G. C. E. (Advanced Level)

CHEMISTRY

Grade 13

Resource Book

Unit 11: Chemical Kinetics
Unit 12: Chemical Equilibrium
Unit 13: Electrochemistry

Department of Science
Faculty of Science and Technology
National Institute of Education
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Chemistry
Resource Book
Grade 13

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Message from the Director General

The National Institute of Education takes opportune steps from time to time for the development of quality in education. Preparation of supplementary resource books for respective subjects is one such initiative.

Supplementary resource books have been composed by a team of curriculum developers of the National Institute of Education, subject experts from the national universities and experienced teachers from the school system. Because these resource books have been written so that they are in line with the G. C. E. (A/L) new syllabus implemented in 2017, students can broaden their understanding of the subject matter by referring these books while teachers can refer them in order to plan more effective learning teaching activities.

I wish to express my sincere gratitude to the staff members of the National Institute of Education and external subject experts who made their academic contribution to make this material available to you.

Dr. (Mrs.) T. A. R. J. Gunasekara
Director General
National Institute of Education
Maharagama.

Message from the Director

Since 2017, a rationalized curriculum, which is an updated version of the previous curriculum is in effect for the G.C.E (A/L) in the general education system of Sri Lanka. In this new curriculum cycle, revisions were made in the subject content, mode of delivery and curricular materials of the G.C.E. (A/L) Physics, Chemistry and Biology. Several alterations in the learning teaching sequence were also made. A new Teachers’ Guide was introduced in place of the previous Teacher’s Instruction Manual. In concurrence to that, certain changes in the learning teaching methodology, evaluation and assessment are expected. The newly introduced Teachers’ Guide provides learning outcomes, a guideline for teachers to mould the learning events, assessment and evaluation.

When implementing the previous curricula, the use of internationally recognized standard textbooks published in English was imperative for the Advanced Level science subjects. Due to the contradictions of facts related to the subject matter between different textbooks and inclusion of the content beyond the limits of the local curriculum, the usage of those books was not convenient for both teachers and students. This book comes to you as an attempt to overcome that issue.

As this book is available in Sinhala, Tamil, and English, the book offers students an opportunity to refer the relevant subject content in their mother tongue as well as in English within the limits of the local curriculum. It also provides both students and teachers a source of reliable information expected by the curriculum instead of various information gathered from the other sources.

This book authored by subject experts from the universities and experienced subject teachers is presented to you followed by the approval of the Academic Affairs Board and the Council of the National Institute of Education. Thus, it can be recommended as a material of high standard.

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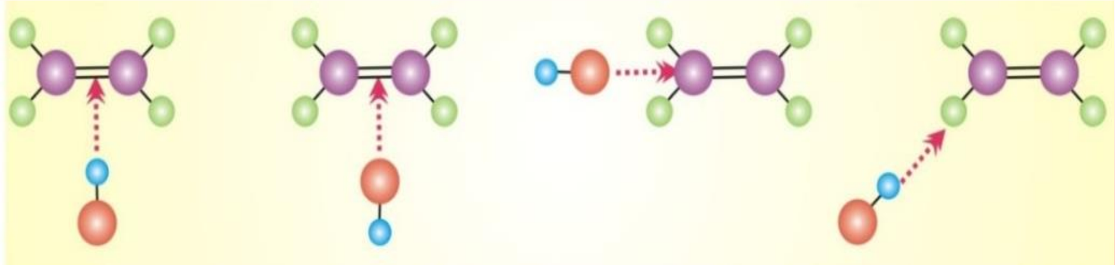


1. Chemical Kinetics

Content

Introduction

In the previous units for example, unit 4 and 5 described the basic aspects of behavior of molecules depending on their physical state and energy requirements for the reaction to occur. Though, we know that the amounts of reactants and products and their molecular nature yet, we have not focused quantitatively on "How fast is the reaction proceed" and requirements to be satisfied to occur a chemical reaction. In this regard the present unit addresses and focuses on the field of *kinetics* where the rates of reactions are concerned. We examine the rate of a reaction, the factors that affect it, the theories that explain those effects, and the stepwise changes reactants undergo as they transform into products. This unit also introduce some general ideas about reaction rates and overview key factors that affect them—concentration/ pressure, physical state, catalyst and temperature. Further, express rate through a rate law and determine its components and see how concentrations change as a reaction proceeds and discuss the meaning of half-life. In addition, we discuss about reaction mechanisms, noting the steps a reaction goes through and picturing the chemical species that exists as reactant bonds are breaking and product bonds are forming.

1.1 Concept of chemical kinetics

We have gained some idea about chemical reactions in unit 5 (energetics). Chemistry is mainly concerned with changes occurring in nature or in substances of interest. Such changes are depicted in a simple way by an equation which is considered a chemical reaction. In the study of any chemical reaction we try to find out the followings.

(a) The feasibility of a chemical reaction, which can be predicted by thermodynamics. For example, energy changes associated with a reaction are expressed by thermodynamic quantities such as ΔH, ΔG, ΔS and we know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible. This also gives us in which direction the reaction occurs.

(b) Extent of a reaction, which explains how far a reaction proceeds to give the desired products and this can be determined from chemical equilibrium (unit 12). This can be quantified with the knowledge of the equilibrium constant.

Along with these, there is another equally important aspect for a given reaction worth paying attention; that is how fast a reaction occurs or the rate of a reaction and factors controlling the rate of a reaction. In this case, time taken by a reaction to reach some known point (extent) has to be studied. Further, how the conversion of reactants to products occurs: that is the mechanism of the reaction has to be known. All these questions can be answered by a branch of chemistry, which deals with the study of reaction rates and their mechanisms, called "chemical kinetics".

If a reaction is to occur, it must be both thermodynamically and kinetically favoured under given conditions such as temperature and pressure of the system. These are relative terms: the reaction must be thermodynamically favoured enough to form the amount of the product desired, and it must be kinetically favoured enough to be completed within the desired time period. For example, nuclear reactions occur very fast (in a fraction of a second) and the conversion of graphite to diamond takes millions of years. This is because it has an enormous activation energy that must be overcome before the reaction may proceed. We must also consider the mechanism of the reaction which is a sequence of events at the molecular level that controls the speed and the desired products of the reaction. Therefore, studying the rates of reactions is very important in many fields. These factors of thermodynamics and kinetics can be simply shown schematically in Figure 1.1 below.

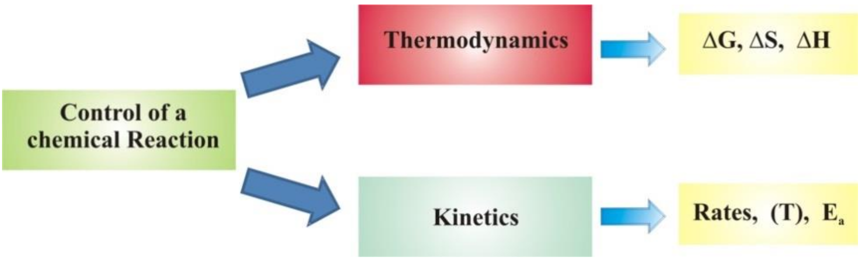


Figure 1.1 Controlling chemical reactions in view of thermodynamics and kinetics

Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions which can alter the reaction rates. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. In these studies, investigations in measurable quantities such as amounts reacted or formed and the rates of consumption or formation come under macroscopic level. At the molecular level, the reaction mechanisms involving orientation, velocities and energy of molecules undergoing collisions have to be considered. These parameters are somewhat hard to measure.

When we consider chemical processes, many chemical processes such as explosive reactions take place in a fraction of a second while the rusting of iron may take a very long time, sometimes in centuries for completion. Ionic reactions in solution, for example the reaction between NaCl(aq) and $AgNO_3$(aq) giving a white precipitate of silver chloride occurs within a very short (but measurable with some advanced techniques) time. In chemical kinetics, at this stage we actually study the rates of reactions which are neither so fast nor so slow. Usually, a chemical reaction involves breaking of bonds in the reactant molecules and making of bonds in the product molecules and it is easy to understand that a reaction that involves breaking of weak bond(s) is faster than a one involving breaking of strong bond(s) at a given temperature. Ionic compounds such as strong electrolytes in solution remain completely ionized and hence in any ionic reaction, no bond is broken. Therefore, an ionic reaction is fast. Different reactions, as they involve variety of bonding in respect of the strength of the bonds to be broken, occur at different rates. Reactions which involve less bond rearrangements are generally faster than those which involve considerable bond rearrangements at a given temperature. Chemical kinetics or reaction kinetics is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and gives information about the mechanisms of reactions and transition states, as well as the construction of mathematical models (rate equations) that can describe the characteristics of a chemical reaction. With this it may worth to categorize reactions with respect to their rates as described below.

Very fast (Instantaneous) reactions

These reactions are so fast and occur as soon as the reactants are bought together. These reactions involve ionic species and are thus known as ionic reactions. There are many reactions occurring on the surfaces of catalysts. They are much faster and usually take place in 10^{-12} to 10^{-18} seconds in the time scale. It is almost impossible to determine the rates of these reactions with conventional techniques. However, there are advanced techniques available with ultra-fast laser spectroscopy which in further allow us even to follow electron transfer processes. Some examples we can consider for these very fast reactions are;

Formation of a precipitate of AgCl when highly concentrated solutions of silver nitrate and sodium chloride are mixed:

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

Neutralisation of a strong acid with a strong base when their aqueous solutions are mixed:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Very slow reactions

There are certain reactions which occur in extremely slow rates or sometimes never happen at the room temperature. It is therefore, difficult to study the kinetics of such reactions. Examples:

Reaction between hydrogen and oxygen at room temperature: This is highly explosive at high temperatures (~ 1000 K).

Reaction between carbon and oxygen; coke does not catch fire spontaneously in air and remains unreacted.

Moderate reactions

Between the above two extremes, there is a large number of reactions which take place at moderate and measurable rates at room temperature and these allow us to study chemical kinetics under laboratory conditions. Some common examples are given below.

Decomposition of hydrogen peroxide:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Decomposition of nitrogen pentoxide:

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

Hydrolysis of an ester:

$$CH_3COOC_2H_5(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + C_2H_5OH(aq)$$

Inversion of sucrose in aqueous solution:

$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$

Reaction between nitrogen dioxide and carbon monoxide:

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Reaction between nitric acid and thiosulfate:

$Na_2S_2O_3(aq) + 2HNO_3(aq) \rightarrow S(s) + 2NaNO_3(aq) + SO_2(g) + H_2O(l)$

Reaction between ferric chloride and potassium iodide:

$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

Reaction between calcium carbonate and hydrochloric acid:

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

The rates of chemical processes can be decreased or increased by changing conditions under which they occur. For example, very slow reaction at room temperature; $CO + 2H_2 \rightarrow CH_3OH$, can be speeded up by maintaining temperature around 400 ^oC, pressure about 300 atm and using a catalyst. The decay of food items can be slowed down by reserving them in refrigerators.

In the study of chemical kinetics, we can predict the rate of a particular reaction under given conditions and that conditions can be adjusted or optimized to make the reactions occur at a desired rate. This is useful in industry to accelerate the formation of industrial products and to predict the mechanism of the reaction.

1.2 Rate of a reaction

Different reactions can occur at different rates. Reactions that occur slowly have a low rate of reaction and reactions that occur quickly have a high rate of reaction. As mentioned above, for example, the chemical change of graphite to diamond and weathering of rocks are very slow reactions; it has a low rate of reaction. Explosions and nuclear reaction are very fast reactions: they have a high rate of reaction.

In general, a reaction can be represented as follows.

$$\text{Reactants} \rightarrow \text{Products}$$

When the reaction proceeds, reactants are consumed while products are formed. As a result, the speed of a reaction or the rate of a reaction can be defined as the change in amount (concentration) of a reactant or product in unit time. That is;

(i) the rate of decrease in amount/ concentration of any one of the reactants, or

(ii) the rate of increase in amount/ concentration of any one of the products at a constant temperature.

Consider a hypothetical reaction at a constant temperature and also assume that the volume of the system remains constant.

$$A \rightarrow B$$

In general, it is more convenient to express the reaction rate in terms of the change in amount with time at a constant temperature. For the reaction above let's consider that at the time t_i *(not at t = 0)* the initial amount of A is $(n_A)_i$ moles and after some time t_t, the amount of A is $(n_A)_t$ moles. Therefore, the change in amount of A within the time interval $(t_t - t_i)$ is $[(n_A)_t - (n_A)_i]$ moles.

$$\therefore \text{ The rate of change in the amount of A } = \frac{[(n_A)_t - (n_A)_i]}{t_t - t_i} = \frac{\Delta(n_A)}{\Delta t}$$

Similarly for the product B we can write,

$$\text{The rate of change in amount of B } = \frac{[(n_B)_t - (n_B)_i]}{t_t - t_i} = \frac{\Delta(n_B)}{\Delta t}$$

In the above, $\Delta(n_A)$; change in amount of the reactant has a negative sign because $(n_A)_t < (n_A)_i$. It is important to note that the change in amount in any chemical process is considered to be a positive quantity. Hence in the case of change in amount in a reactant we use a negative sign. So, the rate of change in amount is always a positive quantity. Therefore, the rate of the above reaction can be written as,

$$\text{Rate} = -\frac{\Delta(n_A)}{\Delta t} = \frac{\Delta(n_B)}{\Delta t}$$

With the above understanding, the rate of a reaction can easily be correlated with the change in amount of either reactant(s) or product(s) of the reaction as the rate of consumption of the reactants or formation of the products.

In this simple description, the rate depends upon the change in amount of reactants or products and the time taken for that change to occur. Thus, the variation of the rate of the reaction A → B can be illustrated as shown in Figure 1.2.

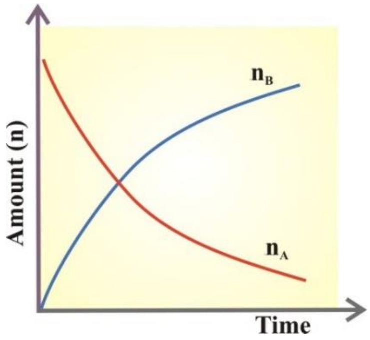
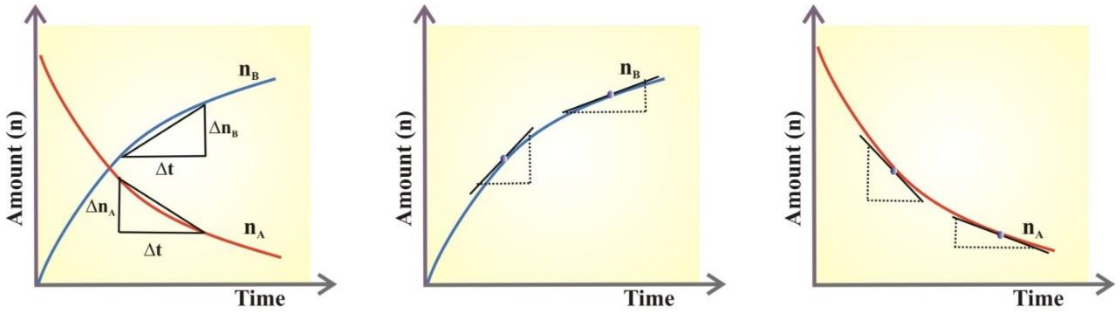


Figure 1.2 The rate of reaction A → B; is the decrease of n_A and increase of n_B with time at a constant temperature. It has to be noted that the rate of the reaction has decreased over the time.

In a mathematical point of view, this quantity $-\frac{\Delta(n_A)}{\Delta t}$ or $\frac{\Delta(n_B)}{\Delta t}$ can be represented as depicted in Figure 1.3(a) where the rate of the reaction is given by the change in amount

$\Delta(n_A)$ *or* $\Delta(n_B)$ over the time interval Δt and usually this rate is defined as *average rate*. Usually the rate changes at a very small time and hence to calculate the rate over the time interval **Δ*t***, the rates at each time within the interval has to be averaged. The rate at a given instance of time is the slope of the tangent drawn to the curve showing the variation of amount with time as shown in Figures 1.3 (b) and (c) for the product B and reactant A, respectively. It is noted that the slope for the rate of change in amount of A (reactant) is negative indicating that the amount decreases with the time and therefore, we use a negative sign in front of the slope when the rate is calculated. It also shows that the rate also decreases with time as the slope decreases with the time because the reactant is consumed during the progress of reaction.



(a) (b) (c)

Figure 1.3 The rate of reaction A → B; **(a)** Description of rate as the change in amount Δn over time period Δt. The definition of rate as the slope of the tangent drawn to the curve showing the variation of amount of the product B with time **(b)** and the reactant A with time **(c)**. In **(c)**, negative slope indicates that the amount of reactants is decreasing over the time. It is also shown in **(b)** and **(c)** that the rate of the reaction decreases with the time as the slope of the tangent decreases.

In the above we have gone through a very basic idea about the description of reaction rate in which the change in amount (number of moles) is considered the measure of the quantity. If we consider the volume of the container in which the reactions occurs as *V* and *it does not change during the progress of reaction* then we can define the rate of the reaction as the change in amount of either reactant(s) or product(s) per unit time per unit volume. If the volume *V* of the system in which the reaction is carrying out is constant, we can write the rate as,

$$\text{Rate } = \frac{\Delta(n_A)}{V\,\Delta t} = \frac{\Delta(C_A)}{\Delta t} \quad \because \quad {(n_A)}/{V} = C_A : \text{concentration}$$

Thus we can then express the rate of the reaction as the change in concentration of either reactant(s) or product(s) per unit time as: Rate $= -\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$.

We can therefore, replace the amount in y-axis in the plots of Figures 1.2 and 1.3 with the concentration and hereafter, we use the concentration to represent the change in quantity of a given reaction as shown in Figure 1.4.

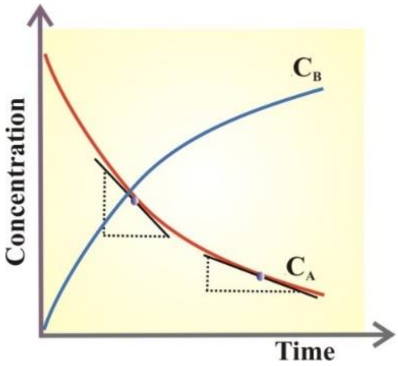


Figure 1.4 The rate of reaction A → B; description of rate as the change in concentration over the time. Rate decreases with the time as is evident from the decrease in the slope of the curve.

We can also see in this plot that the reaction slows down as it proceeds (not the case with reactions) indicating that the reaction rate depends on the concentration of A available to react. Note that when [A] is large, the slope of the curve is steep and hence the reaction is fast. Later in the reaction, [A] is much smaller, and so is the slope. Hence the reaction slows down as A is used up showing that there is a concentration dependence of rate.

Units of rate:

As the rate is defined as the change in concentration at a given time, the units will be **mol dm^{-3} s^{-1}** (if the time is measured in seconds). This unit can easily be applied for the reactions in solutions. When the gas phase reactions are concerned we have to measure the concentrations as partial pressures. Therefore, the units will be **Pa s^{-1}** (or atm s^{-1}).

It can further be understood that the reaction rate will be equal (proportional) to the reciprocal of time (1/t) if the time taken to occur a given change in a reaction is monitored. For a reaction A → B, we write the rate as;

$$\text{Rate} = -\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$$

If the change occurred is a constant and the time taken for that change is t, we write,

$$\text{Rate} = \frac{\text{constant}}{t}$$

or

$$\text{Rate} \ \alpha \ \frac{1}{t}$$

1.3 Reaction rate and stoichiometry

As shown in section 1.2, the rate of a simple reaction of the type A → B at a constant temperature and in a closed rigid vessel (constant volume) can be expressed either as the rate of decrease in concentration of A, $-\frac{\Delta(C_A)}{\Delta t}$ or as the rate of increase in concentration of B, $\frac{\Delta(C_B)}{\Delta t}$. In this reaction we see that one mole of A gives one mole of B, so that the rate can be given as are equal giving $-\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$. Now let us consider a reaction when 2 moles of A giving one mole of B.

$$2A \rightarrow B$$

Because two moles of A are consumed to produce one mole of B, the rate of consumption of A would be twice the rate of production of B. Therefore, we can express the rate of the reaction as;

$$-\frac{1}{2}\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$$

Or we write the same as,

$$-\frac{1}{2}\frac{\Delta[\mathrm{A}]}{\Delta t} = \frac{\Delta[\mathrm{B}]}{\Delta t}$$

Therefore, in general for a reaction: $a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$

We can write,

$$\textbf{Rate} = -\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{1}{b}\frac{\Delta[\mathrm{B}]}{\Delta t} = \frac{1}{c}\frac{\Delta[\mathrm{C}]}{\Delta t} = \frac{1}{d}\frac{\Delta[\mathrm{D}]}{\Delta t}$$

Example 1.1

Consider the decomposition of $H_2O_{2(aq)}$ occurring in a 1.0 dm^3 rigid container at a given temperature according to the following reaction.

$$2H_2O_{2(aq)} \rightarrow 2H_2O(l) + O_2(g)$$

Write the rate of the above reaction in terms of both reactants and products.

Answer

Assuming that the reaction proceeds according to the stoichiometry as shown in the **Figure 1.5**, plot the variations in concentrations of each species in the reaction mixture over the time.

According to the stoichiometry of the reaction; 2 moles of $H_2O_{2(aq)}$ give 2 moles of $H_2O(l)$ and one mole of $O_2(g)$. As the volume of the container is 1.0 dm^3:

Initial concentrations; $H_2O_{2(aq)}$: $H_2O(l)$: $O_2(g)$ = 2.0 : 0.0 : 0.0 mol dm^{-3}

Final concentrations; $H_2O_{2(aq)}$: $H_2O(l)$: $O_2(g)$ = 0.0 : 2.0 : 1.0 mol dm^{-3}

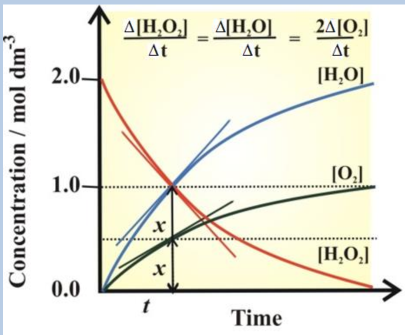


Figure 1.5 The variation of concentrations of the species in reaction $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ at a given temperature

Rate of the reaction can be written as;

$$\text{rate} = -\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t} \quad \text{or} \quad \frac{-\Delta[H_2O_2]}{\Delta t} = \frac{\Delta[H_2O]}{\Delta t} = 2\frac{\Delta[O_2]}{\Delta t}$$

It has to be noted that the above graphs were drawn with the accurate scale according to the stoichiometry and rate of the reaction. Therefore, from the plots after time *t* the rates (slopes) can be calculates as:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = -\frac{(-)2x}{t} = \frac{2x}{t};\ \frac{\Delta[H_2O]}{\Delta t} = \frac{2x}{t} \text{ and } \frac{\Delta[O_2]}{\Delta t} = \frac{x}{t}$$

This clearly implies the definition of the rate of this reaction. Therefore, we can understand that the rates of reactions can be experimentally determined or estimated.

Example 1.2

Write the rates of following reactions in terms of both reactants and products.

(i) $Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

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

Answer

(i) Rate $= -\frac{\Delta[Na_2CO_3(aq)]}{\Delta t} = -\frac{1}{2}\frac{\Delta[HCl]}{\Delta t} = \frac{1}{2}\frac{\Delta[NaCl]}{\Delta t} = \frac{\Delta[CO_2(g)]}{\Delta t}$

(ii) Rate $= -\frac{\Delta[N_2(g)]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

Example 1.3

$N_2O_5(g)$ decomposes as follows:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

It was found that in a closed rigid vessel at a particular instant the rate of decomposition of $N_2O_5(g)$ was 3.0×10^{-7} mol dm^{-3} s^{-1} at a constant temperature. Write the rates of formation of (i) $NO_2(g)$ and (ii) $O_2(g)$.

Answer

We can write the rate of the reaction as;

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5(g)]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2(g)]}{\Delta t} = \frac{\Delta[O_2(g)]}{\Delta t}$$

(i) $$\frac{1}{2} \times 3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1} = \frac{1}{4}\ \frac{\Delta[NO_2(g)]}{\Delta t}$$

$$\frac{\Delta[NO_2(g)]}{\Delta t} = 6.0 \times 10^{-7}\ \text{mol dm}^{-3}\text{s}^{-1}$$

(ii) $$\frac{1}{2} \times 3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1} = \frac{\Delta[O_2(g)]}{\Delta t}$$

$$\frac{\Delta[O_2(g)]}{\Delta t} = 1.5 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Example 1.4

In the reaction taking place in a closed rigid container at a constant temperature:

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

the rate of formation of NO(g) was found to be 2.0×10^{-4} mol dm^{-3} s^{-1}.

Write the rates of (i) the reaction and (ii) the consumption of NOBr(g).

Answer

We can write; $$\text{Rate} = -\frac{\mathbf{1}}{\mathbf{2}}\ \frac{\Delta[NOBr(g)]}{\Delta t} = \frac{\mathbf{1}}{\mathbf{2}}\ \frac{\Delta[NO(g)]}{\Delta t} = \frac{\Delta[Br_2(g)]}{\Delta t}$$

(i) $\therefore$ rate of the reaction = $\frac{\mathbf{1}}{\mathbf{2}} \times\ 2.0\ \times 10^{-4}$ mol dm^{-3} s^{-1}

$$= 1.0\ \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

(ii) $$\frac{\mathbf{1}}{\mathbf{2}}\frac{\Delta[NOBr(g)]}{\Delta t} = 1.0\ \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

$$\therefore\ \frac{\Delta[NOBr(g)]}{\Delta t} = 2.0\ \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Example 1.5

At a given time, the rate of the following reaction with respect to C_2H_4 is 0.20 mol dm^{-3} s^{-1}. Write the rate of the reaction with respect other species in the reaction.

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

Answer

Rate of the reaction:

$$\text{Rate} = -\frac{\Delta[C_2H_4(g)]}{\Delta t} = -\frac{1}{3}\frac{\Delta[O_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[CO_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O\,(g)]}{\Delta t}$$

Given that, $\frac{\Delta[C_2H_4(g)]}{\Delta t} = 0.20 \text{ mol dm}^{-3}\text{ s}^{-1}$

$$\frac{\Delta[O_2(g)]}{\Delta t} = 3 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 3 \times 0.20 \text{ mol dm}^{-3}\text{ s}^{-1} = 0.60 \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$\frac{\Delta[CO_2(g)]}{\Delta t} = 2 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 2 \times 0.20 \text{ mol dm}^{-3}\text{ s}^{-1} = 0.40 \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$\frac{\Delta[H_2O(g)]}{\Delta t} = 2 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 2 \times 0.20 \text{ mol dm}^{-3}\text{ s}^{-1} = 0.40 \text{ mol dm}^{-3}\text{ s}^{-1}$$

From the above examples we can see that the rate of a reaction is not directly equal to either the rate of disappearance of reactants or the rate of appearance of products.

