospheric pressure. On the other hand if the vapour pressure is low, more heat/energy is needed to reach the external pressure.

Therefore, the liquid with the higher vapour pressure at a given temperature has the lower boiling point.

When an ideal mixture is formed by two liquids at the same temperature;
the one with the higher vapour pressure is the one with the lower boiling point.

Constructing a temperature (boiling point) - composition diagram

First what we have to perform is the conversion of vapour pressure – composition diagram to a temperature (boiling point) – composition diagram at constant (external) pressure. Some may think that the task is an easy one with the thought of it as simply a reciprocal of the vapour pressure – composition diagram. Though it looks like a correct argument still we have to consider some facts as follows.

In the ideal mixture aforesaid with $p_A^0 > p_B^0$ at constant pressure $T_{b(A)} < T_{b(B)}$ where T_b is the boiling point (A has a lower boiling point).

For mixtures of A and B, perhaps you might have expected that their boiling points would form a straight line joining the two points. However, it is a curve. You may recall that the vapour pressure of a liquid has an exponential variation with the temperature as discussed in the section 2.5.3 (see the Figure 12.34).

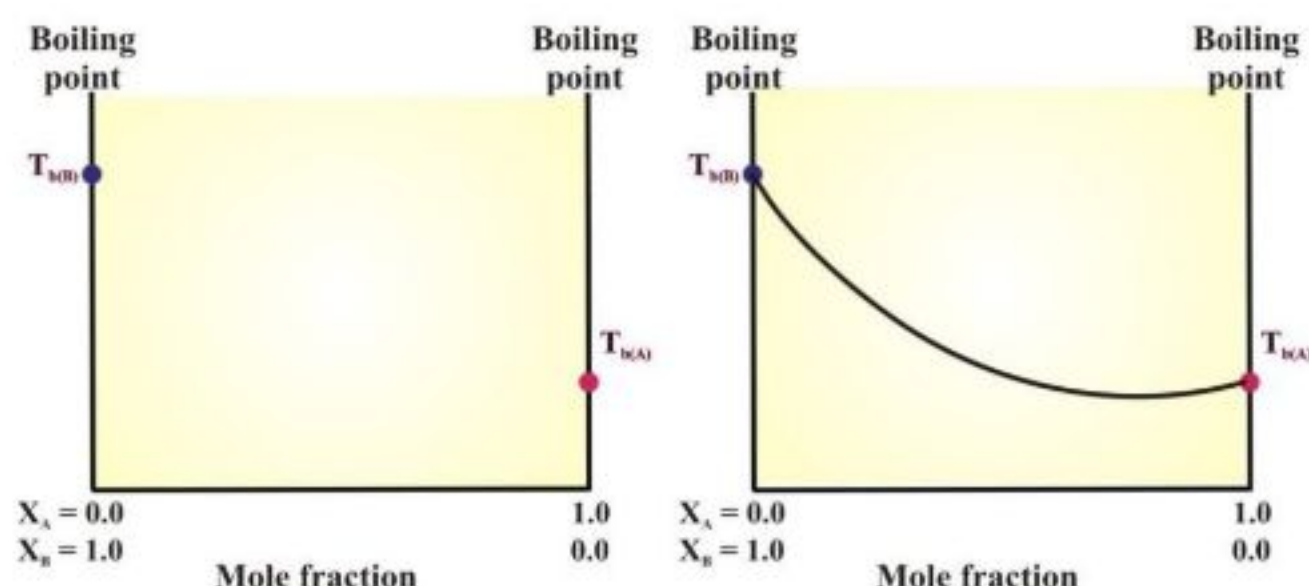


Figure 2.45 Boiling point (temperature) – composition diagrams for an ideal mixture AB at constant pressure. (a) Boiling points of components A and B; (b) variation of boiling point of the mixture.

First we can mark the boiling points on the respective axes with $T_{b(A)} < T_{b(B)}$ as shown in Figure 2.45 (a) and with the idea on the variation of the vapour pressure of the mixture with the composition of the liquid, the two points can be connected as shown in Figure 2.45 (b).

Now we need to know how the vapour pressure changes with the composition of the vapour. When a liquid mixture is boiled at constant pressure, the more volatile substance escapes to form the vapour more easily than the less volatile one. That means, in the present system higher proportion of A (the more volatile component) will be in the vapour than in the liquid. The composition of the vapour at this point can be estimated /determined by condensing the vapour first and analyzing it. Consider the point (P) marked on the diagram as shown in Figure 2.46 (a). The liquid at point P boils at temperature T_p and the composition of the vapour corresponding to T_p can be obtained by drawing a horizontal line through P and T_p . That the point in vapour is marked as Q.

Repeating this exercise with liquid mixtures with different compositions of the liquid, the second curve for the variation of the vapour pressure of the vapour with the composition can be plotted as shown in Figure 2.46 (b). We can see that the area inside the two lines consists of an equilibrium between the liquid and the vapour.