Therefore, for a reaction taking place at constant temperature and constant volume, rate of the reaction is given by;

$$\boxed{\textbf{Rate} = \frac{1}{\nu_j}\frac{\Delta[J]}{\Delta t}}$$

ν_j is the stoichiometric coefficient of the substance J. ν_j is negative for reactants and positive for products.

Example 1.6

Consider the reaction, A $\rightarrow$ 2B, which was started with the initial concentration of 0.50 mol dm^{-3} of reactant A. It drops to 0.00 mol dm^{-3} in 10 seconds. During this time the concentration of B increased from 0.00 mol dm^{-3} to 1.00 mol dm^{-3}. Calculate the rate of this reaction as follows.

Answer

We can write the rate of the reaction as; Rate $= \frac{1}{\nu_j}\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$

$$= -\frac{(0.00 - 0.50)\text{mol dm}^{-3}}{10\text{ s}}$$

$$= 0.05\text{ mol dm}^{-3}\text{ s}^{-1}$$

or

$$\text{Rate} = \frac{1}{\nu_j}\frac{\Delta[B]}{d\,t} = \frac{1}{2}\frac{\Delta[B]}{\Delta t} = \frac{1}{2}\times\frac{(1.00 - 0.00)\text{ mol dm}^{-3}}{10\text{ s}}$$

$$= 0.05\text{ mol dm}^{-3}\text{ s}^{-1}$$

Example 1.7

The decomposition of A at 300 K in a solution with constant volume can be followed by monitoring the concentration of A. Initially (at t = 0), the concentration of A is 2.00 mol dm^{-3} and after 180 seconds, it is reduced to 1.64 mol dm^{-3}. The reaction takes place according to the equation

$$2A(aq) \rightarrow 4B(aq) + C(aq)$$

Calculate the rate of this reaction.

Answer

$\Delta A = 1.64 - 2.00 = -0.36$ mol dm^{-3}

$\therefore -\Delta A = 0.36$ mol dm^{-3}

According to the reaction,

Rate = ½ $[\Delta[A]/\Delta t]$ = ½ × 0.36 mol dm^{-3}/ 180 s

$= 1.0 \times 10^{-3}$ mol dm^{-3} s^{-1}

1.4 Experimental techniques to determine the rates of reactions

As from the example 1.1 and other calculations, we know that the reaction rates are experimentally determined quantities and therefore it is necessary to understand that how the rate of a reaction, is obtained experimentally. In this context, we know to determine the rate of a reaction we have to monitor the concentration of the reactant (or product) as a function of time. That is, in order to determine the rate of a particular reaction, it is necessary to follow either the rate of decrease in concentration of a reactant(s), or the rate of increase in concentration of a product, by choosing an appropriate experimental method at a constant temperature. We can categorize the techniques as non-disruptive and disruptive. In non-disruptive techniques, this is done through a measurement of a rapidly determinable physical property of the reaction mixture. For example, for reactions in solutions, the concentration of a species can often be measured by spectrophotometric techniques if coloured species are involved. If ions are involved, the change in concentration can also be detected by an electrical conductance measurement. Reactions involving gases are monitored by pressure measurements under the constant volume.

Spectrophotometric methods

This is usually employed when at least one of the species involved in the reaction is coloured and its absorbance is monitored as a function of time at a suitable wavelength obtained from the absorption spectrum of either a reactant or a product. As the absorbance is directly proportional to the concentration of the particular species, the rate of the reaction can be monitored by these absorbance measurements as a function of time.

Methods involving the measurement of change in total pressure

As we know, the total pressure of a gas-phase reaction occurring in rigid container at any time will be the sum of the partial pressures of all the gaseous reactants and products. Thus if the stoichiometry of the reaction is known, this can be used to determine either the rate of decrease of a reactant or the rate of increase of a product as a function of the measured total pressure.

Electrical conductance/ conductivity method

Consider, for example, the reaction:

$$R_1COOR_2(aq) + OH^-(aq) \rightarrow R_1COO^-(aq) + R_2OH(aq)$$

The conductivity of hydroxyl ions is much higher than that of the other ions such as ethanoate ions ($R_1 = C_2H_5$). Also the conductivity depends on the concentration of ions and hence, measurement of the conductance is an appropriate method for following the rate of loss of hydroxyl ions in the above process where the decrease in conductivity will be observed.

Optical rotation method

This method is suitable for reactions where the optical activity of the products is different from those of the reactants. For example hydrolysis of sucrose gives glucose and fructose with different optical rotations. An instrument called “polarimeter” is used for the optical rotation measurements. As the optical rotation is related to the concentration, measurement of the optical rotation will then be related to the rate of the reaction.

Refractive index method

This method is especially useful for liquid-phase reactions where the refractive index of reaction mixture changes in the course of the reaction due to increase in the products and decrease in the reactants.

Gas evolution method

If there is one gaseous product in a reaction, the gas evolved can be collected and its volume measured as a function of time. For example, the decomposition of calcium carbonate proceeds by producing CO_2 gas.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

For these types of reactions, the rate can be determined from a measurement of the volume of gas evolved during the reaction (you will practice such in a laboratory under this unit).

Disruptive techniques: Chemical analysis method

In chemical analysis method, a required sample of the reaction mixture is taken out and analyzed, for example, titration to estimate the acid liberated during the hydrolysis of an ester. In the method of chemical analysis, to obtain the composition of the reaction mixture at a given time it is necessary to ensure that no further reaction takes place between sampling and analysis. This is usually achieved by lowering the temperature (quenching) of the mixture immediately after sampling.

1.5 Factors affecting the rate of a chemical reaction

Usually a balanced chemical equation is used to describe the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed in a chemical reaction. As we have some idea from the previous sections, this balanced equation gives us no information about how fast a given reaction will occur. Such information is obtained by studying the chemical kinetics or rates of a reaction. The rate of the reaction depends on various factors: reactant concentrations, temperature, physical nature and surface areas of reactants, catalyst properties and solvent. By studying the kinetics of a reaction, it is possible to gain insights into how to control reaction conditions to achieve a desired outcome.

It is easy to get an idea that the rate of a chemical reaction can be increased by:
Increasing the concentration of a solution or raising the pressure (for a gas phase reaction), increasing the temperature of the reaction system, increasing the surface area of a solid

and by adding a catalyst. In addition to these, solvent used in an experiment to dissolve solute (reactant) can also affect the rate of reaction.

Insight into these can be understood by considering the basic requirements necessary to satisfy to occur a chemical reaction based on collision theory as discussed below.

1.6 Uses molecular kinetic theory (Collision Theory) to explain the effect of factors affecting the rate of chemical reactions

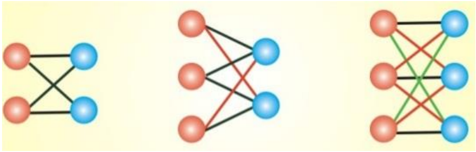
1.6.1 Collision theory

As we know from unit 4 (gaseous state of matter), collision theory explains the motion of molecules, their kinetic energy and how pressure changes in a system accordingly. Now it is easy to understand that for a reaction to occur the molecules must collide all the time and some fraction- but not all of those collisions will lead to transformation of the reactants to the products. This simply means that all the collisions will not result products. For example, at 1 atm and 20 °C, the $N_{2(g)}$ and $O_{2(g)}$ molecules in 1 cm^3 of air experience about 10^{27} collisions per second. If all that was lead for a reaction atmosphere would consist of almost all NO; but only traces are present. This indicates that the number of collisions can't be the only factor which determines the occurrence of a reaction and a reaction rate. Therefore, following must be satisfied to occur a chemical reaction:

1. The molecules must come into contact leading to a collision.
2. They must collide with enough energy to overcome an energy barrier. This minimum energy required is called the activation energy for the reaction.
3. They must collide in favorable orientation that allows the necessary bond-breaking and forming needed to transform the reactants to the products.

Collision:

According to kinetic molecular theory, the reactant molecules are considered to be hard spheres. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency *(Z)*. In its basic form, collision theory deals with one-step reactions, those in which two particles collide and form products: $A + B \rightarrow$ products. Suppose we have only two particles of A and two of B confined in a vessel.



(a) (b) (c)

Figure 1.6 Increase in number of collisions with concentration of the reactants A and B in a constant volume of the reaction mixture. **(a)** Two molecules of A and two molecules of B can undergo four collisions. Likewise, in **(b)** when there are three molecules of A and 2 molecules are present total of six (3 × 2) collisions result. Three molecules of each A and B results nine (3 × 3) collisions as in **(c)**. Note that though the number of collision probabilities could predict like this, all the collisions may not result the product of the reaction.

Figure 1.6 shows that four A-B collisions are possible when there are two A and two B molecules. If we have three A and two B molecules, then there are six possible collisions and likewise when there are three A and three B molecules, we have nine possible collisions. Therefore, it can be noted that this probability of collision shows that the number of collisions depends on the *product* of the numbers of reactant particles, not their sum. Thus, collision theory explains that how the rate of a chemical reaction depends on the number of collisions per unit time per unit volume which in turn explains how the increase in concentration increases the reaction rate. Usually, this collision requirement has a large effect on what media are chosen to perform chemical reactions. Solids tend to be very slow reactors because only the atoms on the surface can have collisions with other atoms of other molecules. That’s why the rusting of iron is very slow. Most reactions are done either in solution or in the gas phase where freedom of movement of the reactant molecules allows them to easily come into contact. Therefore, the more collisions per unit time per unit volume at a given temperature, the faster is the reaction rate.

Collision orientation

It is easy to understand that in a situation involving two molecules they can only react together when they come into contact with each other. In this encounter, they first have to collide, and then they *may* react. This means that though the molecules collide with each other and all the collisions may not result the product. Reactant molecules must collide with a favorable orientation and they must have necessary activation energy to yield the desired product and such collisions are called *effective collisions.* The reaction rate increases with the increase in number of effective collisions and it is in turn proportional to the total number of collisions.

Example:

Consider the single-step decomposition reaction of BrNO given below.

$$2BrNO(g) \rightarrow 2NO(g) + Br_2(g)$$

Now let's see the way the two molecules of BrNO arrange in space as depicted in Figure 1.7. To form $Br_2(g)$ as a product, two Br atoms of the two molecules of BrNO should approach along the same line as shown in the first two collisions. However, if those molecules line up as depicted in third collision, there is no way to collide two Br atoms and hence the collision orientation would not produce the products in the reaction. Therefore, the proper line of approach or the direction of colliding reactant molecules control the rate of reaction.

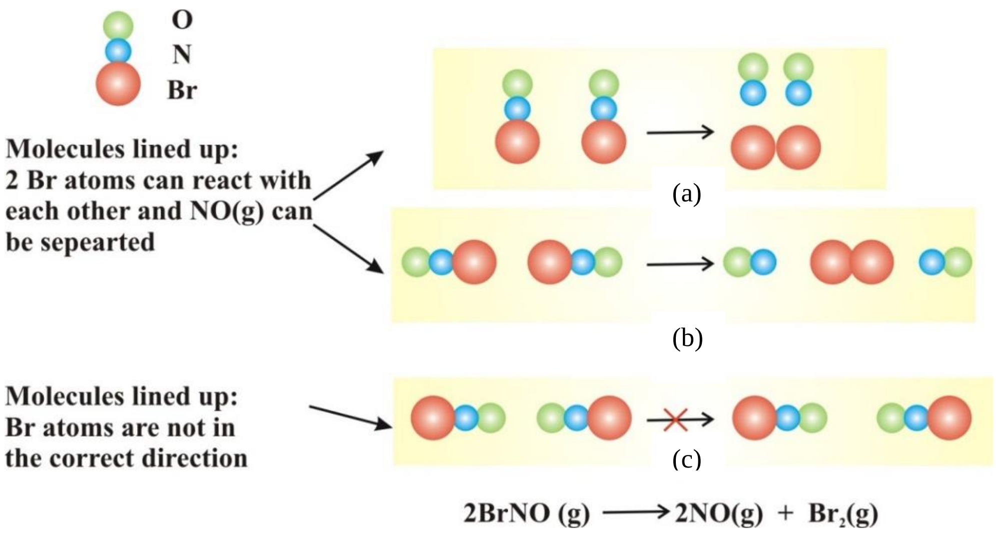
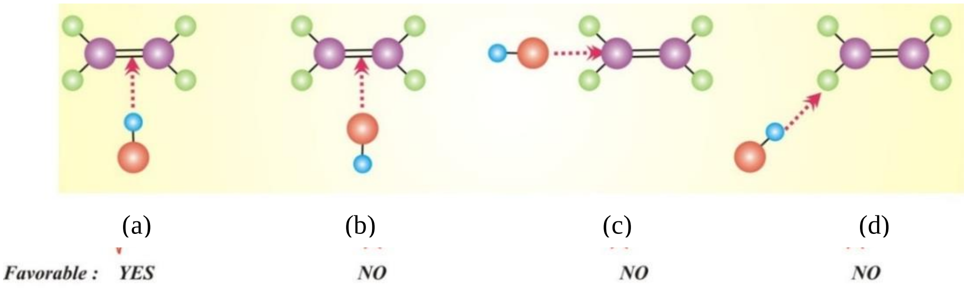


Figure 1.7 Different orientations of collisions between two BrNO molecules. In **(a)** and **(b)**, two molecules lined up properly and result the formation of a Br_2 molecule and two NO molecules. In **(c)** though the molecules lined up, Br atoms are not in the favourable sides/directions to collide and to for in the products.

Consider another single-step reaction between ethene and HCl to produce chloroethane.

$$CH_2{=}CH_2(g) \; + \; HCl(g) \; \rightarrow \; CH_3CH_2Cl(g)$$

As a result of the collision between the two molecules, the C = C double bond is converted into a single bond attaching hydrogen atom to one of the carbons and a chlorine atom to the other. The desired product of the reaction is only possible if the hydrogen end of the H-Cl bond approaches the carbon-carbon double bond. C = C has a high electron density around it and if the Cl atom approaches it, the Cl atom is repelled leading to no products. The collisions leads to the products and the other possible collisions the collisions which do not lead to products are compared in Figure 1.8.



$$CH_2{=}CH_2(g) \ + \ HCl(g) \rightarrow CH_3CH_2Cl(g)$$

Figure 1.8 Possible orientations of collisions between $CH_2{=}CH_2$ and HCl molecules. In **(a)** hydrogen atom of HCl oriented towards the C=C bond and as the C=C bond has negative charge, this collision favours the product. In **(b)**, Cl atom of HCl is repelled thus the reaction is not favoured. In **(c)** and **(d)** product is not favoured.

Surmounting the activation energy barrier

We know that a sample of reactant molecules in motion will have a Boltzmann distribution of molecular kinetic energies. Some molecules will have high energy; some low; many with intermediate energies. Figure 1.9 shows Boltzmann plots for a set of reactants at two different temperatures. Only those reactant molecules with energies greater than a certain minimum (threshold) energy called the ***activation energy, E_a*** (to the right of the plot) will be able to yield products. Because a greater fraction of molecules in the high temperature sample exceed the activation energy, the high-temperature sample will have more effective collisions and will experience a faster reaction rate compared to the sample at low temperature.

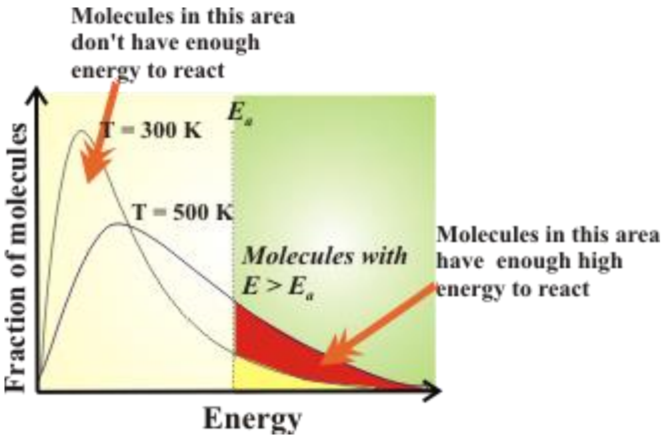


Figure 1.9 The effect of temperature on the distribution of collision energies. At higher temperature fraction of molecules having energy more than the activation energy increases leading to higher reaction rates.

When a favorable collision occurs between molecules overcoming the forces of interactions among the molecules, first an unstable molecule cluster, called the activated complex (transition state) is formed. The life time of the activated complex is very short and transformed to the products (or may break into the reactants again). The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reaction. The energy diagram for this with the example of the decomposition of BrNO(g) is shown in Figure 1.10 More details on this will be discussed later.

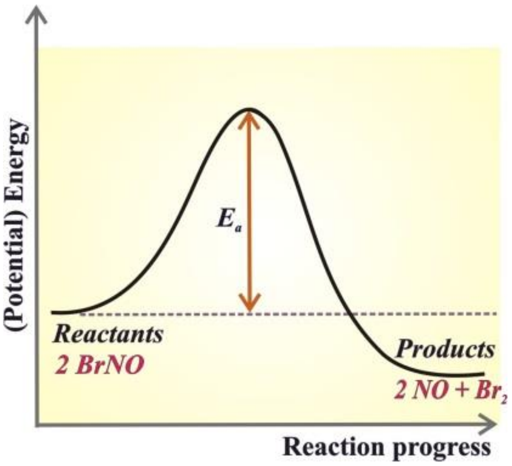


Figure 1.10 Energy diagram in which the activation energy (E_a) is depicted

For example, in the decomposition reaction $2BrNO(g) \rightarrow 2NO(g) + Br_2(g)$, of BrNO(g) two Br-N bonds need to be broken and one Br-Br bond needs to be formed. The energy required to break a Br-N bond is about 243 kJ mol^{-1} and hence this energy must be required to occur the reaction. Based upon the collision model, the energy comes from the kinetic energy of the molecules and once the molecules collide, the kinetic energy is transferred into potential energy which breaks the bonds and rearranges the atoms.

As a summary we can see that a chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after an effective collision and then they can go to the right side of the curve and consequently change into products. If the activation energy for a reaction is low, the fraction of effective/ favourable collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of collisions and the number of effective collisions per unit time per unit volume will increase and hence the rate of reaction will increase.

Concentration effects

In a chemical reaction of the type A + B → *Products:* reactant molecules of A and B (atoms, or ions) come into contact and converted into products. If there is no contact, the reaction rate will be zero. If the number of molecules per unit volume is increased the reaction rate increases as the collisions between them increase. This means that the reaction rate usually increases as the concentration of the reactants increases. In reactions involving liquids or gases, increasing the concentration of the reactants increases the rate of reaction. In a few cases, increasing the concentration of one of the reactants may not have an effect of the rate (Details of this is discussed in a latter section). The reaction between solid $CaCO_3$ and HCl acid can be used to demonstrate this concentration effect:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The rate of reaction can be altered by changing the concentration of the acid. (Also size of the calcium carbonate chips can be changed and it comes under the physical nature of the reactant). In this reaction it has been observed that if the $CaCO_3$ chips are large and in excess, then only a small fraction of the solid reacts. The rate will decrease over time as the hydrochloric acid is consumed because the concentration of HCl decreases over the time. Therefore, the rate of reaction can be monitored by measuring the pH of the solution, the decrease in the mass of calcium carbonate, or the increase in the volume of carbon dioxide. The easiest way is the volume measurement of the evolved CO_2 as it is the only gaseous species formed. In a particular experiment if we allow to react a known amount of $CaCO_3$ separately with a known volume of (~ 100 cm^3) of 0.50, 1.00 and 2.00 mol dm^{-3} HCl solutions, and monitor the volume of CO_2 formed with the time, following results could be observed (Figure 1.11).

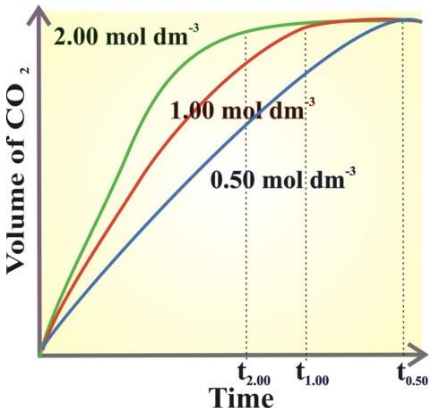


Figure 1.11 The variation in time for the generation of a constant volume of $CO_2(g)$ with the concentration of HCl in a reaction $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ at a given temperature.

From the above graph it can be seen that the time taken to produce a constant volume of CO_2 gas decreases ($t_{2.00} < t_{1.00} < t_{0.50}$) with the increasing concentration of HCl. That is the rate of the reaction increases with the increasing concentration of HCl. The reason for this increased rate is explained by the collision theory. At high concentrations collisions per unit time per unit surface area of ($CaCO_3$) among reactants increase and hence the rate of the reaction.

Though the reaction rate increases with concentration, it has to be noted that in certain type of reactions (multi-step) this phenomenon does not exist. For example, consider a reaction which occurs in a series of steps having widely different rates where some of the steps are fast and some of them are slow.

Suppose two reactants A and B react together to give product P in the following two steps:

$$\mathrm{A(aq)} \rightarrow \mathrm{X(aq)} \quad : \textbf{\textit{slow}}$$

$$\mathrm{B(aq)} + \mathrm{X(aq)} \rightarrow \mathrm{P} \quad : \textbf{\textit{fast}}$$

In the above reaction overall rate of the reaction is controlled by the ***slow*** step in which **A** makes X. This is described as the ***rate determining step*** of the reaction.

If the concentration of A is increased, it is clear that the rate of that step increases as described above. However, if the concentration of B is increased, of course, the rate of the step increases but that does not make any impact on the overall rate of the reaction because that the step happens very fast as soon as any X is formed. Therefore, in such a multi-step reaction, increase in the concentration of a particular reactant which involves in the fast step does not show any impact on the reaction rate. Nucleophilic substitution reactions are some of the examples for this type of reactions.

Pressure effects

Increasing the pressure of a reaction involving gaseous reactants increases the rate of reaction. Changing the pressure of a reaction involving only solids or liquids has no effect on the rate. For example, in the manufacture of ammonia by the Haber process, the rate of reaction is increased by the use of very high pressures. Increasing the pressure of a gas is exactly the same as increasing its concentration for a given mass of gas as can be understood from the *ideal gas equation* as follows.

$$PV = nRT$$

For a given mass of gas, we can rearrange the above equation as;

$P = \frac{n}{V} RT = C\,RT$ for a given volume at a constant temperature. As a product *(RT)* is a constant at constant temperature, pressure is directly proportional to the concentration. It is clear that when the pressure is increased collision between two different particles or two of the same particles increases and hence the rate of reaction. This is true for the systems with the both reacting molecules are in gaseous state at constant volume, or whether one is a gas and the other is a solid as described in the Figure 1.11.

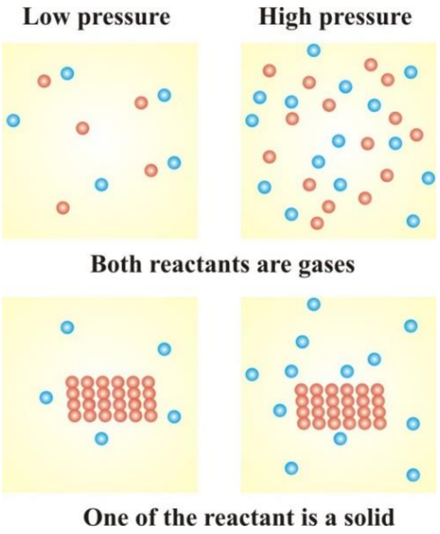


Figure 1.12 Effect of the pressure: Increase in pressure increases the concentrations of gaseous reactants.

Temperature effects

It has been understood that changing the temperature affects the rate of a reaction. As described in the above with the Maxwell-Boltzmann distribution of molecular energies in a gas increase in the temperature leads the rate of reaction to increase. For many reactions (not for all reactions) happening at around the room temperature, the rate of reaction approximately doubles for every 10 °C rise in temperature. Some reactions are virtually instantaneous (very fast). Examples are precipitation reactions from participant ions in solution to make an insoluble solid, or the reaction between hydrogen ions from an acid and hydroxide ions from an alkali in solution. So heating one of these would not make any acceptable or significant difference in the rate of the reaction.

As described in Unit 4 (gaseous state of matter) the increase in temperature of a system increases the average kinetic energy of its constituent molecules/particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time (per unit volume). This leads to increase the fraction of molecules processing energy for productive collisions (or in other words, exceeds the activation energy of the reaction). Both of these factors increase the reaction rate. Hence, the reaction rate of all (most) reactions increases with increasing temperature. Details of this will be discussed in a latter section. Conversely, the rate of reactions decreases with decreasing temperature. For example, refrigeration slows down the growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce.

In addition, in the systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the presence of dilute sulfuric acid and at temperatures around 100 °C, ethanol is converted to diethyl ether:

$$2CH_3CH_2OH(aq) \xrightarrow{H_2SO_4} CH_3CH_2OCH_2CH_3(aq) + H_2O(l)$$

At 180 °C, however, a completely different reaction occurs, which produces ethylene as the major product:

$$CH_3CH_2OH(aq) \xrightarrow{H_2SO_4} C_2H_4(g) + H_2O(l)$$

Physical nature of the reactants

Consider a reaction of two reactant molecules in the same liquid phase. They collide more frequently than when one or both reactants are solids (or when they are in different immiscible liquid phases). If the reactant molecules are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time per unit volume depends on concentration and temperature. If the reaction is heterogeneous, the reactants are in two different phases (solid/gas), and collisions between the reactants can occur only at the interface between the two phases. The number of collisions between reactants per unit time per unit volume is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. Usually rates of reactions depend on the physical state as Gaseous state > Liquid state > Solid state. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

In automobile engines, surface area effect on the reaction rate is used. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided iron burns slowly (or not at all), but spraying finely divided dust into a flame produces a vigorous reaction.

In the case of solid reactant, a more finely powdered solid reacts faster than the same mass present as a single lump because the powdered solid has a greater surface area than the single lump.

For example in the calcium carbonate and hydrochloric acid reaction in the laboratory you can observe that the powdered calcium carbonate reacts much faster with dilute hydrochloric acid than if the same mass was present as lumps of marble or limestone.