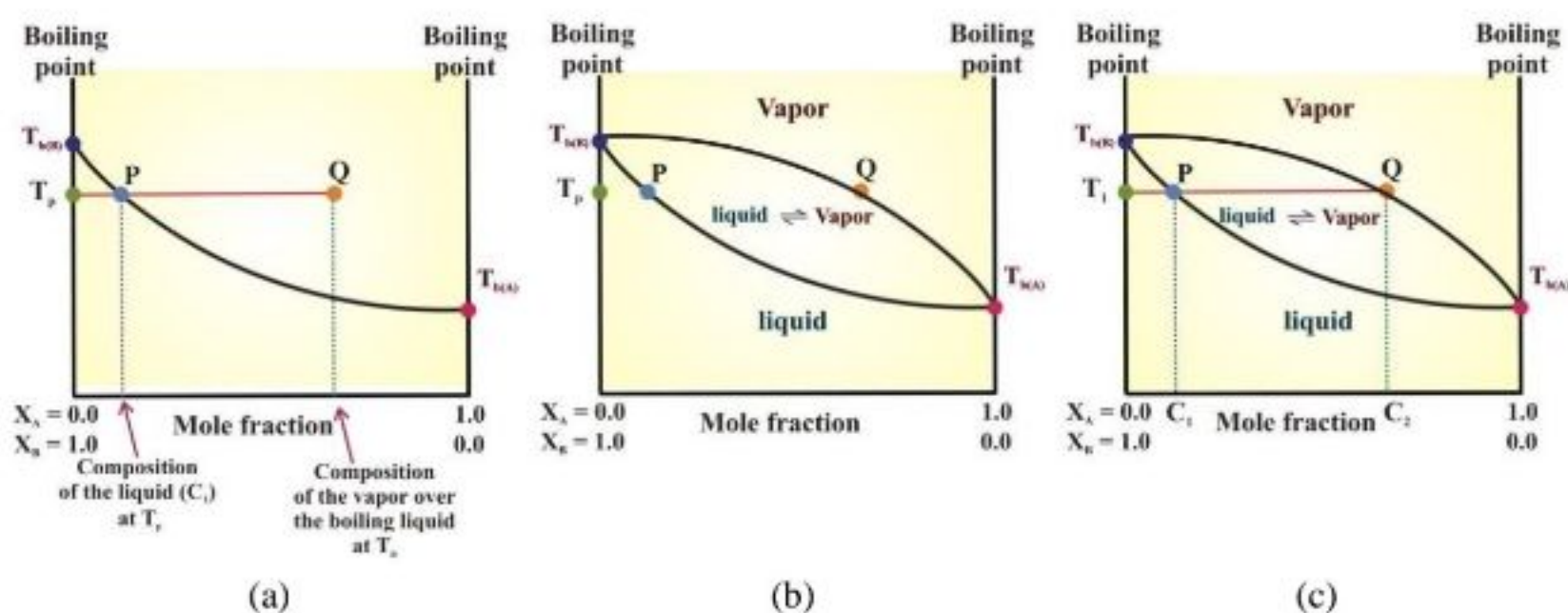


Figure 2.46 Boiling point (temperature) – composition diagrams for an ideal mixture AB at constant pressure. (a) Variation of boiling point of the mixture with the selected liquid composition C_1 which boils at T_p . Extrapolation of the line T_pP gives the composition of vapour at point P. (b) Variation of the boiling point in the vapor and inside envelop where the equilibrium liquid \rightleftharpoons vapor exists. (c) Finds the composition of the liquid corresponds to the point Q as C_2 .

As described in Figure 2.46 (b), by boiling a liquid mixture we can find the temperature at which it boils, and the composition of the vapour over the boiling liquid. For example, in the Figure 2.46 (c), a liquid mixture of composition C_1 boils at a temperature T_1 and the vapour over the top of the boiling liquid will have the composition C_2 . Likewise we can repeat this for other compositions and from the liquid composition curve the boiling point can be determined. Then the composition of the vapour in equilibrium with the liquid of that composition could be estimated. This behaviour is very helpful in separating liquids from mixtures through distillation/ fractional distillation and the details on this will be discussed in a later section. Before going to discuss that application it is worth seeing the characteristics of systems of liquid mixtures showing some deviations from the Raoult law.

Non-ideal mixtures of liquids

A liquid mixture which does not obey Raoult law is called a non-ideal liquid mixture. Such a mixture is formed by the components A and B among which the intermolecular interactions are not equal. These systems differ in behavior from ideal mixtures. In a non-ideal mixture with components A and B, $f_{A-A} \neq f_{B-B} \neq f_{A-B}$, so there is a change in enthalpy during mixing. Therefore, the tendency for the molecules to escape is not the same in the mixture and in the pure liquids.

Vapour pressure - composition diagrams for non-ideal mixtures

As we know, the ideal mixtures obey the Raoult law and dependence of vapour pressure on the composition of the liquid phase at a constant temperature results in a straight line as shown in Figure 2.44 (a), where A is the more volatile one and hence $p_A^0 > p_B^0$.