In the catalytic decomposition of hydrogen peroxide solid manganese(IV) oxide is often used as the catalyst. Oxygen is given off much faster if the catalyst is present as a powder than as the same mass of granules.

For example, in a reaction between magnesium metal and a dilute hydrochloric acid involves collision between magnesium atoms and hydrogen ions. The surface area of the metal here also affects the rate of the reaction. Fine magnesium powder causes evolution of hydrogen gas more rapidly than the magnesium strip.

Not only the physical nature as described earlier but nature of chemical bonds in reactants affects the rate.

Consider the following two reactions:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ ………… (a)

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ ………… (b)

The first reaction (a) is faster than the second because in the first reaction only N = O bond is to be broken where as in the second reaction (b) four C-H bonds are to be broken.

Similarly consider another example of two similar reactions:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ ……….. (c)

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ ……........ (d)

NO bond is weaker than CO bond, hence is broken easily. Thus reaction (c) is faster than (d).

Solvent effects

The nature of the solvent can also affect the reaction rates. The same reaction occurring in different solvents shows different rates depending on the polarities of solvents used.

When the reaction occurs in the same solvent, viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time per unit volume. Thus the reaction rates decrease with increasing solvent viscosity.

Catalyst effects

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate by changing the path of the reaction without undergoing a net chemical change itself. For example, the reaction $CO(g)+ 2H_2(g) \rightarrow CH_3OH(g)$ is very slow at room temperature and can be speeded up by introducing a catalyst. In addition, the decomposition of hydrogen peroxide in the presence of catalyst occurs in much more rapidly compared to the rate of that reaction without a catalyst. Because most catalysts are specific to certain reactions, they often determine the product of a reaction by accelerating only one of several possible reactions that could occur. In particular reactions with a catalyst the increase in concentration of the reactants sometimes may not increase the rate of reaction. For example, when a small amount of finely powdered solid catalyst is used in a reaction with a high enough concentration of reactant in solution the catalyst surface is totally covered up with reacting particles. Increasing the concentration of the solution even more cannot make any effect because the catalyst is already working at its maximum capacity. Details of these effects on the reaction rate and mechanisms will be discussed in a separate section.

1.7 Controlling the rate of a reaction by appropriately manipulating the concentration of reactants

1.7.1 Expressing the rate of a reaction: Average, instantaneous and initial rates

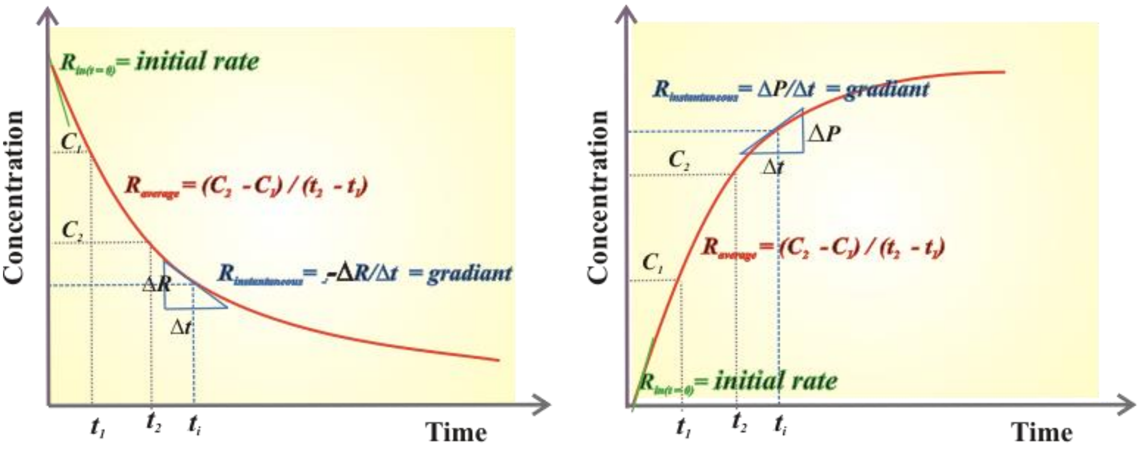
As described earlier *the rate varies as a reaction proceeds.* Consider the following hypothetical gas phase reaction between **A** and **B**.

$$A(g) + B(g) \rightarrow C(g)$$

For every molecule of **A**, a molecule of **B** reacts and hence [**A**] and [**B**] decrease at the same rate and we can write:

$$\text{Rate} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{\Delta[\text{B}]}{\Delta t}$$

Assume that the reaction is started with a known [A] in a closed vessel at 298 K and the concentration of is manured A at 10 second intervals after adding B. The obtained data can be plotted as shown in Figure 1.13. Rate *decreases* during the progress of the reaction because the *reactant* concentration decreases with the time (As **A** molecules react, the number of effective collisions decreases and hence the rate). If we plot the concentration of the products with the time the opposite curve will result. With the help of the plot of concentration vs time, following three types of rates can be defined.



(a) (b)

Figure 1.13 Definitions and graphical expression of reaction rates; average, instantaneous and initial rates: (a); change in rate for the reactants and (b); change in rate for the products. Note that the quantity of rate takes negative sign (as the slope is negative) and that for the products is positive. Therefore, in the calculations rate of consumption of reactants is multiplied by (-1).

Average rate

Over a given period of time, the **average rate** is the slope of the line joining two points along the curve. The average rate over the first 100 s time interval is the change in concentration during that time interval divided by the time taken. For example, when $C_1 = 3.50 \times 10^{-5}$ and $C_2 = 0.50 \times 10^{-5}$ mol dm^{-3},

$$\text{Rate}_{0-100} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,0.50 \times 10^{-5} - \;3.50 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,100 - 0\,]s}$$
$$= \;3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

This shows that during the first 100 s of the reaction, [A] decreases with the *average* of 3.0×10^{-7} mol dm^{-3} each second. However, this does not imply that the rate at any point along the curve is 3.0×10^{-7} mol dm^{-3} s^{-1}. We can clearly understand that the slope of the curve decreases with the time and hence the rate (average) should also decrease.

That means the rate over shorter intervals may be lower or higher than the average. In the above estimation in whole 100 s interval the decrease in [A] does not show the rate over any shorter time period. This *change* in reaction rate is evident when we calculate the average rate over two shorter periods. For example, in the first 10 s the average rate is given by ($C_1 = 3.50 \times 10^{-5}$ and $C_2 = 3.00 \times 10^{-5}$ mol dm^{-3});

$$\text{Rate}_{0-10} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,3.00 \times 10^{-5} - \;3.50 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,10 - 0\,]s}$$
$$= \;5.0 \times 10^{-7}\text{mol dm}^{-3}\ \text{s}^{-1}$$

Likewise the average rate in the 50-60 s interval is when $C_1 = 1.00 \times 10^{-5}$ and $C_2 = 0.75 \times 10^{-5}$ mol dm^{-3}.

$$\text{Rate}_{50-60} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,0.75 \times 10^{-5} - \;1.00 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,60 - 50\,]\ \text{s}}$$
$$= \;2.50 \times 10^{-7}\text{mol dm}^{-3}\ \text{s}^{-1}$$

Instantaneous rate

Average rate which is a constant for the time interval interested cannot be used to predict the rate of a reaction at a particular instant. So, to express the rate at a particular instant of time the instantaneous rate is determined. Rate of the reaction at a certain time is called as an instantaneous rate. The slope of a line tangent to the curve at any point gives the instantaneous rate at that time.

For example, the instantaneous rate at 50.0 s is;
To calculate this it is necessary to calculate the slope of the tangent line drawn to the curve at 50.0 s. Related points considered are (65, 1.25×10^{-5}) and (35, 0.75×10^{-5})

$$\text{Rate}_{50} = -\frac{\Delta[\text{A}]}{\Delta\, t} = -\frac{[(0.75 - \ 1.25)\times 10^{-5}]\ \text{mol dm}^{-3}}{[\ 65 - 35\ ]\text{s}} = 1.70 \times 10^{-7} \text{mol dm}^{-3}\ \text{s}^{-1}$$

It is very clear that the instantaneous rate is different from the average rate and in general, we use the term *reaction rate* to mean *instantaneous* reaction rate.

Initial rate

The instantaneous rate at the moment the reactants are mixed (that is, at $t = 0$) is the **initial rate.** Initial rate is calculated from the slope of the line tangent to the curve at $t = 0$ s (Figure 1.13). Measurements of initial rates is usually used in chemical kinetics to find other kinetic parameters.

When there is a reversible reaction the use of initial rate poses some complications. As a reaction proceeds in the *forward* direction (products → reactants), product increases, causing the *reverse* reaction (products → reactants), to occur more quickly. To find the overall (net) rate, we would have to calculate the difference between the forward and reverse rates. But, for the initial rate, $t = 0$, so product concentrations are negligible. So the rate of the reverse reaction would not affect the estimations.

As such in the simple way the initial rate or the instantaneous rate at t = 0, occurs when reactants have just been mixed and before any product accumulates.

1.7.2 Effect of concentration on reaction rate

Rate law

From the above section it is known that the frequency of effective collisions controls reaction rates. The more effective collisions mean the faster the rate. There are two ways to increase the frequency of collisions between molecules: increase the number of molecules in a constant volume at a given temperature or increase the kinetic energy of them by raising temperature. Increasing the number of molecules in a constant volume means the increase in concentration.

As was explained previously, for many reactions involving liquids or gases, increasing the concentration of the reactants increases the rate of reaction due to the increase in collision frequency. In some cases, increasing the concentration of one of the reactants may not affect the rate and also doubling the concentration of one of the reactants may not double the rate of the reactions always. Therefore, it is necessary to understand the behavior of concentration dependence of the reaction rate quantitatively with some models.

Consider a simple reaction;

$$A \rightarrow B$$

We can write,

$$\text{Rate} \propto [A]$$
$$\therefore \text{ Rate} = k\,[A]$$

where ***k*** is the proportionality constant and is called the "**rate constant".** The above expression is called the **rate law expression** or **rate law** of the reaction A → B. In this reaction we can say that the rate of the reaction is proportional to the concentration of A. If we assure that doubling the concentration of A doubles the rate and we can then write the rate law as;

$$\text{Rate} = k\,[A]^1 = k[A]$$

Consider the following decomposition reaction.

$$NH_4NCO_{(aq)} \rightarrow (NH_2)_2CO_{(aq)}$$

It has been experimentally found that the rate of the above reaction is proportional to the above square of the $NH_4NCO_{(aq)}$ concentration. That is when the concentration of $NH_4NCO_{(aq)}$ is doubled the rate will quadruple. Therefore, the rate law for the reaction can be written as,

$$\text{Rate} = k\,[NH_4NCO_{(aq)}]^2$$

From the above it can be noted that there are three parts appear in the rate law;

***k:* rate constant;** For a given reaction it has a number and (appropriate) units. Rate constant is different for different reactions and is different for the same reaction at different temperatures.

[$NH_4NCO_{(aq)}$]: the concentration of the reactants; If more than one reactant is present, any or all of them may be present in the equation. Sometimes it is the case that one or more reactants will not be appearing in the rate law.

2: the order of the reaction with respect to the relevant reactant; This is more often an integer like 1,2. but fractions are also possible sometimes. If the order is one, 1 is not written in the rate law expression. The order of the reaction can also be more than 2. However, they are not included in this discussion.

Experimentally derived rate laws for two reactions are given below.

$2NO_{(g)} + O_{2(g)} \rightarrow NO_{2(g)}$: Rate = $k\,[NO_{(g)}]^2[O_{2(g)}]$

$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$: Rate = $k\,[NO_{2(g)}]^2$

Now consider a general reaction between reactants A and B;

$$aA + bB \rightarrow \textit{Products}$$

The rate law for the reaction can be written as,

$$\text{Rate} = \boldsymbol{k}\,[A]^{x}[B]^{y}$$

From the above examples concentrations of **A** and **B** have to be raised to some power ***x*** and **y** to show how they affect the rate of the reaction. These powers are called the **orders of the reaction** with respect to **A** and **B**. The sum of *x* and y, **(*x* + y)** is called as the **overall order** of the reaction.

> *i.e the sum of powers of the concentration terms of the reactants written in the rate law expression is called the overall order of that chemical reaction.*

If the order of reaction with respect to **A** is 0 (zero), this means that the concentration of **A** doesn't affect the rate of the reaction. Mathematically, any number raised to the power zero is equal to 1. That is why that particular concentration term disappears from the rate equation.

> *Therefore, rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.*

Let's consider some examples of observed rate laws and note the reaction orders.
For the reaction between NO and H_2 gases,

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

the rate law is

$$\text{Rate} = k\,[NO_{(g)}]^2\,[H_{2(g)}]$$

This reaction is second order with respect to NO. And, even though $H_{2(g)}$ has the stoichiometric coefficient of 2 in the balanced equation, the reaction is first order with respect to $H_{2(g)}$. It is third order overall.

For the reaction between nitrogen monoxide and ozone,

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

the rate law is

$$\text{Rate} = k\,[NO(g)]\,[O_3(g)]$$

This reaction is first order with respect to $NO_{(g)}$ and first order with respect to $O_3(g)$, thus it is second order overall.

For the hydrolysis of 2-bromo-2-methylpropane,

$$(CH_3)_3CBr(l) + H_2O(l) \rightarrow (CH_3)_3COH(l) + HBr(aq)$$

the rate law is

$$\text{Rate} = k\,[(CH_3)_3CBr(l)]$$

This reaction is first order with respect to 2-bromo-2-methylpropane and zero order with respect to $H_2O(l)$, despite its coefficient of 1 in the balanced equation. If we want to note that water is a reactant, we can write the rate law as follows.

$$\text{Rate} = k\,[(CH_3)_3CBr(l)]\,[H_2O(l)]^0$$

This is a first order reaction overall.

The above examples give an important point:

> *Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation and must be determined experimentally. Although the rate constant is really a number with appropriate units, when describing a general rate law, we usually just write* ***k*** *but any value is true only at one temperature.*

The rate of a reaction is always expressed in terms of mol dm^{-3} s^{-1}. We can classify the reactions as *zeroth, first, second, etc.* order reactions. Assuming time is measured in seconds, The corresponding units of the *rate constant can be derived* as follows.

Zero order reactions

Consider the reaction; A → products

If the reaction is zero order, the rate law is,

$$\text{Rate} = k$$

The units of k must be the same as that of rate, **mol dm^{-3} s^{-1}.**

First order reactions

Consider the reaction; A → products

If the reaction is first order, the rate law is,

$$\text{Rate} = k\,[A]$$

$$\text{Units of } k; = \frac{\text{Rate}}{[A]} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}} = \mathbf{s^{-1}}.$$

Second order reactions

Consider a reactions A → products or A + B → products

If the reaction is second order, the rate law is,

$$\text{Rate} = k\,[A]^2 \quad \text{or} \quad \text{Rate} = k\,[A][B]$$

$$\text{Units of } k; = \frac{\text{Rate}}{[A]^2} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol}^2\text{ dm}^{-6}} = \mathbf{mol^{-1}\ dm^{3}\ s^{-1}}.$$

Example 1.8

Methyl acetate reacts with hydroxide ion according to the following equation.

$$CH_3COOCH_3(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + CH_3OH(aq)$$

The rate law is;

$$Rate = k\,[CH_3COOCH_3(aq)][OH^-(aq)]$$

What is the order of reaction with respect to each reactant, and the overall reaction order?

Answer

Because there are no superscripts to the right of each concentration term in the rate law, it means they are each first order. The reaction is first order in $CH_3COOCH_3(aq)$ and first order in $OH^-(aq)$. It is second order overall (1 + 1 = 2).

For example let's consider experimentally derived rate laws for the following reactions;

$2NO(g) + O_2(g) \rightarrow NO_2(g)$: Rate = $k\,[NO(g)]^2[O_2(g)]$

The reaction is second order with respect to $NO(g)$ *and first order with respect to* $O_2(g)$. *Overall order of the reaction is 3.*

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$: Rate = $k\,[NO_2(g)]^2$

The reaction is second order with respect to NO_2 (g) *and zero order with respect to* $CO(g)$. *Overall order of the reaction is 2.*

Example 1.9

Identify the reaction order from each of the following rate constants.

Answer

(i) $k = 5.6 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$

The unit of second order rate constant is $dm^3\ mol^{-1}\ s^{-1}$

$\therefore k = 5.6 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$ *represents the second order reaction.*

(ii) $k = 3 \times 10^{-4}\ s^{-1}$.

The unit of a first order rate constant is s^{-1}

$\therefore k = 3 \times 10^{-4}\ s^{-1}$ *represents the first order reaction.*

Table 1.1 summarizes the difference in rate of a reaction and rate constant to avoid the confusion between them.

Table 1.1 The difference in rate of a reaction and rate constant

Rate of reaction	Rate constant
It is the speed of conversion of reactants into products.	It is a proportionality constant.
It is measured as the rate of decrease of concentration of reactants or the rate of increase of concentration of products with time.	It is equal to the rate of reaction when the concentration of each of the reactants is unity.
It depends upon the initial concentration of reactants.	It is independent of the initial concentration of the reactants. It has a constant value for a given reaction at a fixed temperature.

1.7.3 Graphical representation of change in rate with concentration for zero, first and second order reactions

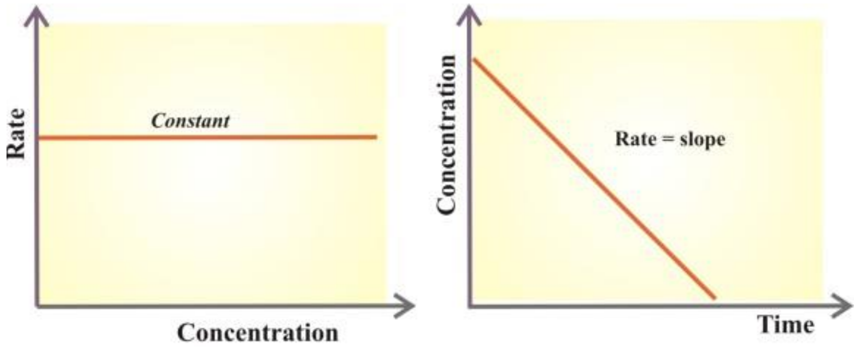
Zero order reactions

Zero order reactions means that the rate of the reaction is independent of the concentration of the reactants or we can say that the rate is proportional to zeroth power of the concentration of reactants. Consider the reaction,

$$A \rightarrow \text{Products}$$

$$\text{Rate} = k\,[A]^0 = k$$

Therefore, for any given concentration of A, the rate does not change implying that the rate is a constant with the concentration. Hence the plot of rate against the concentration is a horizontal straight line as shown in Figure 1.14 (a). In other words, the change in concentration over the time is a constant which can be obtained from the slope of the graph of concentration over the time as shown in Figure 1.14(b).



(a) (b)

Figure 1.14 (a) Variation of reaction rate over the concentration of the reactant and (b) Variation of concentration of the reactant over the time for a zero-order reaction.

The behaviour of the zero order reaction can be treated as follows too.
Consider a reaction:

$$A + B \rightarrow \text{Products}$$

Rate of the reaction is,

$$\text{Rate} = k\,[A]^a[B]^b$$

Assume that the concentration of B is very high and change in its concentration is negligible during the course of reaction. Therefore, the rate of reaction can be written as,

$$\text{Rate} = k'\,[A]^a \quad \text{where } k' = k\,[B]^b$$

As the reaction is zero order with respect to A, Rate = k' = constant

Therefore, the graph of rate verses the concentration is again a horizontal straight line as described above.

Some photochemical reactions and a few heterogeneous reactions are examples for zero-order reactions. Such reactions are not common.

Photochemical reaction between hydrogen and chlorine:

$$H_2\,(g) + Cl_2\,(g) \overset{h\nu}{\rightarrow} 2HCl\,(g)$$

This photochemical reaction is a zero-order reaction. The reaction is studied by placing H_2 and Cl_2 gases over water. The rate of reaction is studied by noting the rate at which water rises in the vessel due to dissolving of HCl formed. The rate of rise of water is the same as the rate of disappearance of H_2 and Cl_2, i.e., the concentration of the gaseous phase will not change with time, although the quantities will change.

Decomposition of N_2O(g) on a hot platinum surface:

$$N_2O(g) \rightarrow N_2(g) + 1/2\ O_2(g)$$

$$\text{Rate} = k\,[N_2O]^0 = k \text{ or,}$$

$$\frac{\Delta[N_2O]}{\Delta t} = k$$

Decomposition of NH_3(g) in the presence of molybdenum or tungsten is a zero-order reaction.

$$2NH_3(g) \xrightarrow{Mo} N_2(g) + 3H_2(g)$$

The surface of the catalyst is almost completely covered by NH_3 molecules. The adsorption of gas on the surface cannot be changed by increasing the pressure or

concentration of NH_3. Thus, the concentration of gas phase remains constant although the product is formed. Therefore, this reaction has zero order kinetics.
Other examples for zero order reactions are:
Iodination of acetone in the presence of $H^+(aq)$ ions:

$$CH_3COCH_3(aq) + I_2(aq) \xrightarrow{H^+(aq)} ICH_2COCH_3(aq) + HI(aq)$$

Experimentally found that the rate equation of this reaction does not containing $[I_2]$ factor, i.e.,

$$\text{Rate} = k\,[CH_3\,COCH_3(aq)\,][H^+(aq)]$$

Indicating that the reaction is zero order with respect to $[I_2(aq)]$

Characteristics of zero order reactions

The concentration of the reactants decreases linearly with time.
The time required for the reaction to be complete, i.e., time at which [A] is zero is given by;

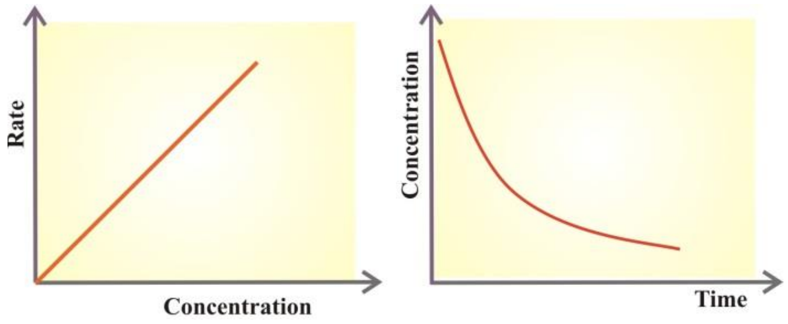
$$t_{\,completion} = \frac{[A]_0}{k} = \text{(Initial concentration)/ (Rate constant)}$$

First order reactions

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant. For example, considering the same reaction; A → products

$$\text{Rate} = k\,[A]$$

This takes the form; $y = mx$ and the graph of rate against the concentration will be a straight line going through the origin (0,0) as shown in Figure 1.15(a). The plot of the variation of concentration over the time will be a curve as shown in Figure 1.15(b).



(a) (b)

Figure 1.15 **(a)** Variation of reaction rate over the concentration of the reactant (gradient = rate constant) and **(b)** Variation of concentration of the reactant over the time for a first-order reaction.

Let us consider this in another way.
We can write,

$$\text{Rate} = k\,[\text{A}]$$

Taking log of both sides; $\log(\text{Rate}) = \log[\text{A}] + \log(k)$

Therefore, the graph of log (Rate) against log[A] will be ***y* = *mx* + *c*** type having the slope of one (1) and the intercept of log *(k)* as shown in Figure 1.17 (will be shown later).

As discussed previously, the rate constant of a first order reaction has only (inverse) time unit. It has no concentration unit. This means that the numerical value of *k* for a first order reaction is independent of the unit in which concentration is expressed. ($k = \frac{\text{rate}}{\text{concentration}} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}}$)Therefore, even if the concentration unit is changed the numerical value of *k* for a first order reaction will remain unchanged. However, it would change with the change in time unit. Say, *k* is 6.0×10^{-3} min^{-1}, then it can also be written as 1.0×10^{-4} s^{-1} .i.e. The numerical value of *k* has changed.

Following are some examples for the first order reactions.

Decomposition of $H_2O_2(aq)$ in aqueous solution

$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

Hydrolysis of methyl acetate in the presence of mineral acids

$$CH_3COOCH_3(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + CH_3OH(aq)$$

Inversion of cane sugar in the presence of mineral acids

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H^+} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

Decomposition of ammonium nitrite in aqueous solution

$$NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O(l)$$

Hydrolysis of diazo derivatives

$$C_6H_5N{=}NCl(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

In the cases where gas phase reactions are considered, it is necessary to use pressure terms instead of concentration terms in the rate law. For example, a reaction $A(g) \rightarrow B(g) + C(g)$ is a first order reaction. If the initial (at t = 0) pressure of the system is P_1 and the pressure of the system changed to P_2 after time t, it is necessary to understand the way we write the rate law of the reaction.

In this case we can assume that the partial pressure of A is decreased by -x due to its decomposition and hence the pressures built up by each of B and C would be +x. Therefore we can construct the system as follows.

	$A(g) \rightarrow$	$B(g) +$	$C(g)$
Initial	P_1	0	0
At time *t*	$P_1 - x$	x	x

Therefore, total pressure at time t = $(P_1-x) + x + x = P_1 + x = P_2$

$\therefore x = P_2 - P_1$

t Pressure of A at t = $P_1-x = P_1 - (P_2 - P_1) = 2P_1 - P_2$

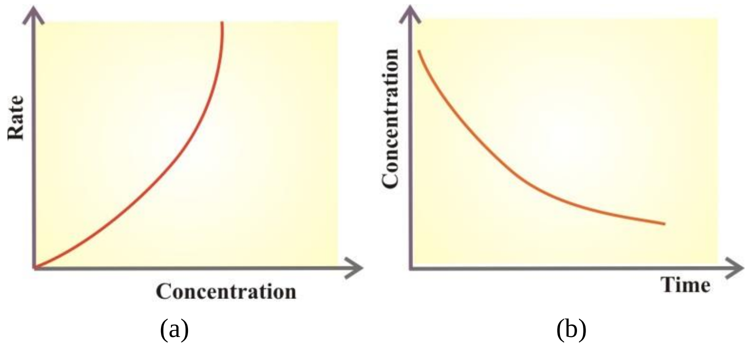
Thus these pressure terms can be used for the estimation of orders and rate constants of the reactions.

Second order reactions

In this class of reactions, the rate of the reaction is proportional to the second power of the concentration of the reactant or if the concentration of the respective reactant is doubled the rate will be quadrupled. For example, considering the same reaction; A → products

$$\text{Rate} = k\,[\text{A}]^2$$

This takes the form; $y = mx^2$ and the graph of rate against the concentration will be a upward-curve passes through the origin (0,0) as shown in the Figure 1.16(a). The variation of concentration against time will be a curve; however, slope would be higher than that for the first order plot as seen in Figure 1.16(b).



(a) (b)

Figure 1.16 (a) Variation of reaction rate over the concentration of the reactant and (b) Variation of concentration of the reactant over the time for a second-order reaction.

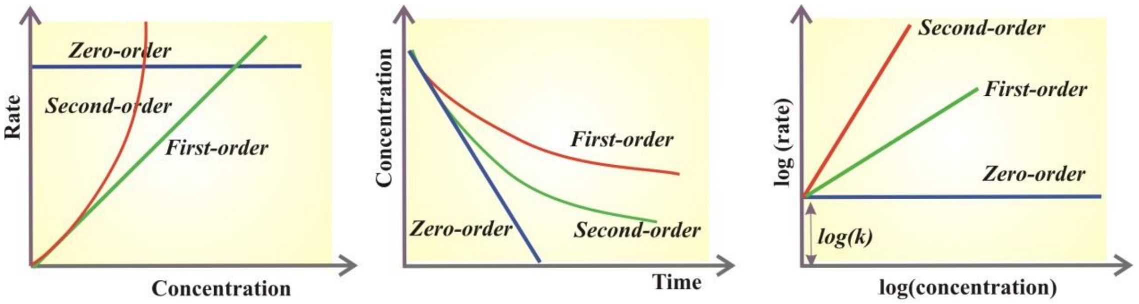
Let us consider this in another way,

We can write,

$$\text{Rate} = k\,[\text{A}]^2$$

Taking log of both sides; log (Rate) = 2 log [A] + log(k)

Therefore, the graph of log(rate) against log[A] will be $\boldsymbol{y = mx + c}$ type having the slope of two (2) and the intercept of log(k). As a summary Figure 1.17 compares the above cases in order to understand the differences in zeroth, first and second order reactions easily.



(a) (b) (c)

Figure 1.17 Comparison of first order, second order and zero order reactions; **(a)** Variation of reaction rate with concentration. The plot is a horizontal line for the zero order reaction because the rate does not change no matter what the value of [A]. The plot is an upward-sloping line for the first order reaction because the rate is directly proportional to [A]. The plot is an upward-sloping curve for the second order reaction because the rate increases exponentially with [A]. **(b)** Variation of concentration over time. The decrease in [A] does not change as time goes on for a zero order reaction. The decrease slows down as time goes on for a first order reaction. The decrease is even more for a second-order reaction. **(c)** Variation of log(rate) with log(concentration). The plot is a horizontal line for the zero order reaction. The plot is a straight line with the slope one for the first order reaction and the plot is a straight line with the slope two for a second order reaction.

Example 1.10

Consider the following first order reaction.

$$N_2O_5(g) \rightarrow 2NO_2(g) + ½O_2(g)$$

At 328 K, when the concentration of $N_2O_5(g)$ was 2.00×10^{-2} mol dm^{-3} the rate of the decomposition was found to be 1.00×10^{-2} mol dm^{-3}s^{-1}. Calculate the first order rate constant of the reaction at 328 K.

Answer

$$\text{Rate} = k\,[A] = 1.00 \times 10^{-2}\ \text{mol dm}^{-3}\ s^{-1}$$

$$\therefore k = \frac{1.00 \times 10^{-2}\ mol\ dm^{-3}\ s^{-1}}{2.00 \times 10^{-2}\ mol\ dm^{-3}} = 0.50\ \ s^{-1}$$

Example 1.11

Consider the reaction between oxygen and nitrogen monoxide.

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

Rate law of the reaction is $\text{rate} = k\ [O_{2(g)}]\ [NO(g)]^2$ at 300 K.

When the concentrations of $O_2(g)$ and NO(g) were 1.00×10^{-2} and 2.00×10^{-2} mol dm^{-3}, respectively, the rate was found to be 3.20×10^{-3} mol dm^{-3} s^{-1} at 300 K. Calculate the rate constant for the reaction at 300 K.

Answer

$$k = \frac{\text{rate}}{[O_{2(g)}]\ [NO(g)]^2}$$

$$= \frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{[1.00 \times 10^{-2} \text{mol dm}^{-3}]\ [2.00 \times 10^{-2}\ \text{mol dm}^{-3}]^2}$$

$$k = 8.00 \times 10^2\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

Example 1.12

Consider the hypothetical reaction given below at a given temperature.

$$aA + bB \rightarrow cC + dD$$

In a particular experiment carried out at a given temperature, the rate of the reaction was found to be 5.00×10^{-4} mol dm^{-3} s^{-1} when the concentrations of A and B are 1.00×10^{-5} mol dm^{-3} and 2.00 mol dm^{-3} respectively. It has also been observed that the rate doubles as the concentration of A is doubled. Calculate the rate constant of the reaction.

Answer

For the reaction we can write the rate law as,

$$\text{rate} = k\ [A]^x\ [B]^y$$

It is given that the rate doubles as the concentration of A is doubled. Therefore, we can conclude/find that the reaction is first order with respect to A. Next, it is necessary to understand the dependence of rate on the concentration of B, which is much higher than the concentration of A ($1.00 \times 10^{-5} <<< 2.00$ mol dm^{-3}). Thus, it is evident that the reaction rate does not depend on the concentration of B, or assuming that [B] remains unchanged during the reaction. Now the rate law of the reaction can be rewritten as,

$$\text{Rate} = k'\ [A]$$

$$k' = \frac{5.00 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{1.00 \times 10^{-5}\ \text{mol dm}^{-3}} = 50\ \text{s}^{-1}$$

Following example gives an idea about the relation between order and the concentration of the reactants. Consider a hypothetical reaction,

$$\mathrm{aA + bB \rightarrow cC + dD}$$

and the rate low of the reaction is given by; Rate = $k\,[\mathrm{A}][\mathrm{B}]^2$

(a) Consider that the initial concentrations of both A and B are 1.0 mol $\mathrm{dm}^{-},{}^{3}$

$$\mathrm{Rate}_1 = k\,[1.0][1.0]^2\ \mathrm{mol}\ {}^3\mathrm{dm}^{-9} = k\ \mathrm{mol}\ {}^3\mathrm{dm}^{-9}$$

If the concentration of A is doubled while keeping the concentration of B constant at 1.0 mol dm^{-3},

$$\mathrm{Rate}_2 = k\,[2.0][1.0]^2\ \mathrm{mol}\ {}^3\mathrm{dm}^{-9} = 2k\ \mathrm{mol}\ {}^3\mathrm{dm}^{-9}$$

i.e. The rate is doubled when the concentration of A is doubled revealing that the reaction is first order with respect to A.

(b) If the concentration of B is doubled while keeping the concentration of A constant at 1.0 mol dm^{-3},

$$\mathrm{Rate}_3 = k\,[1.0][2.0]^2\ \mathrm{mol}\ {}^3\mathrm{dm}^{-9} = 4k\ \mathrm{mol}\ {}^3\mathrm{dm}^{-9}$$

i.e. The rate is quadrupled when the concentration of B is doubled revealing that the reaction is second order with respect to B.

1.7.4 Methods to determine the order of a reaction and rate constant (Rate law)

From the above last two examples, when a concentration of one reactant is in large excess compared to the other reactant it has been assumed that the concentration of that reactant can be considered a constant during the course of reaction. This postulate can be used to investigate the kinetics of reactions involving more than one reactant and the experiments can be designed as such.

There are two fundamentally different approaches to this; follow a particular reaction all the way through, and process the results from that single reaction or investigate the change occurred in the *initial rate* of the reaction as concentrations of the reactants are changed. In the first approach experiments are carried out by keeping the concentrations of all the reactants except one is in large excess. Thus for example, for the reaction:

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$$

The rate law is: Rate = $k\,[\mathrm{A}]^{x}[\mathrm{B}]^{y}$

Let B to be in large excess relative to $[\mathrm{A}]_0$, so that [B] can be considered constant during a course of reaction. Thus we may write:

$$\mathrm{Rate} = k'\,[\mathrm{A}]^{x}$$

where:

$$k' = k\,[\mathrm{B}]^{y}$$

By taking logarithm of both sides we get:

$$\log(\text{Rate}) = \boldsymbol{y}\log[\mathrm{A}] + \log(k')$$

which is the equation of a straight line and by plotting log(Rate) against log[A] with gradient **y** and intercept of log(*k*\`), the order and the rate constant of the reaction would be estimated.

The process can then be repeated by letting A in excess to determine ***x*** and *k*.

Method of initial rates

As we know, the rate laws are not derived from the reaction equation and are derived from experimental data. The method of initial rates is an experimental method to investigate the kinetics of reaction leading to find the rate constant and orders of a given reaction, in which a reaction is run multiple times with different initial concentrations of each reactant. The initial rate of each experiment is compared with the initial concentrations of the reactants to determine its order. The method is most often performed in the following way:

In a simple way of initial rate experiments involve measuring the time taken for some easily measurable or recognizable event that happens very early in a reaction. This could be the time taken for, say, to liberate a *given volume* of a gas, to from a measurable amount of a *precipitate* or for a *colour change* to occur. Further, some *titrations* can be performed by stopping a reaction after a given period of time.

Then the concentration of one of the components of the reaction is changed, keeping everything else such as the concentrations of other reactants, the total volume of the solution and the temperature and so on constant. Then the time taken for the same event to take place has to be measured with that new concentration. This has to be repeated for a range of concentrations of the substance interested in. It is worth to cover a reasonably wide range of concentrations, taking perhaps five or more different concentrations varying from the original one down to half of it or less.

This means that for each reactant, it is needed to run at least a pair of reactions in which that reactant's concentration is doubled (changed) while all other reactant concentrations and conditions are held constant. This isolates the effect on rate to that single reactant.
Most often one of three things happens to the initial rate when the reactant concentration is doubled:

(a) The rate does not change: This means that the rate is independent of that reactant. The reaction is zero order with respect to that reactant.

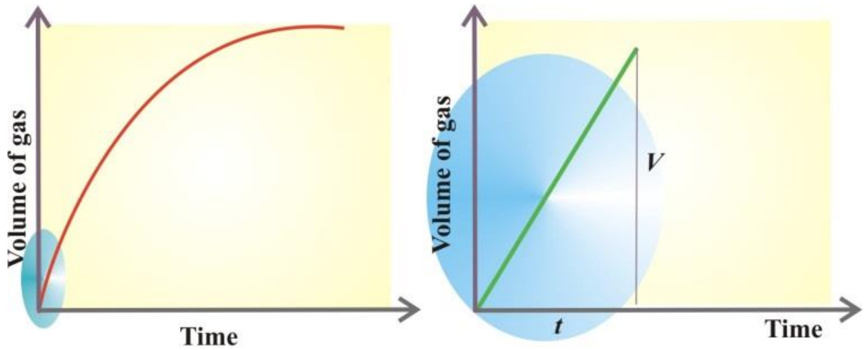
(b) The rate doubles: This means that the rate is proportional to the concentration of that reactant. The reaction is first order with respect to that reactant.

(c) The rate quadruples: This means that the rate is proportional to the square of the concentration of that reactant. The reaction is second order with respect to that reactant.

Once the order for each reactant is found, take any of the experiments and substitute in concentration values and the measured rate to determine the numerical value of the rate constant *k***.**

Exploration of the results from initial rate experiments

Consider a simple example of an initial rate experiment in which a gas being produced. This could be a reaction between a metal and an acid, for example, or the catalytic decomposition of hydrogen peroxide. Assume that the volume of the evolved gas being measured with the time and that can be shown as a plot of volume of gas given off against time as shown in the Figure 1.18.



(a) (b)

Figure 1.18 Measuring the volume of an evolved gas in an initial rate experiment. (**a)** Change in volume over the time, volume increases very fast at the beginning and slows down when the reaction progresses. (**b)** Expanded view of the shaded area of (**a)** Increase in volume at the very beginning of the reaction is linear and therefore it is possible to measure the time taken to produce a constant volume of gas by varying the concentration of the desired reactant at a given temperature.

We know that a measure of the rate of the reaction at any point is found by measuring the slope of the graph. Since we are interested in the initial rate, it is necessary to find the slope at the very beginning (say at *t ~0 s).* Of course, it is impossible to observe some changes at the time = 0, and therefore, we measure the time taken for a given/constant change to happen in the system (like a constant volume). However, since the concentration of the species at the very beginning is almost the initial concentration, it is assumed that during the event measured, the change in concentration of that particular reactant is negligible.

In the Figure 1.18(a), variation of volume over time in the entire range shows a curve. By enlarging the circled area, i.e. enlarging the very beginning of the first curve, it can be seen that it is approximately a straight line at that point (Figure 1.18(b)). That is a reasonable approximation once very early stage in the reaction is considered. This can also be obtained by drawing a tangent line to the curve at the $t \sim 0$. The slope in this case is simply V/t. Now suppose the experiment is carried out again with different (lower) concentrations of the reagent and the time taken to evolve the same volume of the gas is measured at the very beginning of the reaction as earlier. Following types of graphs as shown in Figure 1.19 would result for the formation of a constant volume of a gas in which different time measurements could be obtained.

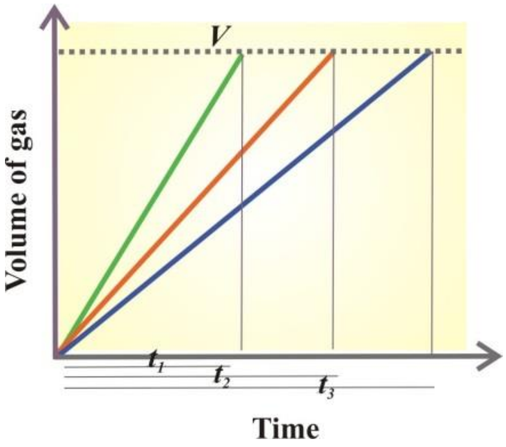


Figure 1.19 Measuring time taken to produce a constant volume of a gas with different concentrations of the reactant in an initial rate experiment. When there is no linearity at the beginning of the reaction, gradient of the tangent has to be determined.

From these experiments the initial rates (in terms of volume of gas produced per second) can be deduced as:

Experimet 1 : Initial rate$_1$ = V/t_1
Experimet 2 : Initial rate$_2$ = V/t_2

In the above two experiments as the time taken to evolve a constant volume (V) of a gas is measured it is easy to compare the initial rates obtained. It is clear from the above two that the initial rate is inversely proportional to the time taken and therefore;

$$\text{Initial rate} \propto \frac{1}{t}$$

Thus, normal in experiments of this type, $\frac{1}{t}$ can be used as a measure of the initial rate without any further calculations. Therefore, the initial rates measured by varying concentrations of respective reactant(s) can be used to determine the orders of reactions and finally the value of the rate constant. Following examples give some insight into this type of experiments.

Example:

Consider a hypothetical reaction at a given temperature:

$$A + 2B \rightarrow C + D$$

The rate law, expressed in general terms, is

$$\text{Rate} = k[A]^m[B]^n$$

To find the values of **m** and **n**, a series of experiments was carried out in which one reactant concentration was changed while the other was kept constant. The initial rate measured in each case is shown in the table shown below. Using the data given in the table calculate the values of ***m, n*** and ***k.***

Table 1.2 Data set for calcultion

Experiment	**Initial [A]/ mol dm^{-3}**	**Initial [B]/ mol dm^{-3}**	**Initial rate/ mol dm^{-3} s^{-1}**
1	2.5×10^{-2}	3.0×10^{-2}	1.75×10^{-3}
2	5.0×10^{-2}	3.0×10^{-2}	3.50×10^{-3}
3	2.5×10^{-2}	6.0×10^{-2}	3.50×10^{-3}

1. *Finding m, the order with respect to A*

   By comparing experiments 1 and 2, in which [A] doubles and [B] is constant, we can obtain m. First, take the ratio of the general rate laws for these two experiments:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k\,[\text{A}]_1^m\,[\text{B}]_1^n}{k[\text{A}]_2^m\,[\text{B}]_2^n}$$

   In experiments 1 and 2, $[\text{B}]_1$ and $[\text{B}]_2 = 3.0 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

   Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[\text{A}]_1^m}{[\text{A}]_2^m}$$

$$\frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{3.50 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}} = \frac{(2.5 \times 10^{-2}\ \text{mol dm}^{-3})^m}{(5.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^m$$

$$\therefore\ \boldsymbol{m = 1}$$

   Thus, the reaction is first order *with respect to* A, because when [A] doubles, the rate doubles.

2. *Finding n, the order with respect to B.*

   Comparing experiments 3 and 1 in which [A] is held constant and [B] doubles:

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{k\,[\text{A}]_1^m\,[\text{B}]_1^n}{k[\text{A}]_3^m\,[\text{B}]_3^n}$$

   In experiments 1 and 3, $[\text{A}]_1$ and $[\text{A}]_3 = 2.5 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

   Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{[\text{B}]_1^n}{[\text{B}]_3^n}$$

$$\frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{3.50 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}} = \frac{(3.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}{(6.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^n$$

$$\therefore\ \boldsymbol{n = 1}$$

   Thus, the reaction is also first order with respect to B, because when [B] doubles, the rate doubles.

   Therefore the rate law of the reaction is

$$\text{Rate} = k\,[\text{A}][\text{B}]$$

   The value of k can be obtained by substituting appropriate values in the rate expression as for the experiment 1 ;

$$1.75 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1} = k\,(2.5 \times 10^{-2})(3.0 \times 10^{-2})\ \text{mol}^2\ \text{dm}^{-6}$$

$$k = \frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{7.50 \times 10^{-4}\ \text{mol}^2\ \text{dm}^{-6}} = 2.3\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$

Note: What would be the initial rate of the above reaction if the concentrations of both A and B are doubled at the same time?

When both [A] and [B] doubled, the rate should quadruple to $7.00 \times 10^{-3}\ mol\ dm^{-3}s^{-1}$ *and therefore, that confirms the rate law derived from the experiment.*

Note especially, that while the order with respect to B is 1, the coefficient of B in the balanced equation is 2. Thus, as mentioned earlier, reaction orders must be determined from experiment.

Example 1.13

Consider the real reaction between oxygen and nitrogen monoxide at 300 K.

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

The general rate law is,

$$\text{Rate} = k\,[O_2(g)]^m[\,NO(g)]^{\,n}$$

Using the data given in the table below derive the rate law of the reaction at 300 K.

Experiment	Initial $[O_2(g)]$ or $[O_2(g)]_0$/ mol dm^{-3}	Initial $[NO(g)]$ or $[NO(g)]_0$/ mol dm^{-3}	Initial rate mol dm^{-3} s^{-1}
1	1.0×10^{-2}	2.0×10^{-2}	3.20×10^{-3}
2	2.0×10^{-2}	2.0×10^{-2}	6.40×10^{-3}
3	1.0×10^{-2}	4.0×10^{-2}	12.80×10^{-3}
4	3.0×10^{-2}	2.0×10^{-2}	9.60×10^{-3}

$[O_2(g)]_0$ and $[NO(g)]_0$ are the initial concentrations.

Answer

1. Finding m, the order with respect to $O_2(g)$.

   By comparing experiments 1 and 2, in which $[O_2(g)]$ doubles and $[NO(g)]$ is constant, we can obtain m. First, take the ratio of the general rate laws for these two experiments:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k\,[O_2]_1^m\,[NO]_1^n}{k[O_2]_2^m\,[NO]_2^n}$$

   In experiments 1 and 2, $[NO]_1 = [NO]_2 = 2.0 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

   Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[O_2]_1^m}{[O_2]_2^m}$$

$$\frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{6.40 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}} = \frac{(1.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}{(2.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^m$$

$$\therefore\ \boldsymbol{m = 1}$$

   Thus, the reaction is first order with respect to O_2, because when $[O_2(g)]$ doubles, the rate doubles.

   Experiment 4 also supports the value of m (m =1); rate increases thrice when the concentration is increased by three times.

2. Finding n, the order with respect to NO(g).

Comparing experiments 1 and 3 in which $[O_2]$ is held constant and [NO] doubles:

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{k\,[\text{O}_2]_1^m\,[\text{NO}]_1^n}{k[\text{O}_2]_3^m\,[\text{NO}]_3^n}$$

In experiments 1 and 3, $[\text{O}_2]_1$ and $[\text{O}_2]_3 = 1.0 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{[\text{NO}]_1^n}{[\text{NO}]_3^n}$$

$$\frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{12.8 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}} = \frac{(2.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}{(4.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^n$$

$$\therefore\ \boldsymbol{n = 2}$$

Thus, the reaction is second order with respect to NO, because when [NO] doubles, the rate increases four times.

Therefore the rate law of the reaction is

$$\text{Rate} = k\,[\text{O}_2(\text{g})]\,[\text{NO}(\text{g})]^2$$

Note: In some cases we may not have exactly simplifying numbers in this calculations. For example if the initial rate of the experiment 1 is 3.10×10^{-3} mol dm^{-3}s^{-1}, then we get $\frac{3.10 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{6.40 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}} = 0.485$ and hence

$$0.485 = \left(\frac{1}{2}\right)^m = (0.500)^m.$$

This can be solved by taking log as;

log (0.485) = *m* log *(0.500)*

$$m = \frac{\log(0.485)}{\log(0.500)} = 1.04 \textit{ or } m = \frac{\log(0.500)}{\log(0.500)} = 1\ \ (as\ 0.485 \sim 0.500)$$

As m has to be an integer, m =1

The value of k can be obtained by substituting appropriate values in the rate expression as for the experiment 1.

$$3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1} = k\,(1.0 \times 10^{-2})(2.0 \times 10^{-2})^2\ \text{mol}^3\ \text{dm}^{-9}$$

$$k = \frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{4.0 \times 10^{-6}\ \text{mol}^3\ \text{dm}^{-9}} = 8.00 \times 10^2\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$$

In addition to the above type of calculations, the data obtained by several experiments can be plotted as a plot of $\frac{1}{t}$ against the varying concentrations of the reactant. If the reaction is first order with respect to that substance, then straight line will result. That's because in a first order reaction, the rate is proportional to the concentration.

If the plot is a curve, then it isn't first order. It *might* be second order (or some sort of fractional order).

The best way for this analysis with several data of initial rates is constructing a *log graph*. As previously discussed, for a reaction involving A, with an order of ***n*** with respect to A, the rate equation is:

$$\textbf{Rate} = k\,[\mathbf{A}]^{n}$$

Taking the log of each side of the equation, you get:

$$\log(\text{Rate}) = n \log[\text{A}] + \log k$$

Therefore the plot of log(Rate) against log[A], would give a straight line with slope *n*, that is the order of the reaction. The intercept of the plot is log(*k)* and hence *k* can be obtained.

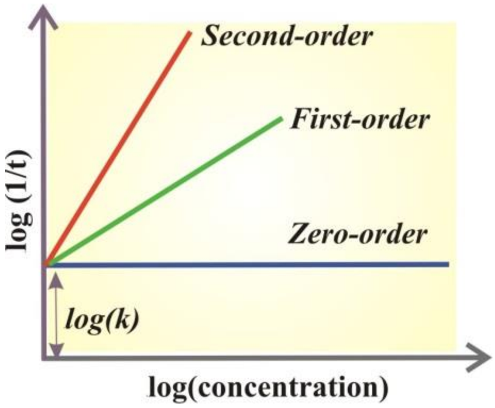


Figure 1.20 Shapes of graphs that could be obtained from initial rate experiments (Figure 1.17(a) can also be obtained)

Some kind of laboratory experiments can be designed and carried out by measuring time measurements to occur for a constant extent of the reaction and then by plotting the appropriate graphs, the order of the reaction(s) can be deduced. Following are some examples which are included in your practical manual.

Thiosulphate-acid reaction

Addition of dilute nitric acid (HNO_3) to sodium thiosulphate ($Na_2S_2O_3$) solution at room temperature results in a slow formation of a pale yellow precipitate of sulphur through the following reaction.

$$Na_2S_2O_3(aq) + 2HNO_3(aq) \rightarrow S(s) + 2NaNO_3(aq) + SO_2(g) + H_2O(l)$$

In this system, there is a simple, but very effective, way of measuring the time taken for a small fixed amount of sulphur precipitate to form. As a precipitate is formed in the reaction, it is possible to measure the time taken to form a fixed amount of precipitate under different concentrations of reactants at a given temperature as follows.

Keep a flask or small beaker on a piece of paper with a cross mark (X) drawn on it, and then look down through the reaction mixture until the cross disappears. First, put a known amount of thiosulphate solution in to a beaker and then add a small amount of dilute acid solution with known different concentrations and measure the time it takes for the cross to disappear (Detailed experiment is discussed in your practical manual). In this experiment, the actual concentration of the sodium thiosulphate does not have to be known because in each case, its relative concentration can be estimated with the total volume of the reaction mixture. The solution with 40 cm^3 of sodium thiosulphate solution plus 10 cm^3 of water has a concentration which is 80% of the original one, for example. The one with 10 cm^3 of sodium thiosulphate solution plus 40 cm^3 of water has a concentration which is 20% of the original one.

After collecting data on the time measurements, the data can be plotted as the variation of 1/t with the thiosulphate concentration and from that the reaction order with respect to the reactant thiosulphate can be deduced. In addition to this, the effect of temperature on the reaction rate could also be investigated as described in the practical manual.

Iodine clock experiments

There are several reactions given the name "iodine clock". They are all reactions which give iodine as one of the products and help measure the time taken for the formation of constant amount of iodine. This is the simplest of them, because it involves the most familiar reagents. For example, kinetics of the reaction of the oxidation of iodide ions by hydrogen peroxide under acidic conditions can be monitored by such “iodine clock” experiments. In the acidic medium iodide ions reacts with hydrogen peroxide as follows.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

In this reaction the amount of iodine ($I_{2(aq)}$) produced can be monitored by using starch when a small amount has been formed. Iodine reacts with starch solution to give a deep blue colored complex turning the solution blue. If a little volume (few drops) of starch solution is added to the reaction mixture initially, as soon as the first trace of iodine was formed, the solution would turn blue. However, just the addition of starch will not help to follow the kinetics as the colour change occurs instantaneously. Therefore, another way to remove the iodine produced is used. As iodine also reacts with sodium thiosulphate solution that can be used to consume some iodine produced.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

If a very small known amount of sodium thiosulphate solution is added to the reaction mixture (including the starch solution), it will react with the iodine that is initially produced, and so the iodine will not affect the starch and no blue colour is displayed. However, when that small amount of sodium thiosulphate has been used up, there is nothing to stop the next bit of iodine produced from reacting with the starch. The mixture suddenly goes blue and the time taken to appear the blue colour can be measured for different experimental conditions.