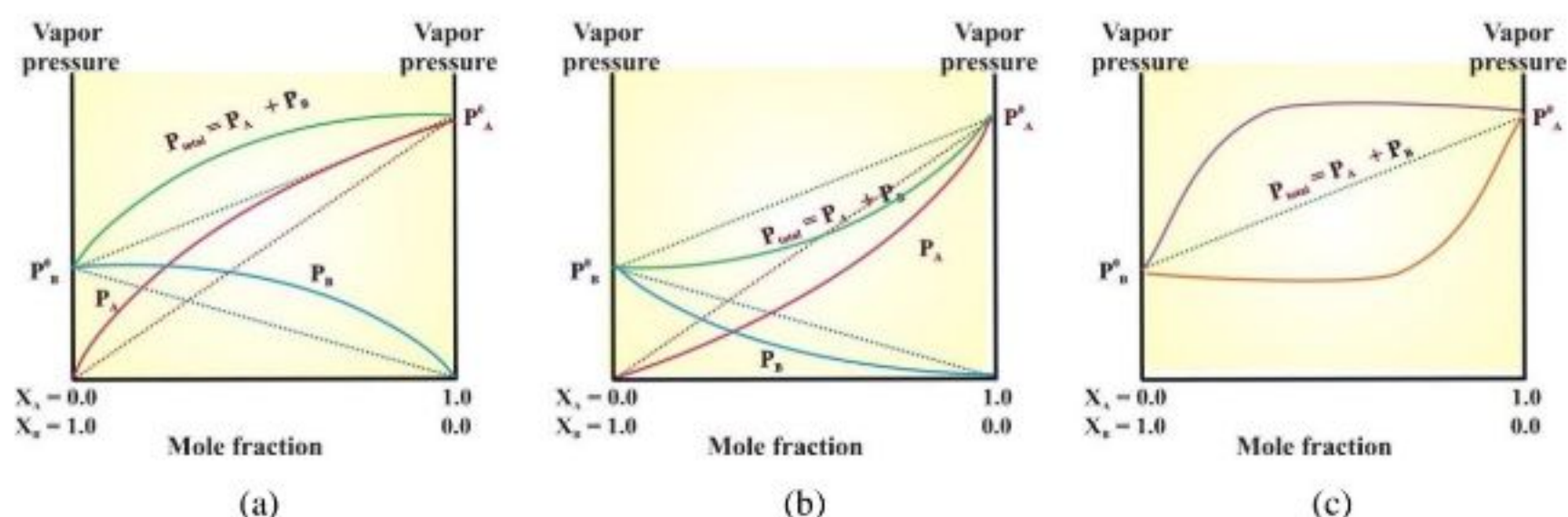


Figure 2.47 Vapour pressure – composition diagrams for non-ideal mixture AB at constant temperature. (a) Positive deviation from Raoult law and (b) negative deviation from Raoult law. (c) Shows mixtures having large positive and negative deviations from Raoult law.

Positive deviations from Raoult law

Some mixtures are formed at constant temperature by components A and B where $f_{A-B} < f_{A-A}$ and f_{B-B} , i.e. the intermolecular forces between molecules of A and B are less than those in pure liquids. Therefore, the tendency for the molecules to escape into the vapour phase is higher than that in the case of an ideal mixture.

Therefore, $p_A > p_A^0 x_A$ and $p_B > p_B^0 x_B$: this results;

$$p_{AB} > (p_A^0 x_A + p_B^0 x_B)$$

This means that the total vapor pressure of the mixture is higher than that of an ideal mixture;

$$p_{AB} > p_{(AB)_{ideal}}$$

These type of mixtures/solutions are said to exhibit **positive deviations** from Raoult law. In mixtures showing a positive deviation from Raoult's Law, the vapour pressure of the mixture is always higher than that expected from an ideal mixture. Thus, the curve in the vapour pressure – composition diagram loops upwards from the ideal line as shown in Figure 2.47 (a). In these mixtures, the vapour pressure which is higher than that of ideal mixtures implies that molecules are breaking away more easily than they do in the pure liquids. As the intermolecular forces between molecules of A and B are less than they are in the pure liquids, less heat is evolved than the heat absorbed to break the original attractions between molecules A-A and B-B when the liquids are mixed. Heat will therefore be absorbed when these liquids are mixed. Thus, the enthalpy change of mixing is positive (endothermic). We can see that along this curve the highest vapour pressure anywhere is still the vapour pressure of pure A as $p_A^0 > p_B^0$. Cases like this, where the deviation is small, behave just like ideal mixtures as far as distillation is concerned. But some liquid mixtures have very large positive deviations from Raoult law and in these cases, the curve becomes distorted as shown in Figure 2.47 (c). For example a mixture of

this kind is ethanol and water that produces a highly distorted curve with a maximum vapour pressure for a mixture containing 95.6% of ethanol by mass.

Negative deviations from Raoult's law

In some mixtures formed at constant temperature by components A and B with $f_{A-B} > f_{A-A}$ and f_{B-B} , the tendency for the molecules to escape into the vapour phase is less than that in the case of an ideal mixture. That is the molecules break away from the mixture less easily than they do from the pure liquids. Thus stronger forces must exist in the mixture than in the original liquids.

Therefore, $p_A < p_A^0 x_A$ and $p_B < p_B^0 x_B$: this results;

$$p_{AB} < (p_A^0 x_A + p_B^0 x_B)$$

This means that the total vapor pressure of the mixture is lower than that of an ideal mixture;

$$p_{AB} < p_{(AB)_{ideal}}$$

These type of mixtures/solutions are said to exhibit **negative deviations** from Raoult law. In mixtures showing a negative deviation from Raoult's Law, the vapor pressure of the mixture is always lower than that expected from an ideal mixture. Thus, the curve in the vapour pressure – composition diagram loops downwards from the ideal line as shown in Figure 2.47 (b). We can see a minimum and along this curve the highest vapour pressure anywhere is still the vapour pressure of pure A as $p_A^0 > p_B^0$. On mixing the liquids to form this type of a mixture, heat is evolved because the new bonds formed are stronger than the original weaker ones which are broken. For example when water and nitric acid is mixed, more heat is evolved because of the formation of ionic species NO_3^- and H_3O^+ (Figure 2.47 (c)).

Boiling point - composition diagrams for non-ideal mixtures

A mixture with positive deviation from Raoult law has a high vapour pressure which means that it has a low boiling point. The molecules escape easily and it is not necessary to heat the mixture much to overcome the intermolecular attractions completely. Therefore, the boiling point - composition curve will have a minimum value lower than the boiling points of either A or B as shown in Figure 2.48 (a). For example, in the mixture of ethanol and water, this minimum occurs with 95.6% of ethanol by mass in the mixture. The boiling point of this mixture is 78.2 °C where as the boiling point of pure ethanol is 78.5 °C, and the boiling point of water is 100 °C.

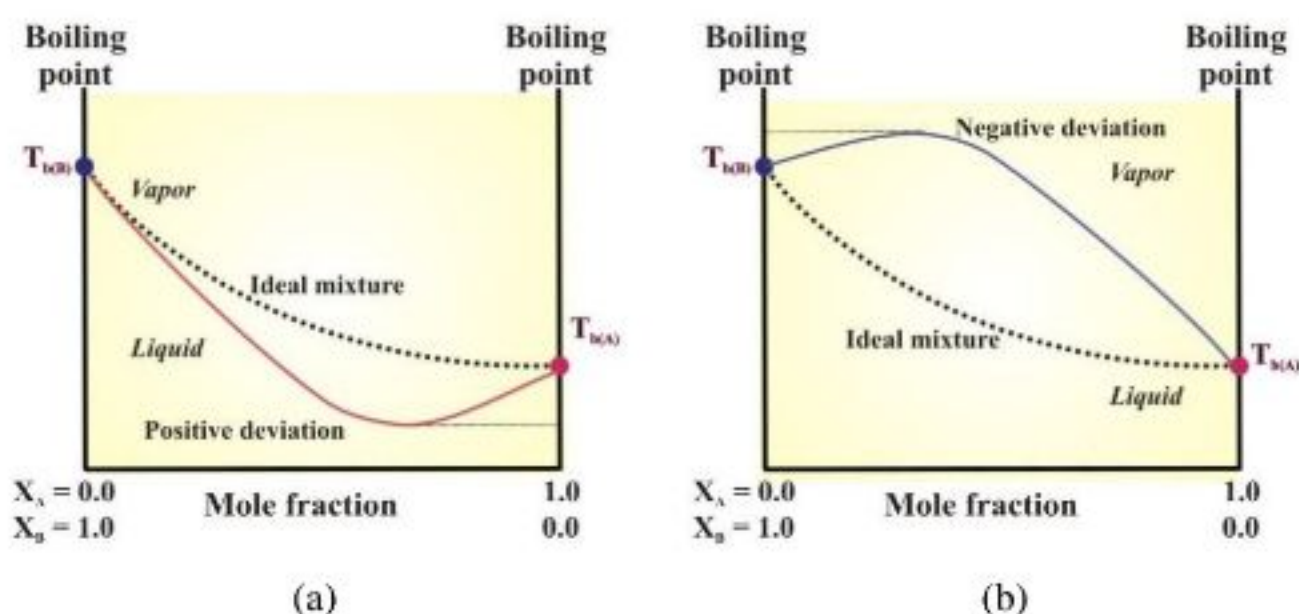


Figure 2.48 Boiling point – composition diagrams for non-ideal mixture AB at constant temperature. (a) Positive deviation from Raoult law and (b) negative deviation from Raoult law.

In the case of the mixtures with negative deviation from Raoult law, molecules break away to form the vapour with much more difficulty than in either of the pure liquids. Therefore, such mixtures can have boiling points higher than either of the pure liquids because it needs extra heat to break the stronger forces in the mixture. Therefore, the variation of boiling point with the composition goes through a maximum value compared to boiling points of pure A and B and is shown in Figure 2.48 (b). For example, in a mixture of nitric acid and water, there is a maximum boiling point of $120.5\text{ }^{\circ}\text{C}$ when the mixture contains 68% by mass of nitric acid. That can be compared with the boiling point of pure nitric acid ($86\text{ }^{\circ}\text{C}$), and water ($100\text{ }^{\circ}\text{C}$). It is easy to understand that this large difference in boiling points is due to the presence of the new ionic interactions as described earlier.