In this experiment, effect of changing the hydrogen peroxide concentration, or the iodide ion concentration, or the hydrogen ion concentration - each time, keeping everything else constant would let you find the orders with respect to each reactant taking part in the reaction.

Note that a similar experiment is included in the practical manual to follow the kinetics of the reaction;

$$2I^{-}(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$$

In addition to the above - mentioned reactions, the method of initial rate can be used to monitor the kinetics of the catalytic decomposition of hydrogen peroxide by monitoring the volume of oxygen gas produced at a given temperature.

Above examples show that the kinetics of reactions can be investigated by carefully designed experiments. It has to be noted that following requirements must be fulfilled once such experiments are carried out.

(i) Controlling the temperature of the system with a good thermostat (this will be learnt during practical) as rates change (exponentially) with temperature.

(ii) Choosing an accurate timing device.

(iii) An appropriate method for determining the concentration of reactant or product. This can be done through a measurement of a rapidly determinable physical property of the reaction mixture.

Following the course of a single reaction

Rather than doing a whole set of initial rate experiments, information about orders of reaction can also be obtained by following a particular reaction from start to finish.

There are two different ways to do this. Withdraw samples of the mixture at intervals and find out how the concentration of one of the reagents is changing by doing an appropriate titrations. Or by measuring some physical property of the reaction which changes as the reaction proceeds - for example, refractive index, absorbance, etc. Then the set of values obtained for concentration can be plotted against time and the rates of reaction at different points need to be extracted from the graph. Finally, by plotting log(rate) against log(concentration) the order of reaction can be estimated.

Half-life of a reaction ($t_{1/2}$)

As the reaction proceeds, the concentration of the reactant(s) decreases and another measure of the rate of reaction relating the concentration to the time is the half-life. The concept of half-life is useful for describing the rough speed of a reaction. The half-life of a reaction is the time it takes for the consumption of reactants by half of the initial amount. In other words, the half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $\mathbf{t_{1/2}}$ and this is affected by temperature. This can be represented by the Figure 1.21.

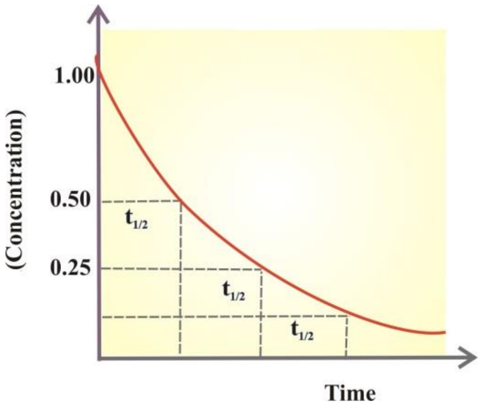


Figure 1.21 Definition of half-life (for a first order reaction)

For example, consider the first order decomposition of hydrogen peroxide. The table below shows the concentration of H_2O_2 in increments of 600 min.

Table 1.3 Concentration of H_2O_2 in increments of 600 min

Time/ min	Number of half-lives	Fraction remaining	$[H_2O_2]$/ mol dm^{-3}
0	0	1	0.020
600	1	1/2	0.010
1200	2	1/4	0.005
1800	3	1/8	0.0025
2400	4	1/16	0.0013
3000	5	1/32	0.00065

Note that in the first 600 min, the concentration drops from 0.020 mol dm^{-3} to 0.010 mol dm^{-3}. That is, it drops in half. The half-life of the reaction is therefore 600 min. Then, when another 600 min passes (from t = 600 to t = 1200) and the concentration drops in half again: from 0.010 mol dm^{-3} to 0.0050 mol dm^{-3} the half-life is still 600 min. Successive half-lives produce reaction mixture with concentration fractions of 1/2, 1/4, 1/8, 1/16 and 1/32 as shown in the table.

Half-life of a first order reaction

Half-life of a first order reaction is given by, $\mathbf{t_{1/2}} = \frac{0.693}{k}$ *

k is the rate constant.

Since k is a constant for a given reaction at a given temperature and the expression does not contains any concentration term, the half-life of a first order reaction is a constant independent of initial concentration of reactant**.**

This means that if we start with 2.00 mol dm^{-3}, and of a reactant reacting with first order kinetics and after 20 minute it is reduced to 1.00 mol dm^{-3}, and the half-life of the reaction will be 20 minutes. In other words, during the first 20 minutes 50% of the reaction completes, then in 40 minutes 75%, in 60 minutes 87.5% and so on. This can also be understood from the Figure 1.21.

Example 1.14

A certain first-order reaction has a half-life of 20.0 minutes.

(i) Calculate *k* for the reaction.

(ii) How much time is required for this reaction to be 75% complete?

Answer

(i) Half-life of a first order reaction is given by $\mathbf{t_{1/2}} = \frac{0.693}{\mathrm{k}}$.

$$20.0 \text{ min} = \frac{0.693}{k}$$

$$k = \frac{0.693}{20 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

(ii) If the reaction is 75% complete that means there is 25% of the reactant is left or the reaction has occurred up to the second half life cycle. Therefore, the time taken to complete the reaction by 75% is two-half-lives, i.e 40 min.

Show that in a first order reaction, time required for completion of 99.9% is 10 times the half-life ($t_{1/2}$) of the reaction.

When 99.9% is completed the remaining amount is 0.100 % or 0.001
The value of remaining concentration after 10 half-life cycles
Can be written as $\frac{1}{2^n} = \frac{1}{2^{10}} = \frac{1}{1024} = 0.001$
Therefore, the time required for the completion of 99.9% of a first order reaction is 10 times the half-life.

Half-life of a zero order reaction is given by;

$$\mathbf{t_{1/2}} = \frac{[\mathrm{A}]_0}{2k} \;*$$

$[\mathrm{A}]_0$ is the initial concentration. Therefore, half-life of the zero-order reaction depends on the initial concentration.

* *Derivation of this equation will not be tested at the G. C. E. (A/L) Chemistry examination.*

1.8 The effect of the physical nature (surface area) on the reaction rate

In the section 1.1 a little description on the effect of the physical nature of the reactant on the rate has been given. When the reactions involve solid reactants, increasing the surface area by turning the solid into a fine powder enhances the rate of reaction due the increase in the number of collisions between reacting particles.

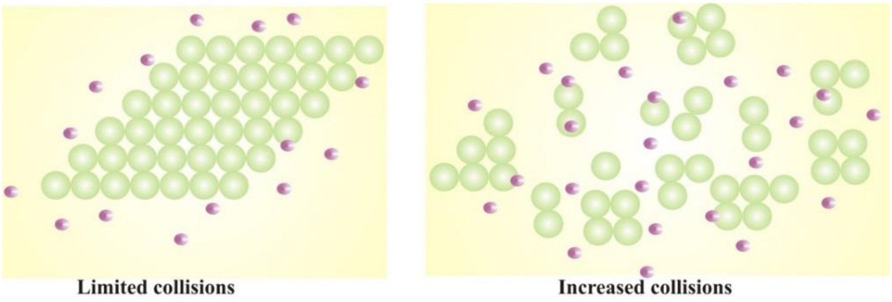
As described earlier, rates of reactions depend on the physical nature as Gaseous state > Liquid state > Solid state. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase. In the case of solid reactant, the more finely powdered solid reacts faster than the same mass present as a single lump because the powdered solid has a greater surface area than the single lump.

For example in the reaction between calcium carbonate and hydrochloric acid you can observe in the laboratory that powdered calcium carbonate reacts much faster with dilute hydrochloric acid than the same mass of marble or limestone in lumps.

In the catalytic decomposition of hydrogen peroxide solid manganese(IV) oxide is often used as the catalyst. Oxygen is given off much faster if the catalyst is present as a powder than when the same mass of it is present as granules.

In these cases with increasing surface area of the solid, the frequency of collisions increases and the rate of the reaction thus increases.

For example, the reaction between magnesium metal and a dilute hydrochloric acid involves collision between magnesium atoms and hydrogen ions. The effect of surface area can be understood by the Figure 1.22.



(a) (b)

Figure 1.22 Effect of particle size on the reaction rate; (a) A particle has a little area to collide with the reactant molecules, molecules collide only with the outer surface. (b) When the solid sample with the same number of atoms is powdered to fine particles, surface area for the collisions with reactant molecules increases and hence the rate of reaction.

1.9 Effect of catalysts on the rate of reactions

Increasing the rate of a reaction has many advantages in industry. Higher temperatures can speed up a reaction, but energy for industrial processes is costly and many organic and biological substances are heat sensitive. More commonly, by far, a reaction is accelerated by a **catalyst,** a substance that increases the rate *without* being consumed. Thus, only a small, non stoichiometric amount of the catalyst is required to speed the reaction.

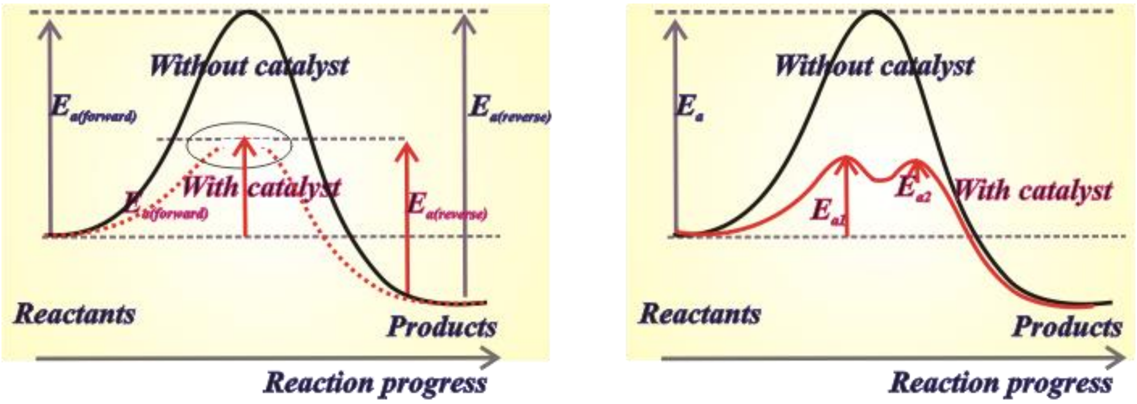
A catalyst is a substance that accelerates a reaction but undergoes no net chemical change. *It functions by providing an alternative path with lower activation energy of the reaction and avoids the slow, rate-determining step of the unanalyzed reaction, and results in a higher reaction rate at the same temperature*.

As we know, there are two basic types of catalysts namely heterogeneous and homogeneous catalyst. Heterogeneous catalyst is in a different phase (for example, a solid catalyst for a gas-phase reaction). A homogeneous catalyst is a one that is in the same phase as the reaction mixture (for example, acid catalyzed reactions in aqueous solution).

The following examples elaborates the function of a catalyst on the reaction rate. The activation energy for the decomposition of hydrogen peroxide in solution is 76 kJ mol^{-1} and the reaction is slow at room temperature. When a little amount of iodide ions is added, the activation energy falls to 57 kJ mol^{-1}, and the rate constant increases by a factor of 2000.

In addition, enzymes (categorized as biological catalysts), are very specific and can have a dramatic effect on the reactions they control. The activation energy for the acid hydrolysis of sucrose is 107 kJ mol^{-1} but the enzyme saccharase reduces it to 36 kJ mol^{-1}, corresponding to an acceleration of the reaction by a factor of 1012 at body temperature (310 K).

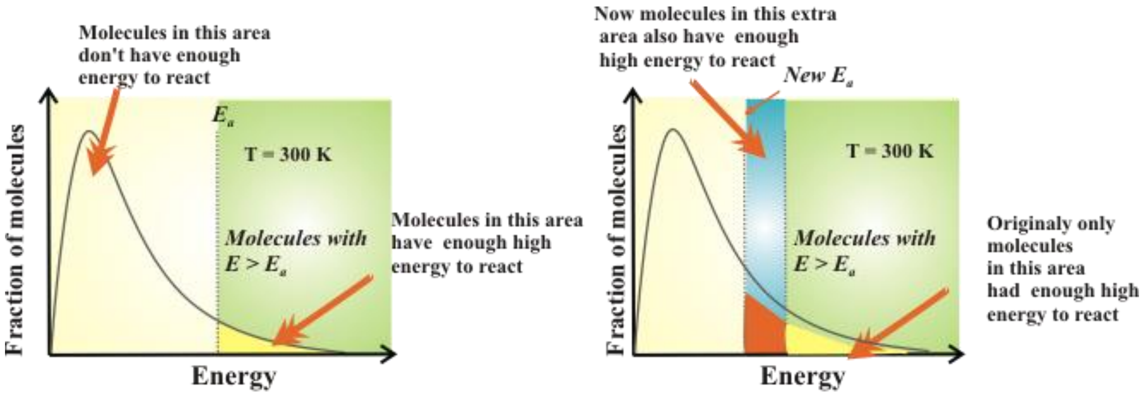
There are some substances which decrease the rate of reaction and such substances are called inhibitors. Obviously, the substances accelerating the rate will be a catalyst. Catalyst are generally foreign substances but sometimes one of the product formed may act as a catalyst. Such a catalyst is called an “auto catalyst” and the phenomenon is called auto catalysis. The function of the catalyst on the reaction rate can be depicted as illustrated in the Figure 1.23



(a) (b)

Figure 1.23 Comparison of the reaction profiles with and without a catalyst. The addition of a catalyst to a reaction increases the rate by providing a new, lower-energy alternative pathway. **(a)** Reaction goes through a different mechanism and (**b)** for example reaction goes through two transition states.

In a chemical reaction collisions result products only if the particles collide with a certain minimum energy or the activation energy for the reaction. The position of activation energy can be marked on a Maxwell-Boltzmann distribution curve as illustrated in Figure 1.24(a).



(a) (b)

Figure 1.24 Comparison of Maxwell - Boltzmann distributions with and without a catalyst at 300 K (same temperature). The addition of a catalyst to a reaction increases the rate by increasing the fraction of molecules having enough energy to react through an alternative pathway by increasing the collision frequency and hence the rate of the reaction.

Only those particles represented by the area to the right of the activation energy will react when they collide. The great majority does not have enough energy, and will simply bounce apart. Therefore, to increase the rate of a reaction it is necessary to increase the number of effective collisions by increasing the fraction of molecules with enough energy. In one way, this can be done by providing an alternative pathway for the reaction to happen with lower activation energy. In other words, the activation energy should be moved to the lower energy side (left) of the Maxwell Boltzmann distribution as shown in Figure 1.24(b). Adding a catalyst to a reaction has exactly this effect on activation energy. i.e. a catalyst provides an alternative path for the reaction with a lower activation energy compared to the un-catalyzed reaction as depicted in Figure 1.23.

It is very important to note that;

> *"A catalyst provides an alternative path for the reaction with lower activation energy." It does not "lower the activation energy of the reaction".*

This means that the original value of the activation energy of the reaction remains the same and the new catalyzed-path has lower activation energy. It is just like going through a tunnel without climbing a mountain.

1.10 Uses of reaction mechanisms to describe the rate of chemical reactions

In any chemical reaction or change, some bonds are broken and new bonds are formed. Usually, these changes such as bond breaking/ formation and rearrangements are too complicated to happen simply in one stage. Instead, the reaction may involve a series of steps one after the other. A reaction mechanism describes the one or more steps involved in the reaction in a way which makes it clear exactly how the various bonds are broken and formed.

A chemical reaction that takes place in one and only one step i.e., all that occurs in a single step is called an **elementary reaction**.

A chemical reaction occurring in a sequence of two or more steps is called a multi-step or complex reaction. As described above, the sequence of steps through which a multi-step reaction takes place is called the reaction mechanism. Each step in a mechanism is an elementary reaction. Reaction mechanisms cannot be calculated or predicted; instead, all reaction mechanisms must be determined experimentally.

Therefore, a chemical reaction in which one or more chemical species react directly to form products in a single step reaction and with a single transition state is called an elementary reaction. In this elementary reaction the molecules collide exactly as the stoichiometric equation of the reaction.

Further, in an elementary reaction no reaction intermediates are involved. Also their presence is not a requirement to describe the chemical reaction on a molecular scale.

1.10.1 Molecularity of a reaction

The molecularity of an elementary reaction is defined as the minimum number of molecules, atoms or ions of the reactant(s) required for the reaction to occur and is equal to the sum of the stoichiometric coefficients of the reactants in the balanced chemical equation.

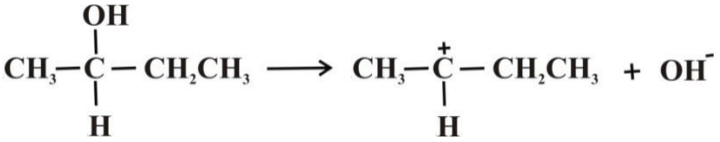
In general, molecularity of a simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.

When multi-step reaction mechanism is written, the minimum number of reacting particles (molecules, atoms or ions) that comes together or collide in the **rate determining step** to form a product or products is called the molecularity of a reaction.

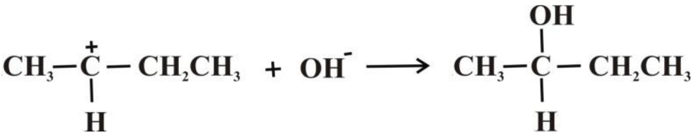
Therefore, chemical reactions can be categorized simply by the number of reacting species in an elementary step. A reaction is **unimolecular** when only a single reactant molecule is involved and is **bimolecular** when two reactant molecules are involved. For example, in a **unimolecular reaction**, a single molecule decomposes itself or changes its atoms into a new arrangement, as in the isomerization of cyclopropane to propene. In a **bimolecular reaction**, a pair of molecules collides and exchange energy while atoms or groups of atoms undergo some other kind of change getting converted into a product or products.

Molecularity is a theoretical concept; it cannot be zero, negative, fractional, infinite and imaginary.

Consider a following reaction in which a bond breaking step involves a single entity breaking up into two pieces. The C-O bond breaks. A single reactant forms two products. Because only one reactant molecule is involved, this step is unimolecular.



The following **bond forming step** which involves bringing two molecular fragments together to form a single product, a C-O bond is formed. Two reactants form a single product. Because two reactant molecules are involved, this step is **bimolecular**.



Usually, there are few reactions with termolecular elementary behaviour as the collision of three molecules at the same time is somewhat difficult (However, such reactions occur through multi steps).

1.10.2 Examples of single step reactions

Many chemical reactions are simple events that occur in a single step. Acid-base reactions mostly occur in a single step. The protonation of ammonia by a hydronium ion involves the transfer of an H^+ ion from H_3O^+ to NH_3. This single step is a concerted bond-breaking and forming process.

$$H_3O^+(aq) + NH_3(aq) \rightarrow H_2O(l) + NH_4^+(aq)$$

The reaction occurs via a single step involving two species and is called as **bimolecular elementary reaction**.

The decomposition of $N_2O_4(g)$ is a single bond breaking step.

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

The reaction occurs via a single step involving one species and is called as **unimolecular elementary reaction**.

Followings examples show some elementary reactions with different molecularities.

Table 1.4 Elementary reactions with different molecularities

Reaction	**Molecularity**
$PCl_5 \rightarrow PCl_3 + Cl_2$	Unimolecular
$2HI \rightarrow H_2 + I_2$	Bimolecular
$NO + O_3 \rightarrow NO_2 + O_2$	Bimolecular
$2SO_2 + O_2 \rightarrow 2SO_3$	Termolecular
$2CO + O_2 \rightarrow 2CO_2$	Termolecular
$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$	Termolecular

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g.

$$4HBr(aq) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)$$

$$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

In the first reaction molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions do not occur in a single step and involve two or more steps; each step has its own molecularity not greater than three. Following describes the basic features of reactions which occurs through multistep.

1.10.3 Multistep reactions

Chemical processes that occur in a series of elementary steps has their own set of rules.

(i) The overall reaction is the sum of the elementary reaction steps.

(ii) A species that is formed in one step and then used up in a later step is an **intermediate**.

(iii) A species that is used in one step and increase the rate of the reaction, then regenerated in a later step is acting as a **catalyst**.

(iv) Neither intermediates nor catalysts are seen in the overall reaction rate law.

Example 1:

The decomposition of ozone takes place in two steps.

Step 1: $O_3(g) \rightarrow O_2(g) + O(g)$; unimolecular, bond breaking

Step 2: $O_3(g) + O(g) \rightarrow 2O_2(g)$: bimolecular, bond forming and breaking

As learned in Unit 5, the idea of adding a series of reactions to give a net reaction is used here to determine the overall reaction that takes place in a series of steps.

In this case, O(g) is present on both sides.

Step 1: $O_3(g) \rightarrow O_2(g) + O(g)$

Step 2: $O_3(g) + O(g) \rightarrow 2O_2(g)$

$2\,O_3(g) + O(g) \rightarrow 3\,O_2(g) + O(g)$

∴ Overall reaction: $\mathbf{2\,O_3(g) \rightarrow 3\,O_2(g)}$

In this example, it can be seen that the O(g) atom formed in the step 1 is consumed in the step 2 and it doesn't appear in the overall reaction. That doesn't mean that it does not exist at least for a little while. A chemical species that is formed in one step of a mechanism and then used in a later step is called an intermediate. Intermediates never appear in the overall reaction equation. Sometimes they can be observed while the reaction progresses, but other times they are formed and used up so quickly and are not seen.

Example 2:

The decomposition of hydrogen peroxide in the presence of iodide ion occurs in two steps.

Step 1. $H_2O_2(aq) + I^-(aq) \rightarrow IO^-(aq) + H_2O(l)$; bimolecular

Step 2. $IO^-(aq) + H_2O_2(aq) \rightarrow I^-(aq) + H_2O(l) + O_2(g)$: bimolecular

∴ Overall reaction $2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$

In this case, the $IO^-(aq)$ ion is formed in the first step and then consumed in the second step. $IO^-(aq)$ is an intermediate in this reaction. Conversely, $I^-(aq)$ ion is used in the first step and then regenerated in the second step. Therefore, $I^-(aq)$ act as a catalyst in this reaction

Example 3:

Chlorofluorocarbons break down in the upper atmosphere to give chlorine atoms. These are involved in the breakdown of ozone via the following mechanism.

Step 1. $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$

Step 2. $ClO(g) + O_3(g) \rightarrow Cl(g) + O_2(g)$

Overall reaction: $2O_3(g) \rightarrow 2O_2(g)$

Reactions in step 1 and 2 are both bimolecular. Cl(g) is a reactant in the Step 1, but is regenerated in Step 2. Cl is therefore a catalyst. ClO is generated in Step 1, but is consumed in Step 2. ClO is therefore an intermediate.

1.10.4 The rate laws of elementary reactions

The rate law for elementary reactions can deduced directly from their molecularity. For example, the rate law of a unimolecular elementary reaction is first-order with respect to the reactant. Consider the reaction where P denotes products (several different species may be formed).

$$\mathrm{A} \rightarrow \mathrm{P}$$

$$\text{Rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = k\,[\mathrm{A}]$$

A unimolecular elementary reaction is first-order because the number of A molecules that decays in a short interval is proportional to the number available to decay. Therefore the rate of decomposition of A is proportional to its molar concentration.

An elementary bimolecular reaction has a second-order rate law:

$$2\mathrm{A} \rightarrow \mathrm{P}$$

$$\text{Rate} = k\,[\mathrm{A}]^2$$

Or we can write the reaction as;

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$$

$$\text{Rate} = k\,[\mathrm{A}][\mathrm{B}]$$

A bimolecular elementary reaction is second order because its rate is proportional to the rate at which the reactant species meet, which in turn is proportional to their concentrations. Therefore, if we consider that a reaction is a single-step, bimolecular process, we can write down the rate law.

Note that the converse of this rule does not follow, that is, for example *second order rate law does not imply that the reaction is bimolecular*. Also, care must be taken to ensure that the reaction /step that we are considering is really elementary. For example, the reaction

$H_2(g) + I_2(l) \rightarrow 2HI(g)$ may look simple, but it is not elementary, and in fact, it has a very complex reaction mechanism, and hence the rate law cannot be deduced by merely looking the reaction.

With the above descriptions, for an elementary reaction of the general type;

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$$

rate law is written as,

$$\text{Rate} = k\,[\mathrm{A}]^a\,[\mathrm{B}]^b$$

The order of an elementary reaction with respect to a given reactant is exactly same as the stoichiometric coefficient. Therefore, for the above elementary reaction, order with respect to the reactant A is ***a*** and the order with respect to the reactant B is ***b*.** The overall order of the reaction is (***a* + *b*).**

It is very important to understand the difference between molecularity and reaction order:

The ***reaction order*** is an empirical quantity, and obtained from the experimental rate law.

The ***molecularity*** refers to an elementary reaction proposed as an individual step in a mechanism.

The following table summarizes some examples.

Table 1.5 Summary of molecularity

Molecularity	**Elementary step**	**Rate law**
Unimolecular	A → Products	Rate = k [A]
Bimolecular	A + A → Products	Rate = k $[A]^2$
Bimolecular	A + B → Products	Rate = k [A] [B]
Termolecular	A + A + A → Products	Rate = k $[A]^3$
Termolecular	A + A + B → Products	Rate = k $[A]^2[B]$
Termolecular	A + B + C → Products	Rate = k [A][B][C]

1.10.5 Reaction mechanisms and the rate law

As described earlier, a species acting as an intermediate or a catalyst does not appear in the rate law. Then it is necessary to understand how the rate law is derived for such systems. Usually, in a mechanism there are some steps that occur very slowly and some other steps that occur very rapidly. The overall rate of a reaction is controlled by the rate of the slowest step. The slowest step of a reaction is known as the **rate determining step (RDS)**. Therefore, in experiments, when the rates are measured, the rate of the rate determining step is actually measured as long as there is a lot of differences among the rates of the various steps.

Consider the following example; in which the reaction occurs in two steps. First the reactant A is transformed into another species B; then in the next step it acts as a reactant which is transformed into the desired product P.

$$A \xrightarrow{k_1} \mathrm{B}$$

$$\mathrm{B} \xrightarrow{k_2} \mathrm{P}$$

k_1 and k_2 are the rate constants of respective steps.

Assume that $k_2 >> k_1$. In such a case, whenever a molecule B is formed, it decays rapidly to P indicating that the rate of the reaction depends only on the first step and that the step would be the rate determining step of the reaction.

Consider another example in which the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ occurs through following mechanism.

$$NO_2(g) + NO_2(g) \xrightarrow{k_1} NO_3(g) + NO(g) : \text{ slow; rate determining step}$$
$$NO_3(g) + CO(g) \xrightarrow{k_2} NO_2(g) + CO_2(g) : \text{ fast}$$

In this reaction the first step is the rate determining step and hence we can say that the rate of reaction depends only on the rate constant k_1. This can further be proven from the experiments in determining the empirical rate law of the reaction. The empirical rate law of the reaction is

$$\text{Rate} = k\,[NO_2]^2$$

i.e. the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is 2nd order with respect to $NO_2(g)$ and zero-order with respect to CO(g).