Fractional distillation

Consider Figure 2.44 (c) and assume that the vapour relevant to the liquid composition C_1 is collected and condensed to get a new liquid mixture with the composition C_2 which is reboiled. This liquid will boil at a new temperature T_2 , and the vapour over the top of it would have a composition C_3 as shown in Figure 2.49. We can see that the vapour with composition C_3 is very close to pure A. Therefore, by repeating this process of condensing the vapour and reboiling the resultant liquid will eventually end up with pure A. This process is the basis of the technique called ***fractional distillation*** which is very useful in separating liquid mixtures to their pure components.

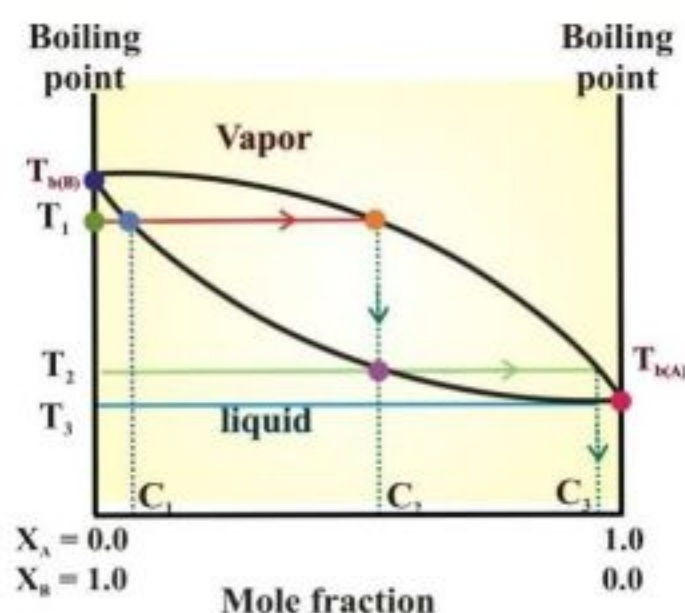


Figure 2.49 Concept of fractional distillation

If we continue the process of condensing and reboiling described in Figure 2.49, reboiling liquid C_3 will give a vapour still richer in the more volatile component A and we will be able to collect a liquid which is virtually pure B. Therefore, we can notice that *the more volatile component from a mixture of liquids can be separated by successive boiling-condensing-reboiling operations*. However, the repeating of this process is really time consuming and it needs some high efficiency in the view of industrial applications. Also it is not quite clear how a component with high boiling point is obtained. Fractionating columns are used to overcome this barrier by automating this condensing and reboiling process. Figure 2.50 shows a sketch of a complete set up used for fractional distillation with a fractionating column.

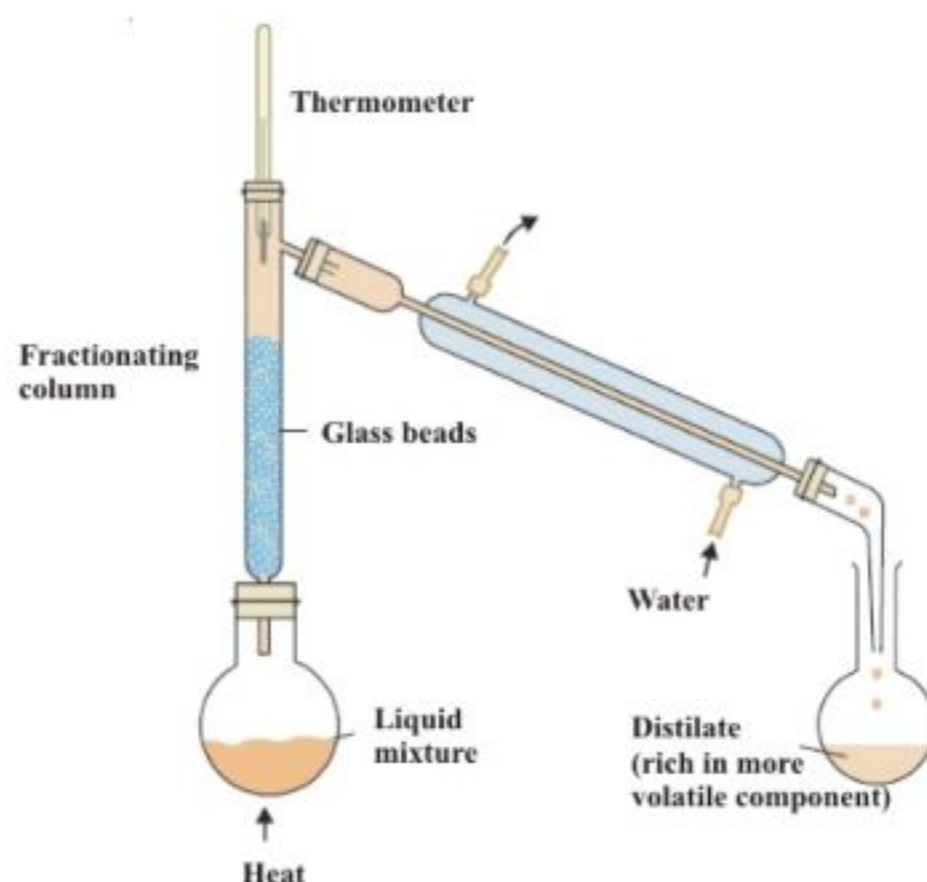


Figure 2.50 A sketch of the complete set up use for the fractional distillation with fractionating column

The fractionating column is packed with glass beads or spikes attached to the walls of a column to facilitate the vapour to condense. These glass beads or spikes make a lot of surface area inside the column allowing the maximum possible contact between the liquid falling down and the hot vapour rising leading to efficient boiling – condensation cycles. A thermometer bulb is placed exactly at the outlet of the fractionating column and the column is connected to a water-cooled condenser.

Consider boiling of a mixture with composition C_1 .

Analysing the vapor;

As we know, the vapour over the top of the boiling liquid is richer in the more volatile component with low boiling point, and will have the composition C_2 (Figure 2.49). The vapour produced on top of the liquid now starts to travel up along the fractionating column and eventually it will reach a height at which the temperature is low enough to condense it giving a liquid on/in glass beads or spikes. The composition of that liquid is still C_2 . Once the vapour is condensed, it will start to fall down along the column and will meet new hot vapour rising. Now as the falling liquid mixes up with the hot vapour that will cause it to reboil.

Assume now the composition of the vapour as C_3 . As described above, this new vapour will again move further up the fractionating column until it gets to a temperature where it can condense. Then the whole process repeats itself. We can see that each time the vapour condenses to a liquid, the liquid will start to fall down the column through the glass beads. It will be reboiled by the up-coming hot vapour producing a vapour rich in the more volatile component A. If the boiling points of the two liquids are very close, we need longer fractionating columns.

Analysing the liquid

As the vapour is richer in the more volatile component A, the liquid remaining in the flask will be getting richer in the other component B. During this repeating process of boiling and condensations and as the condensed liquid falling down the column constantly reboiled by the up-coming vapour, each reboiling makes it rich in the less volatile component.

Therefore, over the time, component A passes out from the top of the column into the condenser and the liquid in the flask will become richer in B. By controlling the temperature carefully, a binary mixture is separated in which the component A (with lower boiling point) passes into the collecting flask and B will remain in the original flask.

2.6.2 Immiscible liquid – liquid systems

Immiscible liquids are those which do not mix to give a mixture with a single phase at a given temperature and pressure. Oil and water are examples of immiscible liquids, where oil floats on top of water. Therefore, we can understand that when immiscible liquids are mixed together, they separate out into different layers with the denser liquid settling to

the bottom and the other floating on top of that. In such a case, if the liquids are in a closed container with static condition and there are no interactions between molecules of two liquids, the vapour pressure of the system will simply be the vapour pressure of the one which is floating on top because there is no way for the liquid in the bottom to travel up.

Let us assume that the mixture is stirred or the static situation is perturbed and the two liquids are broken up into drops. Therefore, the top layer of liquid does not alter the bottom layer - molecules to evaporate, though it may slow it down from reaching its equilibrium. Now, at any time there will be drops of both liquids on the surface giving indication that both of them contribute to the overall vapour pressure of the mixture. As such it is desirable to assume that the molecules of both liquids are in equilibrium with their respective molecules in the gas phase and both of those contribute to the total vapour pressure of the system. Therefore, the total vapour pressure of the system would be the sum of partial pressures of the components; assuming that the component liquids are A and B,

$$p_T = p_A^{\circ} + p_B^{\circ}$$

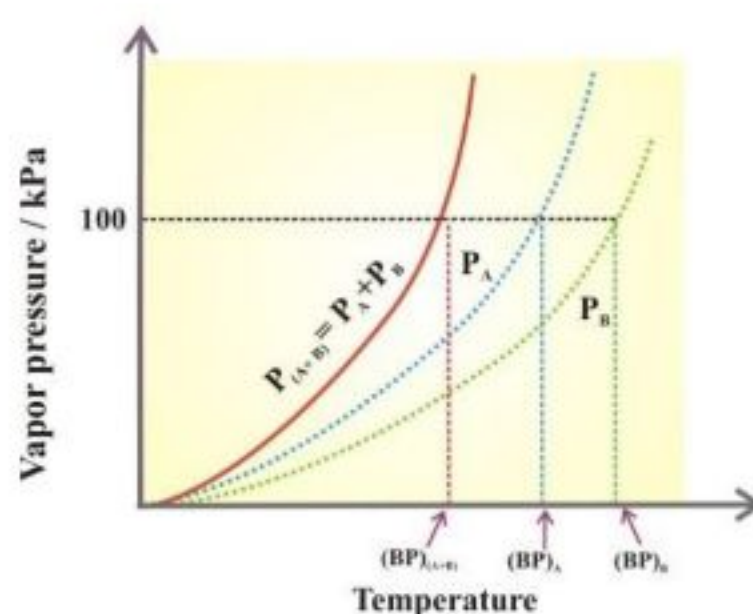


Figure 2.51 Variation of vapor pressure of totally immiscible liquid – liquid system

As the two liquids are immiscible, the variation in their vapor pressures with temperature is independent of each other as depicted in Figure 2.51. Once we sum-up these partial pressure values, the total vapour pressure curve intersects the 100 kPa line at a point which has a lower boiling point compared to pure A and B. Therefore, in these types of mixtures of immiscible liquids, it is very important to note that the boiling point of the mixture will be lower than the boiling points of the pure components.