In the mechanism given above NO_3 functions as a **reaction intermediate,** which is formed and used up during the reaction. Even though it does not appear in the overall balanced equation, a reaction intermediate is essential for the reaction to occur. Intermediates are less stable than the reactants and products.
Rate laws for the two elementary steps written above are;

$$\text{Rate}_1 = k_1\,[NO_2]^2$$
$$\text{Rate}_2 = k_2\,[NO_3][CO]$$

Three key points to notice about this mechanism are

(i) If $k_1 = k$, the rate law for the rate-determining step (step 1) becomes identical to the observed rate law.

(ii) Because the first step is slow, $[NO_3]$ is low. As soon as any NO_3 forms, it is consumed by the fast second step, so the reaction takes as long as the first step does.

(iii) CO does not appear in the rate law (reaction order = 0) because it takes part in the mechanism *after* the rate-determining step.

Example:
Consider the reaction between nitrogen dioxide and fluorine as an example:

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

The experimental rate law is that it is first order in NO_2 and in F_2.
$\therefore$ Rate = $k\,[NO_2(g)]\,[F_2(g)]$

The accepted mechanism is

Step 1; $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$: slow; rate determining

Step 2; $NO_2(g) + F(g) \rightarrow NO_2F(g)$: fast

Note that here the free fluorine atom is a reaction intermediate.

Let us consider the mechanism and how the rate law of the reaction is explained.
Sum of the two elementary reaction steps is the overall balanced equation.

Step 1; $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$

Step 2; $NO_2(g) + F(g) \rightarrow NO_2F(g)$

Overall reaction: $\mathbf{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)}$

And both steps are bimolecular.

The rate laws for the elementary steps are:

$Rate_1 = k_1 [NO_2(g)] [F_2(g)]$

$Rate_2 = k_2 [NO_2(g)] [F(g)]$

It can be seen that the step 1 is the rate-determining step, and with $k_1 = k$, it is the same as the overall rate law.

In this mechanism it has to be noted that the second molecule of NO_2 is involved *after* the rate-determining step, so it does not appear in the overall rate law.

From the above examples it can be noted that though the reaction proceeds through several steps, rate law of the reaction follows the rate determining step (slowest step) of the mechanism.

Consider the reaction between 2-bromo-2-methylpropane with hydroxide (OH^-) ions:

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

In the overall reaction the bromine atom is replaced by an OH group.

The first step that happens is that the carbon-bromine bond breaks to give ions via a unimolecular reaction;

$$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + :Br^- \quad : slow$$

Carbon-bromine bonds are reasonably strong, so this is a slow change. If there is a high concentration of hydroxide ions, the positive ions will combine with them and this step of the reaction will be very fast. A new covalent bond is made between the carbon and the oxygen, using one of the lone pairs on the oxygen atom via a bimolecular (fast) reaction;

$$(CH_3)_3C^+ + :OH^- \rightarrow (CH_3)_3COH \quad : fast$$

The mechanism shows that the reaction takes place in two steps and describes exactly how those steps happen in terms of bonds being broken or made. It also shows that the steps have different rates of reaction; one slow and one fast.

The emperical rate law of the above reaction has been found to be as follows,

$$\text{Rate} = k[(CH_3)_3CBr]$$

The reaction is first order with respect to the $(CH_3)_3CBr$, and zero order with respect to the hydroxide ions. The concentration of the hydroxide ions does not affect the rate of the overall reaction.

If the hydroxide ions were taking part in the slow step of the reaction, increasing their concentration would speed up the reaction. Since its concentration does not seem to matter, they must be taking part in a later fast step.

Increasing the concentration of the hydroxide ions will speed up the fast step, but that will not have a noticeable effect on the overall rate of the reaction as that is governed by the speed of the slow step.

Example: *Predicting a suitable mechanism*
Suppose an elementary bimolecular reaction between A and B which was experimentally found to be first order with respect to both A and B.
So the rate equation is:
Rate = k [A][B]

Let us consider the following two mechanisms;
Mechanism 1

$$\mathrm{A} \rightarrow \mathrm{C} + \mathrm{D} \;; slow$$
$$\mathrm{B} + \mathrm{C} \rightarrow \mathrm{E} \;; fast$$

Mechanism 2

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{D} + \mathrm{E} \;; slow$$

In this case, the reaction is first order with respect to both A and B, so one molecule of each must be taking part in the slow step. That means, mechanism 2 is the possible one.

Mechanism 1 must be wrong. One molecule of A is taking part in the slow step, but no B. The rate equation for that would be:
Rate = k[A]

1.10.6 Consecutive (elementary) reactions

As noted from the above reaction steps/mechanisms, the reaction which goes through an intermediate can be expressed as,

$$\mathrm{A} \overset{k_1}{\rightarrow} \mathrm{I} \overset{k_2}{\rightarrow} \mathrm{P}$$

The above reaction is defined as a consecutive unimolecular reaction because one reactant is involved in each step and the first step is the rate determining step of the reaction. For such a process:

(i) The concentration of A decreases through unimolecular decomposition of A, and is not replenished. Thus we have the rate equation

$$\mathrm{Rate} = -k_1[\mathrm{A}]$$

(ii) The intermediate I is formed from A at a rate k_1[A], and decreases through decay to P at rate k_2[I]. This event happens very fast.
(iii) The product P is formed from I at a fast rate k_2[I], and it does not decrease.

Therefore, from these it can be simply noted that
(i) The concentration of the reactant A decreases with time;
(ii) The concentration of the intermediate I rises to a maximum and then falls to zero within a short time interval;
(iii) The concentration of the product P rises from zero to some value depending on the stoichiometry of the reaction.

These can be illustrated as shown in the Figure 1.25.

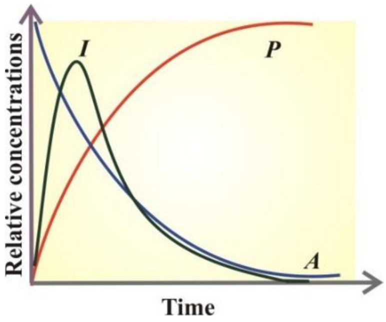


Figure 1.25 The concentrations of A, I, and P in the consecutive reaction $A \overset{k_1}{\rightarrow} I \overset{k_2}{\rightarrow} P$. Intermediate I is formed and consumed in the next step making its concentration zero with the time.

We can look at the above in another direction as follows.

The reaction $A \overset{k_1}{\rightarrow} I \overset{k_2}{\rightarrow} P$ occurs in two steps.

Step 1; $A \overset{k_1}{\rightarrow} I$

Step 2; $I \overset{k_2}{\rightarrow} P$

Overall reaction: $A \overset{k}{\rightarrow} P$

From the above we can deduce how the concentrations of A, I, and P will change over time. It is important to consider the relative rates of each step to understand the variation in concentrations of the species participating in the reaction. In any case, the concentration of A will decrease as the reaction proceeds, and the concentration of the product P will increase. But what would be the concentration of the intermediate, I? It is formed in one step and consumed in another. Its concentration must be zero at the start of the reaction, and must be zero when the reaction is complete, but non-zero in between. This is best observed by examining concentration-time curves. Figure 1.26 shows concentration-time curves of these species in three cases.

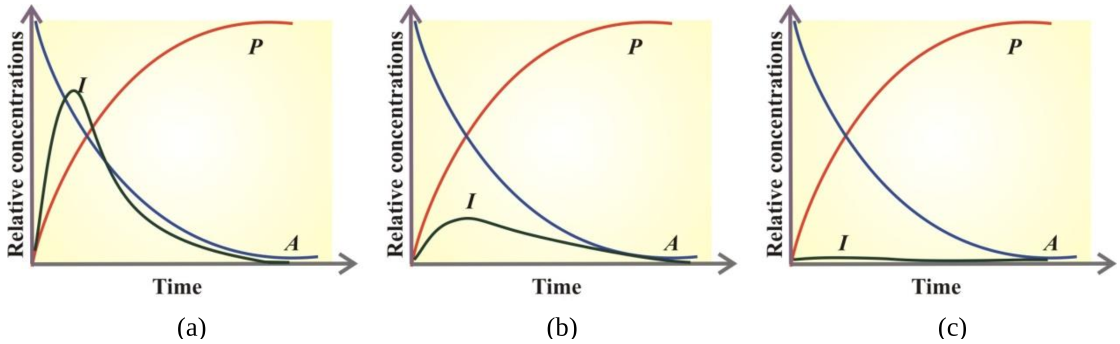


Figure 1.26 **(a)** Step 1 faster than Step 2. **(b)** Step 2 a little faster than Step 1. (c) Step 2 much faster than Step1.

In (a) the first step is somewhat faster than the second step. Initially, as A → I occurs, the rate of formation of I is greater than its rate of consumption in Step 2. So, the concentration of I increases over time. Then, as reactant A is depleted and the concentration of I increases, the rate of formation of I decreases and its rate of consumption increases. At this point, the concentration of I starts to decrease. Eventually the concentrations of both A and I drop to near zero as the reaction nears completion. (b) shows a case where Step 2 is somewhat faster than Step 1. In this case, I is consumed more quickly and its concentration does not build up as much as in (a). (c) shows a case where Step 2 is much faster than Step 1. In this case, I is consumed almost instantly as it is formed. The concentration of I never rises to an appreciable level and I may never be concentrated enough to observe in an experiment.

If a case like (c) occurs, it is important to know that the intermediate ever existed or not. Additional experiments can be designed to show that the intermediate was present, even if not directly observed. One of the methods is the addition of another reagent that would react with the postulated intermediate and observing the expected product. Then we can have evidence for the existence of the intermediate.

1.10.7 Cases where a pre-equilibrium exists in a mechanism

Example 1:

Suppose the mechanism for a reaction $A + B \rightarrow P$

$$A \rightleftharpoons I \; ; fast$$

$$I + B \rightarrow P \; : slow$$

This time the slow step is the second step and the intermediate I reaches an equilibrium with the reactants A and B. This mechanism involves a **pre-equilibrium**, in which an intermediate is in equilibrium with the reactants.

A pre-equilibrium arises when the rates of formation of the intermediate and its decay back into reactants are much faster than its rate of formation of the products.

The rate of the reaction will be governed by the slow step, and so the rate equation of the slow step is : Rate = k [B] [I]

In the rate law the concentration of the intermediate I is appearing and however, it is known that I is in equilibrium with A. Therefore the equilibrium constant K_c for the first step is;

$$K_c = \frac{[\mathrm{I}]}{[\mathrm{A}]}$$

$$\therefore \quad [\mathrm{I}] = K_c[\mathrm{A}]$$

Therefore the rate of the reaction is:

$\text{Rate} = k\ [\mathrm{B}]\ K_c\ [\mathrm{A}] = k\ K_c\ [\mathrm{A}][\mathrm{B}]$

This can further be modified with the relation between rate constants and equilibrium constant of the reaction. If the rate constants for the forward and backward reactions are k_f and k_r, respectively, we can write;

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

Finally,

$$\therefore \text{Rate} = k\ \frac{k_f}{k_r}[\mathrm{A}][\mathrm{B}]$$

$$\text{Rate} = k'\ [\mathrm{A}][\mathrm{B}]$$

The above shows that the rate law is similar to that of an elementary bimolecular reaction.

Consider another example.

Suppose the mechanism for a reaction A + B → P

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{I}\ ;\ fast$$

$$\mathrm{I} + \mathrm{A} \rightarrow \mathrm{P}\ :\ slow$$

The overall reaction is ; $2\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$

The rate of the reaction will be governed by the slow step, so the rate equation of the slow step is : Rate = k [A] [I]

In the rate law the concentration of the intermediate I is appears. However, it is known that I is in equilibrium with A and B, so the equilibrium constant K_c for the first step is;

$$K_c = \frac{[\mathrm{I}]}{[\mathrm{A}][\mathrm{B}]}$$

$$\therefore \quad [\mathrm{I}] = K_c[\mathrm{A}][\mathrm{B}]$$

$$\therefore \ Rate \ = kK_c[\mathrm{A}][\mathrm{A}][\mathrm{B}]$$

$$\therefore Rate = k'[\mathrm{A}]^2[\mathrm{B}]$$

The rate law obeys the termolecular elementary reaction.

Example 2:

The gas phase reaction between $H_2(g)$ and $I_2(g)$ is one example for the above type of reactions.

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

This has a fas*t* pre-equilibrium step in which molecular iodine converts to atoms.

$$I_2(g) \rightleftharpoons 2I(g)$$

Then that atomic iodine reacts with molecular hydrogen to form HI in a slow second step.

$$H_2(g) + 2I\,(g) \rightarrow 2HI(g)$$

The rate of the reaction is governed by the slow step, so the rate equation of the slow step is: $\text{Rate} = k\,[H_2(g)]\,[I(g)]^2$

In the rate law, the concentration of the intermediate, I appears. However, it is known that I is in equilibrium with $I_2(g)$. Therefore the equilibrium constant $\boldsymbol{K_c}$ for the first step is;

$$K_c = \frac{[I(g)]^2}{[I_2(g)]}$$

$$\therefore\ [I(g)]^2 = K_c[I_2(g)]$$

$$\therefore\ \text{Rate} = kK_c[I_2(g)][H_2(g)]$$

$$\therefore \text{Rate} = k'[I_2(g)][H_2(g)]$$

Therefore, the rate of reaction depends on the concentrations of both $I_2(g)$ and $H_2(g)$.

Example 3:

In this example in which the first step of the reaction is a *fast* and *reversible*. Consider the oxidation of nitrogen monoxide given below.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The observed rate law is

$$\text{Rate} = k\,[NO(g)]^2\,[O_2(g)]$$

the reaction has the mechanism;

Step 1 : $NO(g) + O_2(g) \rightleftharpoons NO_3(g)$: fast

Step 2 : $NO_3(g) + NO(g) \rightarrow 2NO_2(g)$: slow; rate determining step

The sum of the above two steps gives the overall reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ and both steps are bimolecular.

Rate law for the slow step is;

$$\text{Rate} = k\,[NO_3(g)]\,[NO(g)]$$

For the step 1, equilibrium constant is,

$$K_c = \frac{[\mathrm{NO_3(g)}]}{[NO(g)][O_2(g)]}$$
$$\therefore [\mathrm{NO_3(g)}] = K_c[\mathrm{NO(g)}][\mathrm{O_2(g)}]$$
$$\therefore \mathrm{Rate} = kK_c[\mathrm{NO(g)}][\mathrm{O_2(g)}][\mathrm{NO}]$$
$$\mathrm{Rate} = k'[\mathrm{NO(g)}]^2[\mathrm{O_2(g)}]$$

This derived rate law is constant with the empirical rate law given earlier. Therefore, the mechanism of the reaction is correct.

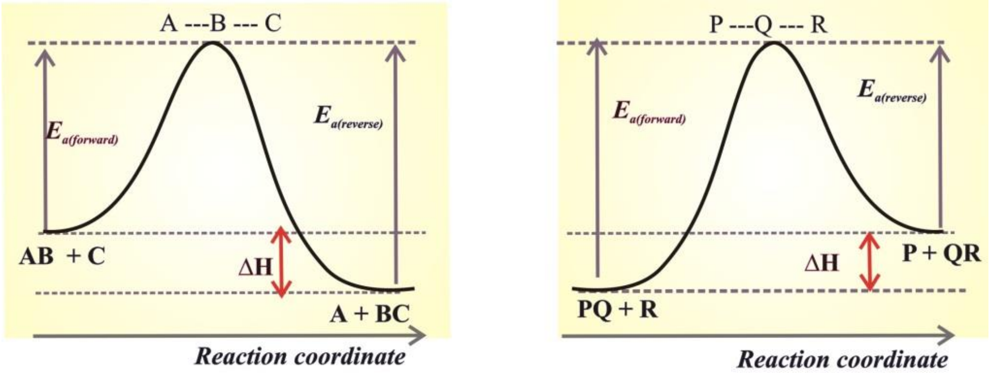
1.11 Energy profiles of reactions

First, consider an elementary reaction which occurs through a single step A → products. As described in earlier sections about the requirements to be satisfied for a chemical reaction to occur when two molecules approach each other, repulsion between their electron clouds continually increase, so they slow down as some of their kinetic energy is converted to potential energy. If they collide, but the energy of the collision is *less* than the activation energy, the molecules bounce off from each other.

According to Maxwell-Boltzmann distribution, however, in a fraction of collisions in which the molecules are moving fast enough, *their kinetic energies push them together with enough force to overcome the repulsions and surmount the activation energy.* Usually in this fraction of sufficiently energetic collisions, the molecules are oriented effectively. In those cases, nuclei in one molecule attract electrons in the other, atomic orbitals overlap, electron densities shift, and some bonds lengthen and weaken while others shorten and strengthen. At some point during this smooth transformation, *a species with partial bonds exists* that is neither a reactant nor a product. This very unstable species, called the **transition state** (or **activated complex**) exists only at the instant of highest potential energy. Thus, *the activation energy of a reaction is used to reach the transition state.* Reaching the transition state does not guarantee that a reaction will proceed to products because *a transition state can change in either direction*. In this case, if the new bond continues to strengthen, products form; but, if the existing bond becomes stronger again, the transition state reverts to reactants.

A useful way to depict these events is with a reaction energy diagram or energy profile which plots how potential energy changes as the reaction proceeds from reactants to products (the *reaction progress or reaction coordinate*). The diagram shows the relative energy levels of reactants, products, and transition state, as well as the forward and reverse activation energies and the enthalpy of reaction. Simply the energy profiles can be depicted for single step exothermic and endothermic reactions as shown in Figure 1.27 considering some hypothetical reactions given below.

AB + C → A + BC: $\Delta H <$ O and PQ + R → P + QR : $\Delta H >$ O.



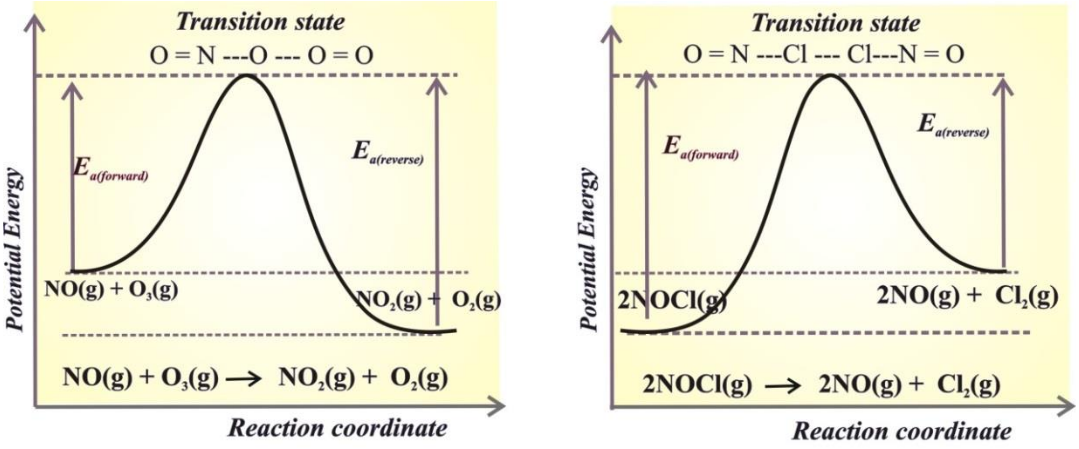
(a) (b)

Figure 1.27 Energy profiles for **(a)** exothermic and **(b)** endothermic reactions going through a single transition state.

Figure 1.27(a) shows that, overall, the reaction is exothermic. The products have lower energy than the reactants, so energy is released when the reaction happens. It also shows that the molecules have to possess enough energy (activation energy) to get the reactants over the "activation energy barrier".

For an endothermic reaction, a simple energy profile is shown in Figure 1.27(b).

For example, following two reactions occur through a single step with a single transition state. The reaction; $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ is exothermic while the reaction $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$ is endorthermic. Their transition states are also shown along with the potential energy in Figure 1.28.



(a) (b)

Figure 1.28 Energy profiles for two gas-phase reactions of **(a)** exothermic and **(b)** endothermic nature. In each case, the structure of the transition state is predicted from the orientations of the reactant atoms that must become bonded in the product.

As another example, the reaction below shows a reaction in which a bromine atom of bromoethane is being replaced by an OH group to produce ethanol.

$$CH_3Br(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq)$$

In the reaction one of the lone pairs of electrons on the negatively charged oxygen in the OH^- ion is attracted to the carbon atom with the bromine attached.

As the bromine is more electronegative than carbon, and so the electron pair in the C-Br bond is slightly closer to the bromine. The carbon atom becomes slightly positively charged and the bromine slightly negative. As the hydroxide ion approaches the slightly positive carbon, a new bond starts to be set up between the oxygen and the carbon. At the same time, the bond between the carbon and bromine starts to break as the electrons in the bond are repelled towards the bromine.

At some point, the process is exactly half complete. The carbon atom now has the oxygen half-attached, the bromine half-attached, with three other groups still there and then the process undergo completion. The structure in which the bonds are half-made and half-broken is the **transition state**, and is at the maximum potential energy.

It has to be noted that the transition state is entirely unstable. Any tiny change in either direction will send it either forward to make the products or back to the reactants again. There is no anything special about a transition state except that it has this maximum energy.

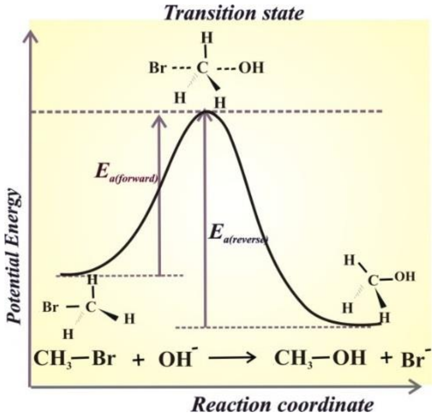


Figure 1.29 Energy profile for the reaction $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

Example 1.15

The reaction, $O_3(g) + O(g) \rightarrow 2O_2(g)$ has the activation energy of 19 kJ mol^{-1} for the forward reaction and the ΔH for the reaction is -392 kJ mol^{-1}. Draw an energy profile for the reaction with approximate relative positions of the species. Estimate the activation energy for the backward reaction.

Answer

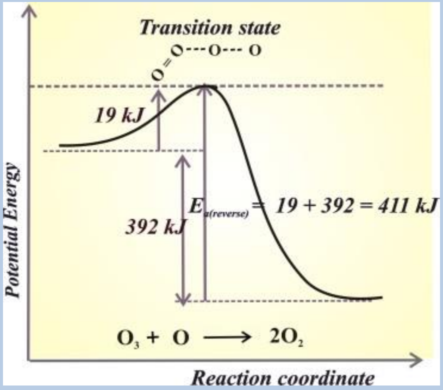


Figure 1.30 Energy profile for the reaction $O_3(g) + O(g) \rightarrow 2O_2(g)$.

Calculation of the activation energy of the backward reaction is indicated in the figure and the postulated structure of the transition state is also drawn.

Energy profiles for reactions which go via an intermediate

In this case, consider the following reaction which goes through an intermediate.

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

In the overall reaction the bromine atom is replaced by an OH group.

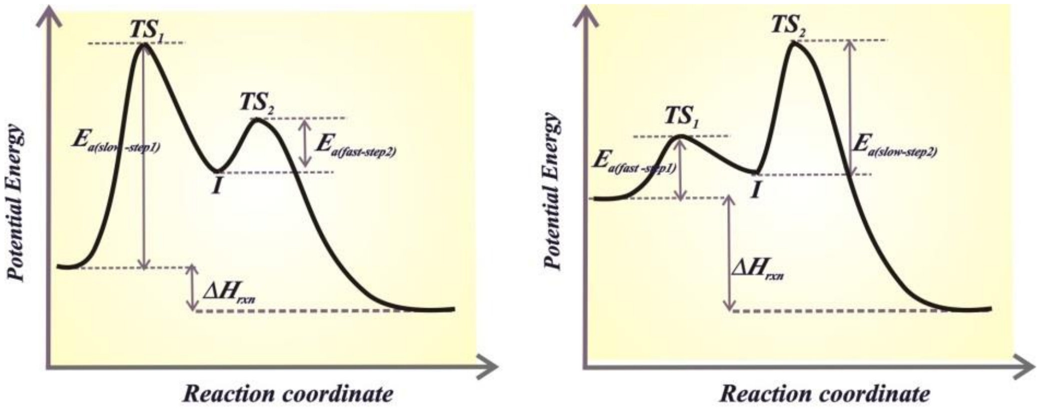
As mentioned earlier the reaction occurs via two steps as follows.

$$(CH_3)_3CBr \rightleftharpoons (CH_3)_3C^+ + :Br^- \quad \text{: slow}$$

$$(CH_3)_3C^+ + :OH^- \rightleftharpoons (CH_3)_3COH \quad \text{: fast}$$

The main difference in this case is that the positively charged ion can actually be detected in the mixture. It is very unstable, short-lived and soon reacts with a hydroxide ion (or picks up its bromide ion again). But, it does have a real presence in the system. The stability (however temporary and slight) of the intermediate is shown by the fact that there are small activation barriers to its conversion either into the products or back into the reactants again.

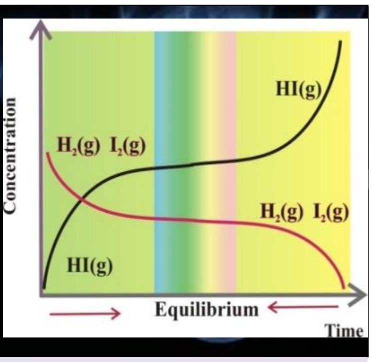
Notice that the barrier on the product side of the intermediate is lower than that on the reactant side meaning the fast second step as shown in Figure 1.30(a). That means, there is a greater chance of it to find the extra bit of energy to convert into products. It would need a greater amount of energy to convert back to the reactants again. The "TS_1" and "TS_2" both represent transition states between the intermediate and either the reactants or the products. During either conversion, there will be some arrangement of the atoms which causes an energy maximum.



(a) (b)

Figure 1.31 Energy profiles for two reactions, each of which has a two-step mechanism. **(a)** The reaction starts with a slow step, and **(b)** The reaction starts with a fast step. Both overall reactions are exothermic. Note these key points: Each step in the mechanism has its own peak with the transition state at the top. The intermediates are reactive, unstable species, so they are higher in energy than the reactants or product. The slow (rate-determining) step (step 1 in (**a)** and step 2 in (**b**) has a larger E_a than the other step.