This principle is very useful in purification of temperature sensitive compounds, particularly those that decompose at their boiling points. As the mixture boils at a lower temperature than those of the components, it is easy to extract high-boiling compounds by the application of steam distillation. For example, phenylamine $C_6H_5NH_2$ oxidizes rapidly at its normal boiling temperature ($184\text{ }^{\circ}C$). However, a mixture of phenylamine

and water will boil at a temperature lower than 100 °C. With the understanding of the Figure 2.51, we can treat this mixture as follows.

At 98 °C, the saturated vapour pressures of the two pure liquids are:

phenylamine	7.07 kPa
water	94.30 kPa

The total vapor pressure of the mixture would then be the sum of these which is 101.37 kPa and this is slightly higher than the normal external pressure. Therefore, the mixture would boil at a temperature just less than 98 °C which is little lower than the boiling point of pure water (100 °C) and much lower than the boiling point of phenylamine (184 °C).

Thus, the isolation of this compound from a mixture can easily be carried out by steam distillation. In this procedure, steam is continuously passed through the heated mixture and the vapour is condensed by a water-cooled condenser. Then the condensed vapour of pure components is collected in a container. It is necessary to keep in mind that the steam distillation technique is useful to separate/purify a substance when the substance is immiscible with water or insoluble in water, has a high molecular mass, has high vapour pressure at around 100 °C and the impurities present are non volatile under the conditions used.

2.7 Partition/ Distribution coefficient

When two immiscible solvents **A** and **B** are placed in a beaker, they will not mix and instead form separate layers. At a constant temperature, when a solute **X** which is soluble in both solvents in the same molecular-form and non-reactive is added, and the system is shook vigorously, the solute **X** gets dissolved in both solvents depending on its solubility in each solvent. This can further be explained as the solute is *distributed* or *partitioned* between the two solvents. After allowing the system to settle, layers of the solvents will separate and **X** molecules of the solute pass through the boundary between two solvents back and forth. Finally a dynamic equilibrium will be reached with the constant concentrations of **X** in each layer.

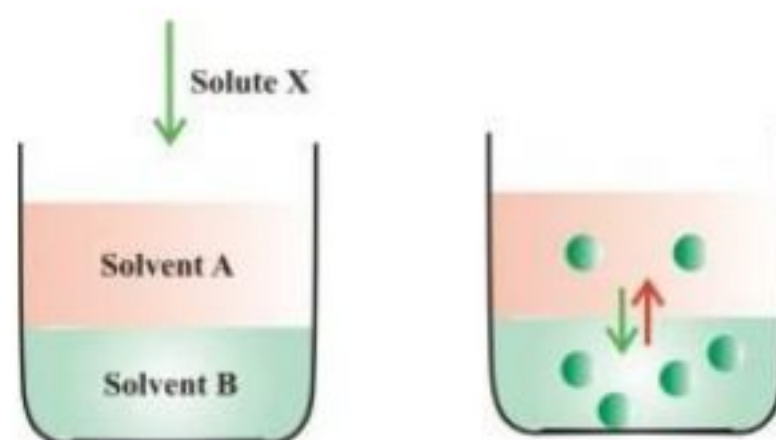


Figure 2.52 Skeptual diagram for the distribution of solute X in A and B solvents

At the same temperature, if more of the solute X is added to the system, *the solute will distribute itself between the layers keeping the same ratio of the solute concentrations at constant temperature.* Therefore, at a constant temperature, the equilibrium constant for the system can be written as:

$$\frac{\text{Concentration of X in A}}{\text{Concentration of X in B}} = \text{constant}$$

i.e.

When a solute X distributes itself between two immiscible solvents A and B at constant temperature and X is in the same molecular condition in both solvents,

$$\frac{[X_A]}{[X_B]} = K_D$$

The constant K_D is called the Distribution coefficient or the partition coefficient or the distribution ratio.

When a solute is shaken with two immiscible solvents at a constant temperature, at equilibrium both the solvents are saturated with the solute. Since the solubility also represents concentration, we can write the distribution law as

$$\frac{[X_A]}{[X_B]} = \frac{S(X)_A}{S(X)_B} = K_D$$

$S(X)_A$ and $S(X)_B$ are the solubilities of the solute in the two solvents. Hence knowing the value of the Distribution coefficient K_D and the solubility of solute in one of the solvents, the solubility of solute in the second solvent can be calculated.

Example 2.46

A solid X is added to a mixture of benzene and water at 25 °C. After shaking well and allowing to settle, 20.00 cm³ of the benzene layer was found to contain 0.20 g of X and 100.00 cm³ of water layer contained 0.40 g of X. X has its normal molecular weight in both solvents. Calculate the K_D .

Answer

$$\text{Concentration of X in benzene, } C_b = \frac{0.20 \text{ g}}{20.00 \text{ cm}^3} = 1.0 \times 10^{-2} \text{ g cm}^{-3}$$

$$\text{Concentration of X in water, } C_w = \frac{0.40 \text{ g}}{100.00 \text{ cm}^3} = 4.0 \times 10^{-3} \text{ g cm}^{-3}$$

$$\therefore K_D = \frac{C_b}{C_w} = \frac{1.0 \times 10^{-2} \text{ g cm}^{-3}}{4.0 \times 10^{-3} \text{ g cm}^{-3}} = 2.5$$

Note: It is not necessary to find the concentration in mol dm⁻³ always. As K_D is a dimensionless quantity, units are cancelling out. It is important to remember that the units of both concentrations should be the same.

Example 2.47

At 25 °C an aqueous solution of iodine containing 0.05 g dm^{-3} is in equilibrium with a carbon tetrachloride (CCl_4) solution containing 4.00 g dm^{-3} . The solubility of iodine in water at 25 °C is 0.40 g dm^{-3} . Find the solubility of iodine in carbon tetrachloride.

Answer

$$K_D = \frac{C_{\text{CCl}_4}}{C_{\text{H}_2\text{O}}} = \frac{4.00 \text{ g dm}^{-3}}{0.05 \text{ g dm}^{-3}} = 80$$

$$\therefore \frac{(\text{Solubility})_{\text{CCl}_4}}{(\text{Solubility})_{\text{H}_2\text{O}}} = \frac{(\text{Solubility})_{\text{CCl}_4}}{0.40 \text{ g dm}^{-3}} = 80$$

$$\therefore (\text{Solubility})_{\text{CCl}_4} = 32.00 \text{ g dm}^{-3}$$

Understanding K_D as a constant at constant temperature

As we are considering a system in dynamic equilibrium with the distribution of solute X, the rate (r_1) at which molecules of X pass from solvent A to B is proportional to its concentration (C_1) in A. The rate (r_2) at which molecules of X pass from solvent B to A is proportional to its concentration (C_2) in B. At equilibrium, the rate of migration of solute from one solvent to the other is equal at a constant temperature.

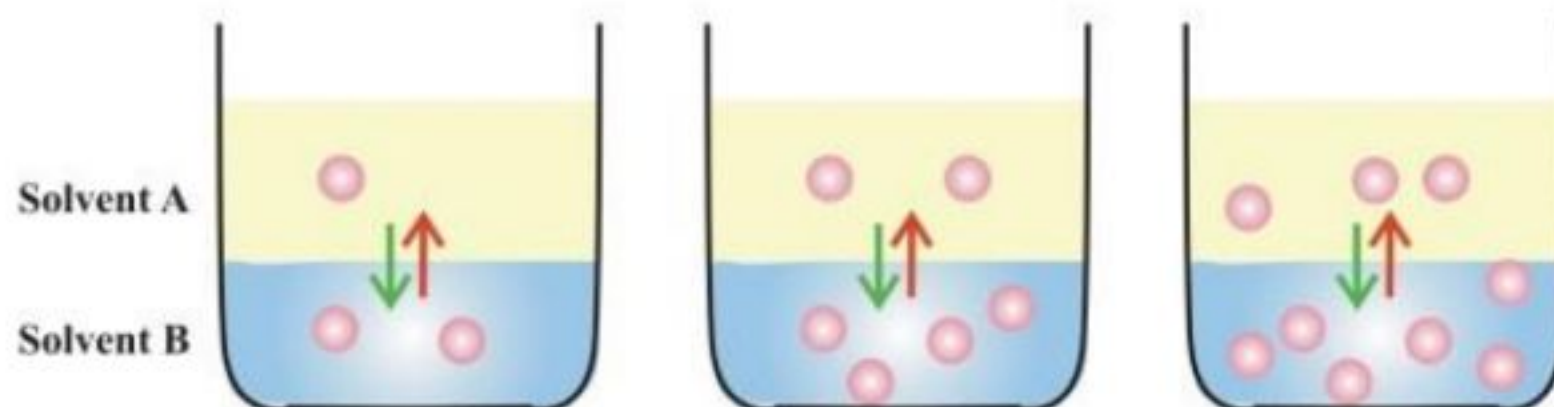


Figure 2.53 Distribution of X solute increases to keep the K_D constant at constant temperature

Thus we have,

$$r_1 \propto C_1 \text{ and } r_2 \propto C_2$$

$$\therefore r_1 = k_1 C_1 \text{ and } r_2 = k_2 C_2$$

k_1 and k_2 are rate constants.

At equilibrium,

$$r_1 = r_2 \quad \text{therefore,} \quad k_1 C_1 = k_2 C_2$$
$$\frac{C_1}{C_2} = \frac{k_2}{k_1} = K_D$$

Usually following conditions are necessary to apply this distribution law.

- (i) Constant temperature: The temperature should be constant throughout the experiment.
- (ii) Same molecular state: The molecular state of the solute should be the same in the two solvents.
- (iii) Equilibrium concentrations: The concentrations of the solute are measured or estimated after the equilibrium has been established.
- (iv) Dilute solutions: The concentrations of the solute in the two solvents should be low. The law does not hold when the concentrations are high.
- (v) Solvents should be immiscible.