2. Chemical Equlibrium



Contents

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,

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{C} + \mathrm{D} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

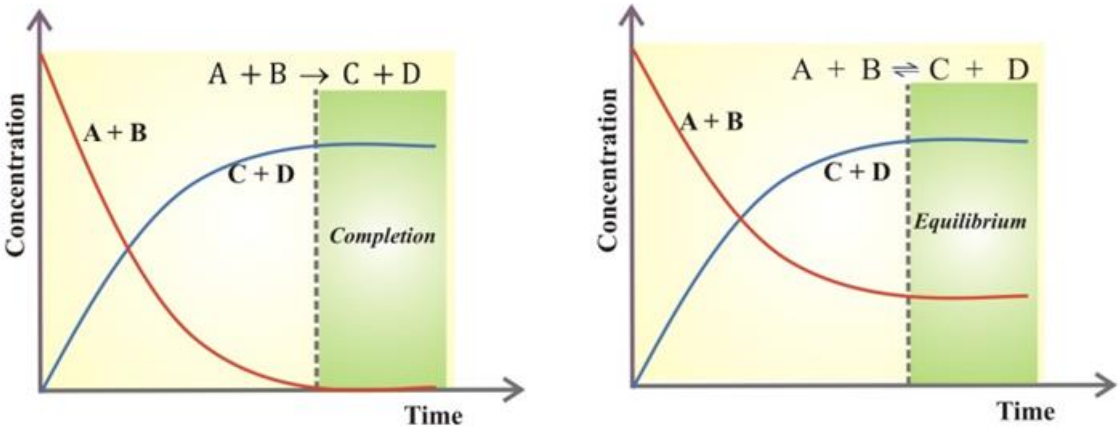
In this reaction, the reverse reaction to form back the reactants never occurs even when the reaction vessel is a closed one. Reactions which go to completion and never proceed in the reverse direction are called **irreversible reactions**.

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 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,

$$A + B \rightleftharpoons C + D \qquad \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

To indicate that the reaction can proceed in both forward and reverse directions, we write the balanced equation with two arrows, ⇌, 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.



(a) (b)

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.

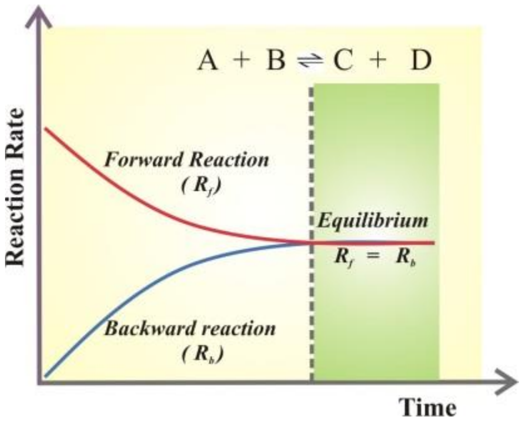


Figure 2.2 When the two rates become equal at a given temperature, an equilibrium state is attained with equalizing the rates of forward and backward reactions and there are no further changes in concentrations.

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 ($N_2O_4(g)$) to nitrogen dioxide ($NO_2(g)$). $NO_2(g)$ is responsible for the brown color we associate with smog. In a sealed vessel containing $N_2O_4(g)$, the red-brown colour of $NO_2(g)$ appears. Therefore the reaction can be followed visually because the product ($NO_2(g)$) is coloured, whereas the reactant ($N_2O_4(g)$) is colourless.

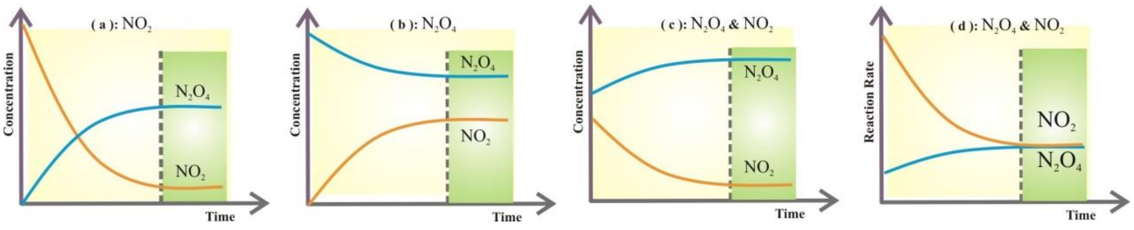
$$N_2O_4(g) \rightleftharpoons 2\,NO_2(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

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

(i) When gaseous $N_2O_4(g)$ is injected into an evacuated flask brown colour appears immediately, indicating the formation of $NO_2(g)$ molecules. The colour intensifies with the time as the dissociation of $N_2O_4(g)$ continues until eventually equilibrium is reached and remains at a constant intensity. At this point, the concentrations of both $N_2O_4(g)$ and $NO_2(g)$ remain constant.

(ii) We can also bring about an equilibrium state by starting with pure $NO_2(g)$. As some of the $NO_2(g)$ molecules combine to form $N_2O_4(g)$, the colour fades and remains at constant intensity once the equilibrium is attained.

(iii) Another way to create this equilibrium state is to start with a mixture of $NO_2(g)$ and $N_2O_4(g)$ and monitor the system until the color stops changing. The important thing to keep in mind is that at equilibrium, the conversions of $N_2O_4(g)$ to $NO_2(g)$ and $NO_2(g)$ to $N_2O_4(g)$ are still going on. We do not see a colour change because the two rates are equal, i.e. the removal of $NO_2(g)$ molecules takes place as fast as the production of $NO_2(g)$ molecules, and $N_2O_4(g)$ molecules are formed as quickly as they dissociate. Figure 2.3 summarizes these three situations.



(a) (b) (c) (d)

Figure 2.3 $N_2O_4(g) \rightleftharpoons NO_2(g)$ equilibrium system: **(a)** Initially, the system contains gaseous $NO_2(g)$ and no gaseous $N_2O_4(g)$. The concentration of $NO_2(g)$ decreases with time as the concentration of $N_2O_4(g)$ increases. **(b)** Initially the system contains gaseous $N_2O_4(g)$ and no gaseous $NO_2(g)$. The concentration of $N_2O_4(g)$ decreases with time as the concentration of $NO_2(g)$ increases. **(c)** Initially a mixture of $NO_2(g)$ and $N_2O_4(g)$ is present. Note that even though equilibrium is reached in all cases, the equilibrium concentrations of $NO_2(g)$ and $N_2O_4(g)$ 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.: solid ⇌ liquid, liquid ⇌ gas, solid ⇌ 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),

$$H_2O(l) \rightleftharpoons H_2O(s)$$

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),

$$H_2O(l) \rightleftharpoons H_2O(g)$$

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 sublimes 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.

$$S(\text{rhombic}) \rightleftharpoons S(\text{monoclinic})$$

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,

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

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,

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

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.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

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,

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

According to the law of mass action;

Rate of forward reaction: $R_f = k_f$ [A] [B]

Rate of backward reaction: $R_r = k_r$ [C] [D]

[A], [B], [C] and [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 $NO_{2(g)}$ and $N_2O_{4(g)}$ in a $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ system at 25°C some interesting pattern is seen: Analysis of the equilibrium concentration data shows that although the ratio $[NO_{2(g)}]/[N_2O_{4(g)}]$ gives random values, the ratio $[NO_{2(g)}]^2/[N_2O_{4(g)}]$ gives a nearly constant value. i.e.

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

is a constant at a given temperature.

Likewise, similar kind of results was observed for the $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ reaction giving the ratio $[HI]^2/[H_2]\,[I_2]$ 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:

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

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,

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

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\ [H_{2(g)}]^3}$$

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 $\grave{K}_c$ from K_c.). i.e.

$$\grave{K}_c = \frac{[N_{2(g)}]\ [H_{2(g)}]^3}{[NH_{3(g)}]^2} = \frac{1}{K_c}$$

Because the equilibrium constants K_c and $\grave{K}_c$ 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 $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3\,(g)}$ at 500 K: $[N_2] = 3.0 \times 10^{-2}$ mol dm^{-3}, $[H_2] = 4.0 \times 10^{-2}$ mol dm^{-3} and $[NH_3] = 2 \times 10^{-3}$ mol dm^{-3}. Calculate the equilibrium constants for both forward and reverse reactions at 500 K.

Answer

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3\,(g)}$

$$K_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\ [H_{2(g)}]^3}$$

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

$$\grave{K}_c = \frac{[N_{2(g)}]\ [H_{2(g)}]^3}{[NH_{3(g)}]^2} = \frac{(3 \times 10^{-2})(4 \times 10^{-2})^3(\text{mol dm}^{-3})^4}{(2 \times 10^{-3})^2\ (\text{mol dm}^{-3})^2}$$

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

or

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

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 $\boldsymbol{K}$ *(either* $\boldsymbol{K_c}$ *or* $\boldsymbol{K_p}$ *which pertains to the gas phase reactions)* is much greater than 1 (that is, $K >>>1$), 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, $K <<< 1$), 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.

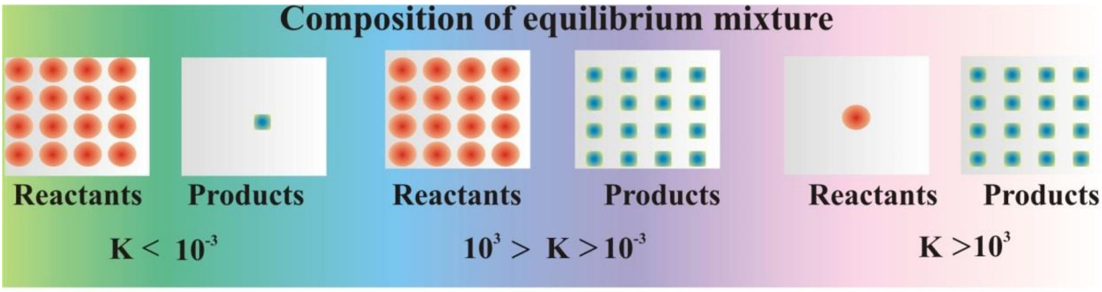


Figure 2.4 Representation of the extent and equilibrium position of a reaction with respect to the magnitude of equilibrium constant, $\boldsymbol{K}$

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 $k_f >> k_r$, $\boldsymbol{K}$ is a large number, and the concentration of products at equilibrium predominate. This corresponds to an essentially irreversible reaction. Conversely, when $k_f << k_r$, $\boldsymbol{K}$ 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, $\boldsymbol{K_c > 10^3}$, products predominate over reactants. If it is very large, the reaction proceeds nearly to completion.
- If, $\boldsymbol{K_c < 10^3}$**,** reactants predominate over products. If it is very small, the reaction proceeds hardly at all.
- If, $\boldsymbol{10^3 \geq K_c \geq 10^{-3}}$, appreciable concentrations of both reactants and products are present.

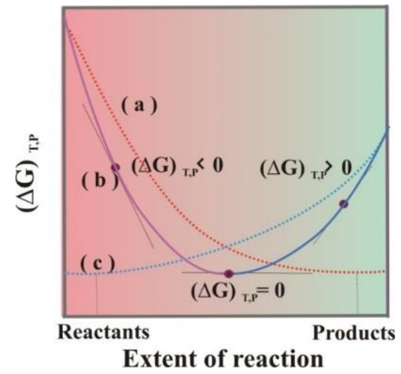


Figure 2.5 Representation of a spontaneous reaction towards minimum Gibbs function at equilibrium at given temperature and pressure. As the reaction proceeds the slope of the Gibbs function changes. Equilibrium point corresponds to the zero slope.

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^o*). In general,* ΔG_r *of a given reaction at a given temperature is given by;* $\Delta G_r = \Delta G_r^o + RT\ln Q$*, and we know that at equilibrium,* $\Delta G_r = 0$ *indicating that any reaction has its own (characteristic)* ΔG_r^o *value. In other words, for a reaction at a given temperature,* $\Delta G_r^o \neq 0$*, or* $\Delta G_r^o = -RT\ln K$*. (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.

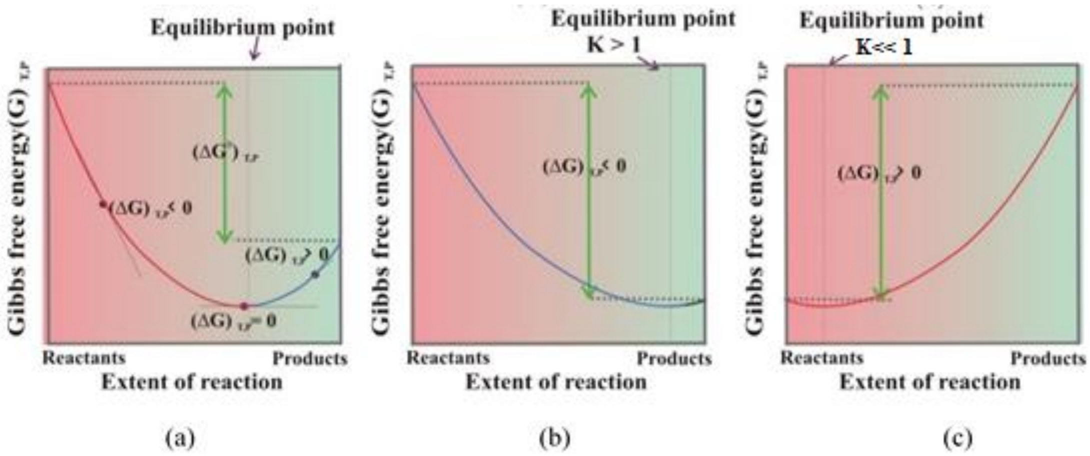


Figure 2.6 Details of Figure 2.5 **(a)** Variation of Gibbs free energy with composition for a reaction with spontaneous tendency. **(b)** A reaction which goes to a completion in which the equilibrium point lies very close to products ($K > 1$) and **(c)** A reaction which never reaches completion or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

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 magnetude and sign of ΔG_r^θ.

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

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

$\Delta G_r^\theta > 0$ *: 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 $2NO_{2(g)} \rightleftharpoons N_2O_{4(g)}$ with the equilibrium constant K is written as $NO_2 \rightleftharpoons 1/2\ N_2O_4$, the equilibrium constant K''; can be written as follows.

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

$$K'' = \frac{[N_2O_4(g)]^{1/2}}{[NO_2(g)]}$$

We can see that the K'' and K has the relation, $\boldsymbol{K'' = (K)^{1/2}}$ 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 $N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$ is 0.25. What is the equilibrium constant K'' for the reaction $\frac{1}{2}N_2(g) + 3/2H_2(g) \rightleftharpoons NH_3(g)$ at 800 K?

Answer

We can write

$$K = \frac{[NH_{3(g)}]^2}{[N_{2(g)}]\ [H_{2(g)}]^3}$$

$$K'' = \frac{[NH_{3(g)}]}{[N_{2(g)}]^{1/2}[H_{2(g)}]^{3/2}} = K^{1/2} = (0.25)^{\frac{1}{2}} = 0.50$$

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, $\boldsymbol{K_c}$ 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 $\boldsymbol{P}$ 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, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, we can write,

$$\boldsymbol{K_p} = \frac{(P_{NO_{2(g)}})^2}{(P_{N_2O_{4(g)}})}$$

Where $P_{NO_{2(g)}}$ and $P_{N_2O_{4(g)}}$ are the equilibrium partial pressures (in Pa) of $NO_2(g)$ and $N_2O_4(g)$, respectively. The subscript in $\boldsymbol{K_p}$ indicates that equilibrium concentrations are expressed in terms of pressure. In general, $\boldsymbol{K_c}$ is not always equal to $\boldsymbol{K_p}$, 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 $\boldsymbol{K_p}$ and $\boldsymbol{K_c}$ can be derived as follows. First, let us consider the following equilibrium in the gas phase:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

We can write,

$$\boldsymbol{K_c} = \frac{[\mathrm{HI(g)}]^2}{[\mathrm{I_2(g)}]\ [\mathrm{H_2(g)}]}$$

$$\boldsymbol{K_p} = \frac{(P_{\mathrm{HI(g)}})^2}{(P_{\mathrm{H_2(g)}})\,(P_{\mathrm{I_2(g)}})}$$

Applying ***P = CRT*** relation, we can write,
$P_{\mathrm{HI(g)}} = [\mathrm{HI(g)}]\,RT$, $P_{\mathrm{H_2(g)}} = [\mathrm{H_2(g)}]\,RT$ and $P_{\mathrm{I_2(g)}} = [\mathrm{I_2(g)}]\,RT$ and substituting these in

$$\boldsymbol{K_p} = \frac{(P_{\mathrm{HI(g)}})^2}{(P_{\mathrm{H_2(g)}})\,(P_{\mathrm{I_2(g)}})} = \frac{[\mathrm{HI(g)}]^2(RT)^2}{[\mathrm{I_2(g)}](RT)\ \ [\mathrm{H_2(g)}](RT)} = \frac{[\mathrm{HI(g)}]^2(RT)^{(2-2)}}{[\mathrm{I_2(g)}]\ \ [\mathrm{H_2(g)}]} = \boldsymbol{K_c}$$

In this example, ***Kp*** = ***Kc*** i.e., both equilibrium constants are equal. However, this is not always the case. For example in reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$,

$$K_c = \frac{[\mathrm{NH_3(g)}]^2}{[\mathrm{N_2(g)}]\ \ [\mathrm{H_2(g)}]^3} \text{ and } K_p = \frac{(P_{\mathrm{NH_3(g)}})^2}{(P_{\mathrm{N_2(g)}})\ \ (P_{\mathrm{H_2(g)}})^3}$$

Assuming ideal behaviour,

$$K_p = \frac{[\mathrm{NH_3(g)}]^2(RT)^2}{[\mathrm{N_2(g)}](RT)[\mathrm{H_2(g)}]^3(RT)^3}$$
$$= \frac{[\mathrm{NH_3(g)}]^2(RT)^{(2-4)}}{[\mathrm{N_2(g)}][\mathrm{H_2(g)}]^3}$$
$$= \frac{[\mathrm{NH_3(g)}]^2(RT)^{(-2)}}{[\mathrm{N_2(g)}][\mathrm{H_2(g)}]^3}$$

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, $aA(g) \rightleftharpoons bB(g)$,

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

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 dm^3 at temperature T (K),
$P_AV = n_ART$ and $P_BV = n_BRT$.

Therefore we can write
$P_A = C_ART$ and $P_B = C_BRT$ and when the C_A and C_B are expressed in mol dm^{-3},

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

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

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

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

As a summary we can write the relation between $\boldsymbol{K_P}$ and $\boldsymbol{K_C}$ for a reaction,

$\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{cC} + \mathrm{dD}$ as,

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

$\Delta n =$ 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 atm/ 101325 Pa (~ 100 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 1bar ($P^{\ominus} = 1$ atm, 100 kPa). Therefore a pressure of 400 kPa in standard state can be expressed as 400 kPa/100 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,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, K_c and K_p have no unit.

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, 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 $CH_4(g) + 2H_2S(g) \rightleftharpoons CS_2(g) + 4H_2(g)$

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

$$K_\mathrm{p} = \frac{\left(P_{\mathrm{H_2(g)}}\right)^4 \left(P_{\mathrm{CS_2(g)}}\right)}{\left(P_{\mathrm{CH_4(g)}}\right)\left(P_{\mathrm{H_2S(g)}}\right)^2} = \frac{(0.1\ \mathrm{Pa})^4\,(0.52\ \mathrm{Pa})}{(0.20\ \mathrm{Pa})\ \ (0.25\ \mathrm{Pa})^2}\left(1.0 \times 10^5\ \mathrm{Pa}\right)^2$$

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

$$K_\mathrm{p} = K_\mathrm{c}\,(RT)^{\Delta n}$$

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

Therefore, $K_\mathrm{p} = K_\mathrm{c}\,(RT)^2$ *and* $K_\mathrm{c} = \frac{K_P}{(RT)^2}$

$$K_\mathrm{c} = \frac{K_P}{(RT)^2} = \frac{4.2 \times 10^7\ \mathrm{Pa}^2}{\left(8.314\ \mathrm{J\,K^{-1}\,mol^{-1}} \times 1000\ \mathrm{K}\right)^2} = \frac{4.2 \times 10^7 \left(10^{-3}\ \mathrm{J\,dm^{-3}}\right)^2}{\left(8314\ \mathrm{J\ mol^{-1}}\right)^2}$$

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

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

$$K_\mathrm{p} = \frac{\left(\frac{P_{\mathrm{H_2(g)}}}{P^{\theta}}\right)^4 \left(\frac{P_{\mathrm{CS_2(g)}}}{P^{\theta}}\right)}{\left(\frac{P_{\mathrm{CH_4(g)}}}{P^{\theta}}\right)\left(\frac{P_{\mathrm{H_2S(g)}}}{P^{\theta}}\right)^2} = \frac{(0.1)^4\,(0.52)}{(0.20)\ \ (0.25)^2} = 4.2 \times 10^{-3}$$

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

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

The equilibrium constant is; $K_{\grave{\mathrm{c}}} = \frac{[\mathrm{CH_3COO^-(aq)}]\ \ [\mathrm{H_3O^+(aq)}]}{[\mathrm{CH_3COOH(aq)}]\ \ [\mathrm{H_2O(l)}]}$

Here, liquid water, $H_2O(l)$ is present as a medium for the reaction. In 1 dm^3 (1 L, or 1000 g of water, there are 1000 g/(18 g mol^{-1}) or 55.5 moles, of water. Therefore, the “concentration” of water or [$H_2O(l)$] 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 [H_2O(l)] as a constant. Therefore, we can write the equilibrium constant as;

$$K_c = \frac{[\mathrm{CH_3COO^-(aq)}]\ \ [\mathrm{H_3O^+(aq)}]}{[\mathrm{CH_3COOH(aq)}]}$$

Where, $K_c = K_c^{`}\,[\mathrm{H_2O(l)}]$

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.

$$\mathrm{H_2O(l)} \rightleftharpoons \mathrm{H_2O(g)}$$

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.

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

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.

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}$$

Considering the stoichiometric equation, we can write,

$$K_c^{`} = \frac{[\mathrm{CaO(s)}]\ [\mathrm{CO_2(g)}]}{[\mathrm{CaCO_3(s)}]}$$

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 [$CaCO_{3(s)}$] and [$CaO_{(s)}$] are both constants, the modified equilibrium constant for the thermal decomposition of calcium carbonate will be

$$K_c = [\mathrm{CO_{2(g)}}],$$

where,

$$K_c = K_c^{`}\ \frac{[\mathrm{CaCO_3(s)}]}{[\mathrm{CaO(s)}]} \text{ is a constant.}$$

Likewise we can write $K_p = P_{CO_2(g)}$

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,

$$Hg(l) + Hg^{2+}(aq) \rightleftharpoons Hg_2^{2+}(aq)$$

$$K_c^{`} = \frac{[Hg_2^{2+}(aq)]}{[Hg^{2+}(aq)][Hg(l)]}$$ and we can write,

$$K_c = \frac{[Hg_2^{2+}(aq)]}{[Hg^{2+}(aq)]} \quad \text{where,} \quad K_c = K_c^{`}\,[Hg(l)]$$

In this case, it's not appropriate to write an expression for $\boldsymbol{K_p}$ 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.

$$Ag_2O(s) + 2HNO_3(aq) \rightleftharpoons 2AgNO_3(aq) + H_2O(l)$$

$$K_C = \frac{[AgNO_3(aq)]^2}{[HNO_3(aq)]^2}$$

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 $\rightleftharpoons$ E + F 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,

$$\mathrm{A + B \rightleftharpoons C + D}$$
$$\mathrm{C + D \rightleftharpoons E + F}$$
$$K_\mathrm{c}^{`} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} \text{ and } K_\mathrm{c}^{''} = \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{C}][\mathrm{D}]}$$

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

$$\begin{array}{ll} \mathrm{A + B \rightleftharpoons C + D} & \\ \mathrm{C + D \rightleftharpoons E + F} & + \\ \hline \mathrm{A + B \rightleftharpoons E + F} & \end{array}$$

The equilibrium constant for the overall reaction is,

$$K_\mathrm{c} = \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{A}][\mathrm{B}]}$$

We can see that the expression of K_c is the product of $K_\mathrm{c}^{`}$ and $K_\mathrm{c}^{''}$

$$K_\mathrm{c}^{`}\,K_\mathrm{c}^{''} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} \times \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{C}][\mathrm{D}]} = \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{A}][\mathrm{B}]}$$

Therefore,

$$K_\mathrm{c} = K_\mathrm{c}^{`}\,K_\mathrm{c}^{''}$$

***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 °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 mol dm^{-3}.

$$\mathrm{N_2(g) + O_2(g) \rightleftharpoons 2NO(g)}: \qquad K_\mathrm{c}^{`} = 2.0 \times 10^{-25} \;\ldots\ldots\text{(I)}$$
$$\mathrm{2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)}: \qquad K_\mathrm{c}^{''} = 6.4 \times 10^{9} \;\ldots\ldots\text{(II)}$$

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

$$\mathrm{N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)} \qquad K_\mathrm{c} = ?$$

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

$$K_\mathrm{c}^{`} \times K_\mathrm{c}^{''} = \frac{[\mathrm{NO(g)}]^2}{[\mathrm{N_2(g)}][\mathrm{O_2(g)}]} \times \frac{[\mathrm{NO_2(g)}]^2}{[\mathrm{NO(g)}]^2[\mathrm{O_2(g)}]} = \frac{[\mathrm{NO_2(g)}]^2}{[\mathrm{O_2(g)}]^2[\mathrm{N_2(g)}]} = K_\mathrm{c}$$

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

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 ⇌ E + F.
Suppose the same reaction has a mechanism with two elementary steps.

$$\mathrm{A} + \mathrm{B} \underset{k^{\prime}_{r}}{\overset{k^{\prime}_{f}}{\rightleftharpoons}} \mathrm{C} + \mathrm{D}$$

$$\mathrm{C} + \mathrm{D} \underset{k^{\prime\prime}_{r}}{\overset{k^{\prime\prime}_{f}}{\rightleftharpoons}} \mathrm{E} + \mathrm{F}$$

We can write, $K_c^{\prime} = \frac{k^{\prime}_{f}}{k^{\prime}_{r}} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]}$ and $K_c^{\prime\prime} = \frac{k^{\prime\prime}_{f}}{k^{\prime\prime}_{r}} = \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{C}][\mathrm{D}]}$

$$K_c^{\prime}K_c^{\prime\prime} = \frac{k^{\prime}_{f}}{k^{\prime}_{r}} \times \frac{k^{\prime\prime}_{f}}{k^{\prime\prime}_{r}} = \frac{[\mathrm{C}][\mathrm{D}]}{[\mathrm{A}][\mathrm{B}]} \times \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{C}][\mathrm{D}]} = \frac{[\mathrm{E}][\mathrm{F}]}{[\mathrm{A}][\mathrm{B}]} = K_c$$

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:

$$\mathrm{aA} + \mathrm{bB} \rightleftharpoons \mathrm{cC} + \mathrm{dD}$$

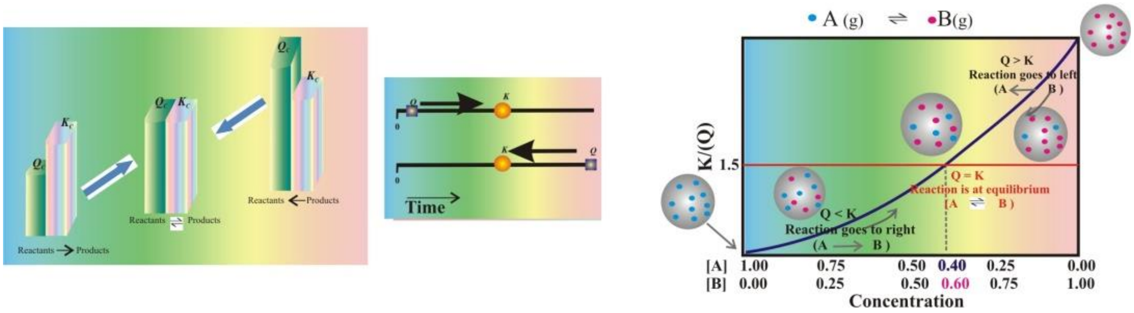
$$Q_c = \frac{[\mathrm{C}]_t^{\mathrm{c}}[\mathrm{D}]_t^{\mathrm{d}}}{[\mathrm{A}]_t^{\mathrm{a}}[\mathrm{B}]_t^{\mathrm{b}}}$$

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 $(Q_\mathrm{c} < K_\mathrm{c})$, 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 $(Q_\mathrm{c} > K_\mathrm{c})$, movement toward equilibrium decreases by converting products to reactants (that is, net reaction proceeds from right to left). If Q_c equals K_c $(Q_\mathrm{c} = K_\mathrm{c})$, 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:

- $Q_\mathrm{c} > K_\mathrm{c}$: *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.



(a) (b) (c)

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 diferent 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 $[A] = [B] = [C] = 3 \times 10^{-4}$ mol dm^{-3}. In which direction will the reaction proceed?

Answer

For the reaction the reaction quotient $\boldsymbol{Q_c}$ is given by,

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

$\boldsymbol{Q_c > K_c}$

Therefore, the reaction will proceed in the reverse direction.

Example 2.5

At elevated temperatures, methane ($CH_4(g)$) reacts with water to produce hydrogen and carbon monoxide as:

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$$

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

$[CH_4(g)] = 1.2 \times 10^{-2}$ mol/ 2.0 $dm^3 = 6.0 \times 10^{-3}$ mol dm^{-3}

Similarly, we can calculate $[H_2O(g)] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[CO(g)] = 8.0 \times 10^{-3}$ mol dm^{-3}, and $[H_2(g)] = 3.0 \times 10^{-3}$ mol dm^{-3}.

$$Q_c = \frac{[CO(g)][H_2(g)]^3}{[CH_4(g)][H_2O(g)]}$$

$$= \frac{(8 \times 10^{-3})\ (3 \times 10^{-3})^3}{(6 \times 10^{-3})(4 \times 10^{-3})}$$

$$= 9.0 \times 10^{-6}$$

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

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

Answer

The initial concentration of $[N_2(g)]$ is $1.5/20 = 7.5 \times 10^{-2}$ mol dm^{-3}. Similarly, $[H_2(g)] = 1.0 \times 10^{-1}$ mol dm^{-3} and $[NH_3(g)] = 4.0 \times 10^{-1}$ mol dm^{-1}. Substituting these concentrations into the Q expression gives

$$Q_c = \frac{[NH_{3(g)}]^2}{[N_{2(g)}][H_{2(g)}]^3} = \frac{(4 \times 10^{-1})^2}{(7.5 \times 10^{-2})(1.0 \times 10^{-1})^3}$$

$$= 2.1 \times 10^4$$

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.

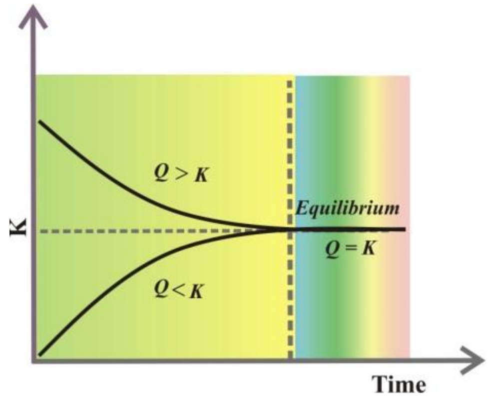


Figure 2.8 The figure explaining the variation of Q over time: If the initial Q is less than K it increases with time favouring the forward reaction; if it is greater than K, it decreases with time favouring the backward reaction until the condition is reached at which $Q = K$.

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 $H_2(g)$ with $I_2(g)$ is 64.0 at 800 K:

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

If 1.00 mol of $H_2(g)$ is allowed to react with 1.00 mol of $I_2(g)$ in a 10.0 dm^3 closed-rigid-reaction vessel at 800 K, what are the concentrations of $H_2(g)$, $I_2(g)$, and HI(g) at equilibrium? What is the composition of the equilibrium mixture in moles?

Answer

The initial concentrations are $[H_2(g)] = [I_2(g)] = 1.00 \text{ mol}/10.0 \text{ dm}^3$
$= 0.10 \text{ mol dm}^{-3}$.

For convenience, define an unknown, x, as the concentration (mol dm^{-3}) of $H_2(g)$ that reacts. According to the balanced equation for the reaction, x mol dm^{-3} of $H_2(g)$ reacts with x mol dm^{-3} of $I_2(g)$ to give $2x$ mol dm^{-3} of HI(g). This reduces the initial concentrations of $H_2(g)$ and $I_2(g)$ from 0.10 mol dm^{-3} to $(0.10 - x)$ mol dm^{-3} at equilibrium.

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

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
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, $K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$

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

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})

$\therefore [H_2(g)] = [I_2(g)] = 0.02 \text{ mol dm}^{-3}$ and $[HI(g)] = 0.16 \text{ mol dm}^{-3}$

$\therefore$ The composition in moles: $H_2(g) = I_2(g) = 0.02 \text{ mol dm}^{-3} \times 10.0 \text{ dm}^3 = 0.2 \text{ mol}$

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

Example 2.8

For the same reaction and temperature as in the previous example, suppose that the initial concentrations of $H_2(g)$, $I_2(g)$, and $HI(g)$ 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 $H_2(g)$ and $I_2(g)$, at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be $2x$.

	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
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, $K_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} = 64 = \frac{(0.02 \ +2\,x)^2}{(0.006 - x)(0.004 - x)}$

Multiplication gives us a quadratic equation;

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

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 mol dm^{-3} or 0.002 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 mol dm^{-3}.

Now the equilibrium concentrations are:

$[H_2(g)] \ = (0.006 - \ 0.002) \ = 0.004 \text{ mol dm}^{-3}$

$[I_2(g)] \ = (0.004 - \ 0.002) \ = \ 0.002 \text{ mol dm}^{-3}$

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

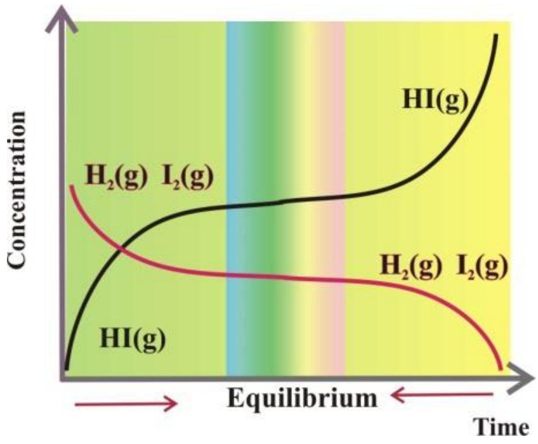


Figure 2.9 Chemical equilibrium in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ can be attained from either direction. This explains that the reaction can start from either side (right and left) with a mixture of $H_2(g)$ and $I_2(g)$ or with HI(g). When it starts with $H_2(g)$ and $I_2(g)$ mixture eventually those decrease in amount while the amount of HI(g) increases. In the other way, if the reactions starts with HI(g), amounts of $H_2(g)$ and $I_2(g)$ increase with the time while the amount of HI(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 $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. The total pressure at equilibrium was found to be 9.0×10^5 Pa. Calculate partial pressures of each and hence $\boldsymbol{K_p}$ and $\boldsymbol{K_C}$ at equilibrium.

Answer

Assuming ideal behaviour for $N_2O_4(g)$;

$PV = nRT$

$P_{N_2O_4} = 0.15 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 400 \text{ K} \approx 5.0 \times 10^5 \text{ Pa}$

Therefore, initial pressure = 4.98×10^5 Pa

Consider the reaction,

	N_2O_4 (g)	$\rightleftharpoons$	$2NO_2$
Initial Pressure/ Pa:	5.0×10^5		0
Pressure change/ Pa:	x		$2\,x$
Pressure at equilibrium/ Pa:	$(5.0 \times 10^5 - x)$		$2\,x$

At equilibrium, total pressure; $P_{\text{total}} = P_{N_2O_4} + P_{NO_2}$

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

$$x = 4.0 \times 10^5\ Pa$$

$$P_{N_2O_4} = 1.0 \times 10^5 \text{ Pa and } P_{NO_2} = 8.0 \times 10^5 \text{ Pa}$$

$$K_p = \frac{(P_{NO_2})^2}{(P_{N_2O_4})} = \frac{(8.0 \times 10^5 \text{ Pa})^2}{(1.0 \times 10^5 \text{ Pa})} = 6.4 \times 10^6 \text{ Pa}$$

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

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

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.

$$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$$

What are the equilibrium partial pressures of CO(g) and CO_2(g) at 1000 K if the initial partial pressures are $P_{CO(g)} = 1.0 \times 10^5$Pa and $P_{CO_2(g)} = 0.50 \times 10^5$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.

	$FeO(s) + CO(g)$ $\rightleftharpoons$	$Fe(s) + CO_2(g)$
Initia pressure/ Pa	1.0×10^5	0.50×10^5
Change pressure/ Pa	$- x$	$+x$
Equilibrium pressure (Pa)	$(1.0 \times 10^5 - x)$	$(0.50 \times 10^5 + x)$

$$K_P = \frac{(P_{CO_2(g)})}{(P_{CO(g)})} = 0.25 = \frac{(0.50 \times 10^5 + x)}{(1.0 \times 10^5 - x)}$$

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

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

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

$$P_{CO_2(g)} = 0.30 \times 10^5 \text{ Pa}$$

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 $P_{CO(g)}$ and $P_{CO_2(g)}$. 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:

$H_2(g) + C_2H_4(g) \rightleftharpoons C_2H_6(g)$.

Equilibrium constant of the reaction $K_c = 9.6 \times 10^{18}$ at 25 °C. If a mixture of 0.200 mol dm^{-3} $H_2(g)$ and 0.155 mol dm^{-3} $C_2H_4(g)$ 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 mol dm^{-3}) is higher than the amount of $C_2H_4(g)$ (0.155 mol dm^{-3}), it is clear that all the $C_2H_4(g)$ is consumed to produce 0.155 mol dm^{-3} of $C_2H_6(g)$. Therefore the remaining amount of $H_2(g)$ is (0.200 -0.155) mol dm^{-3}= 0.045 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.

	$H_2(g)$	+	$C_2H_4(g)$	$\rightleftharpoons$	$C_2H_6(g)$
Initial/ mol dm^{-3}	0.045		0.0		0.155
Change/ mol dm^{-3}	$+ x$		$+ x$		$- x$
Equilibrium/ mol dm^{-3}	$(0.045+x)$		x		$0.155 - x$

$$K_c = \frac{[C_2H_6(g)]}{[H_2(g)][C_2H_4(g)]} = 9.6 \times 10^{18} = \frac{(0.155 - x)}{(0.045+x)x} \approx \frac{(0.155)}{(0.045)x} \quad \text{(since } x \text{ is very small)}$$

$$x = 3.6 \times 10^{-19} \text{ mol dm}^{-3}$$

$[H_2(g)]$ = 0.045 mol dm^{-3}
$[C_2H_4(g)]$ = 3.6×10^{-19} mol dm^{-3}
$[C_2H_6(g)]$ = 0.155 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 Chātelier.

Le Chātelier'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,

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

If $H_{2(g)}$ 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 $H_{2(g)}$ is consumed, i.e., more of $H_{2(g)}$ and $I_{2(g)}$ react to form $2HI_{(g)}$ and finally the equilibrium shifts to right (forward). This is in accordance with the Le Chātelier'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.

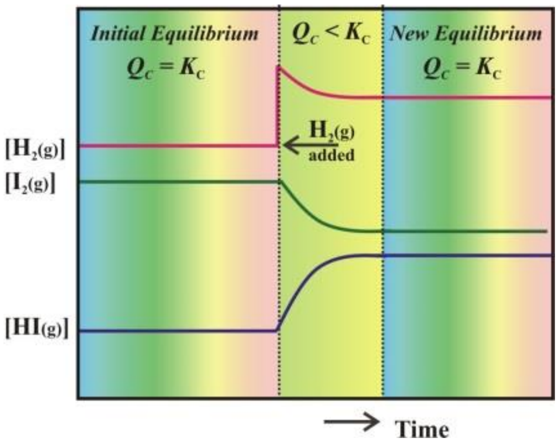


Figure 2.10 Effect of addition of H_2 on the change of concentration for the reactants and products in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

This behaviour can be explained in terms of the reaction quotient, $\boldsymbol{Q_c}$

$$Q_c = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]}$$

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 $H_2(g)$ 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. $[Fe(SCN)_3]$ dissolves readily in water to give a red solution. The red colour is due to the presence of hydrated $[FeSCN]^{2+}$ ion. The equilibrium between undissociated $[FeSCN]^{2+}$ and the Fe^{3+} and SCN^- ions is given by

$$\underset{\textit{red}}{[FeSCN]^{2+}(aq)} \rightleftharpoons \underset{\textit{pale yellow}}{Fe^{3+}(aq)} + \underset{\textit{colourless}}{SCN^-(aq)}$$

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

Further, if we write the above equilibrium as;

$$\underset{\textit{pale yellow}}{Fe^{3+}(aq)} \quad + \quad \underset{\textit{colourless}}{SCN^{-}(aq)} \quad \rightleftharpoons \quad \underset{\textit{red}}{[FeSCN]^{2+}(aq)}$$

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 $Fe^{3+}(aq)$ or $SCN^{-}(aq)$ ions. For example, oxalic acid ($H_2C_2O_4$), reacts with $Fe^{3+}(aq)$ ions to form the stable complex ion $[Fe(C_2O_4)_3]^{3-}$, thus decreasing the concentration of free $Fe^{3+}(aq)$. In accordance with the Le Chatelier's principle, the concentration stress of removed $Fe^{3+}(aq)$ is relieved by dissociation of $[Fe(SCN)]^{2+}$ to replenish the $Fe^{3+}(aq)$ ions. Because the concentration of $[Fe(SCN)]^{2+}$ decreases, the intensity of red color decreases.

This effect can be explained by the reactions shown below.

$$3H_2C_2O_4(aq) + Fe^{3+}(aq) \rightarrow [Fe(C_2O_4)_3]^{3-}(aq) + 6H^{+}(aq)$$

and

$$[FeNCS]^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + SCN^{-}(aq)$$

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

$$HgCl_2(aq) + 4SCN^{-}(aq) \rightarrow [Hg(SCN)_4]^{2-}(aq) + 2Cl^{-}(aq)$$

and

$$[FeNCS]^{2+}(aq) \rightleftharpoons Fe^{3+}(aq) + SCN^{-}(aq)$$

Example:

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

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad K_C = 0.291 \text{ at } 700\text{ K}$$

Suppose we have an equilibrium mixture of 0.50 mol dm^{-3} $N_2(g)$, 3.00 mol dm^{-3} $H_2(g)$, and 1.98 mol dm^{-3} $NH_3(g)$ at 700 K and that we disturb the equilibrium by increasing the $N_2(g)$ 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 $N_2(g)$ by converting some of the $N_2(g)$ to $NH_3(g)$. It is clear that the number of gaseous molecules decreases in the forward direction allowing the release in the stress. i.e. as the $N_2(g)$ concentration decreases, the $H_2(g)$ concentration must also decrease and the $NH_3(g)$ concentration must increase in accordance with the stoichiometry of the balanced equation.

These changes can be explained by the following Figure 2.11.

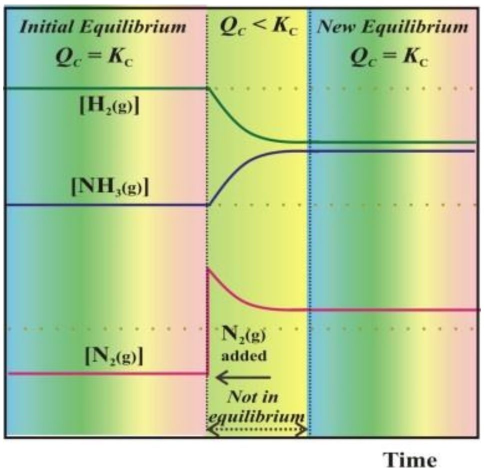
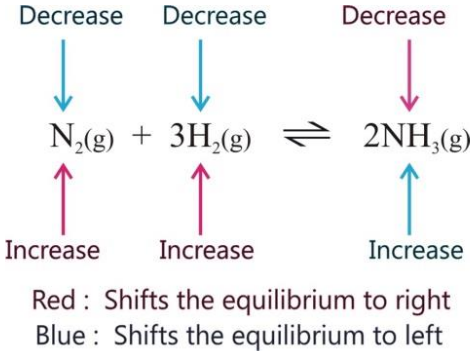


Figure 2.11 Effect of addition of N_2 on the change of concentration for the reactants and products in the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

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 $\boldsymbol{Q_c}$. For the initial equilibrium mixture of 0.50 mol dm^{-3} $N_{2(g)}$, 3.00 mol dm^{-3} $H_2(g)$, and 1.98 mol dm^{-3} $NH_3(g)$ at 700 K, $\boldsymbol{Q_c}$ equals the equilibrium constant $\boldsymbol{K_c}$ (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 $N_2(g)$ 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 :

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

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 $N_2(g)$ and $H_2(g)$ to $NH_3(g)$ 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} $N_2(g)$, 2.43 mol dm^{-3} $H_2(g)$, and 2.36 mol dm^{-3} $NH_3(g)$, 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 ⇌ gas systems:

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

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(l) + 3CO_2(g)$$

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 *Qc*.

(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;

$$Q_c = \frac{[CO_2(g)]^3}{[CO(g)]^3}$$

When the equilibrium is disturbed by reducing [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, $[CO_2]$ must decrease and [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:

$$PbCO_3(s) \rightleftharpoons PbO(s) + CO_2(g)$$

Because $PbCO_3$ and PbO are solids, the equilibrium constant is simply $K = [CO_2(g)]$. At a given temperature, therefore, any system that contains solid $PbCO_3$ and solid PbO will have exactly the same concentration of $CO_2(g)$ at equilibrium, regardless of the ratio or the amounts of the solids present. This can be understand by Figure 2.12, which shows a plot of $[CO_2(g)]$ versus the amount of solid $PbCO_3$ added. Initially, the added $PbCO_3$ decomposes completely to $CO_2(g)$ because the amount of $PbCO_3$ is not sufficient to give a $CO_2(g)$ concentration equal to K. Thus the left portion of the graph represents a system that is not at equilibrium because it contains only $CO_2(g)$ and PbO(s). In contrast, when just enough $PbCO_3$ has been added to give $[CO_2(g)] = K$, the system has reached equilibrium, and adding more $PbCO_3$ has no effect on the $CO_2(g)$ concentration: so the graph is a horizontal line. Thus any $CO_2(g)$ 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 $CO_2(g)$ lies above the horizontal line, so it corresponds to a $[CO_2(g)]$ that is greater than the equilibrium concentration of $CO_2(g)$ ($Q > K$). To reach equilibrium, the system must decrease $[CO_2(g)]$, which it can do only by reacting $CO_2(g)$ with solid PbO to form solid $PbCO_3$. Thus the reaction will proceed to the left side, until $[CO_2(g)] = K$. Conversely, the point labelled as **B** in the figure, the concentration of gaseous $CO_2(g)$ lies below the horizontal line, so it corresponds to a $[CO_2(g)]$ that is less than the equilibrium concentration of $CO_2(g)$ ($Q < K$). To reach equilibrium, the system must increase $[CO_2(g)]$, which it can do only by decomposing solid $PbCO_3$ to form $CO_2(g)$ and solid PbO. The reaction will therefore proceed to the right as written, until $[CO_2(g)] = K$.

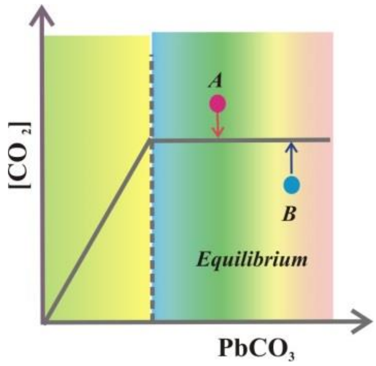


Figure 2.12 Initially the concentration of $CO_2(g)$ increases linearly with the amount of solid $PbCO_3$ added, as $PbCO_3$ decomposes to $CO_2(g)$ and solid PbO. Once the $CO_2(g)$ concentration reaches the value that corresponds to the equilibrium concentration, however, adding more solid $PbCO_3$ has no effect on $[CO_2(g)]$, 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.

$$CdO(s) + H_2(g) \rightleftharpoons Cd(s) + H_2O(g)$$

Equilibrium constant $\boldsymbol{K_c}$ is $[H_2O(g)]/ [H_2(g)]$. For example, if $[H_2O(g)]$ is doubled at equilibrium, then $[H_2(g)]$ must also be doubled for the system to remain at equilibrium. A plot of $[H_2O(g)]$ versus $[H_2(g)]$ at equilibrium is a straight line with a slope of $\boldsymbol{K_c}$. Again, only those pairs of concentrations of $H_2O(g)$ and $H_2(g)$ 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 $[H_2O(g)]/ [H_2(g)]$ ratio is less than the ratio of an equilibrium mixture ($Q < K$). Thus the reaction will proceed to the right as written, consuming $H_2(g)$ and producing $H_2O(g)$, 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 $[H_2O(g)]/ [H_2(g)]$ ratio is greater than the ratio of an equilibrium mixture ($Q > K$). Thus the reaction will proceed to the left as written, consuming $H_2O(g)$ and producing $H_2(g)$, which causes the concentration ratio to move down and to the right toward the equilibrium line.

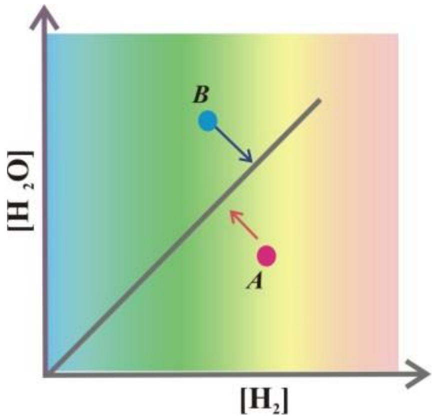


Figure 2.13 For any equilibrium concentration of $H_2O(g)$, there is only one equilibrium concentration of $H_2(g)$. Because the magnitudes of the two concentrations are directly proportional, a large $[H_2O(g)]$ at equilibrium requires a large $[H_2(g)]$ and vice versa. In this case, the slope of the line is equal to $\boldsymbol{K_c}$.

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:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)} \quad K_c = 0.29 \text{ at } 700\text{ K}$$

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 mol dm^{-3} $N_2(g)$, 3.00 mol dm^{-3} $H_2(g)$ and 1.98 mol dm^{-3} $NH_3(g)$ at 700 K, where Q_c equals the equilibrium constant $\boldsymbol{K_c}$ (0.291) because the system is at equilibrium:

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

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.

$$Q_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]} = \frac{[3.96]^2}{[1.0][6.0]^3} = 0.073 < K_c$$

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 $\Delta H = +58\ kJ\ mol^{-1}$. This reaction can be written as follows:

$$58\ \text{kJ} + N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

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

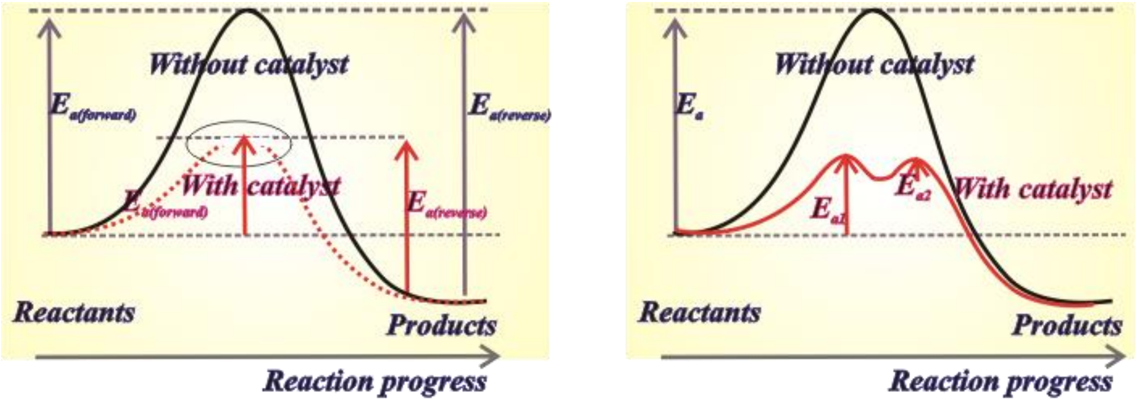
Increasing the temperature (adding heat to the system) is a stress that will drive the reaction to the right. Thus increasing the temperature increases the ratio of $NO_{2(g)}$ to $N_2O_{4(g)}$ at equilibrium, which increases equilibrium constant ***K***.

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 providng 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.



(a) (b)

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 providng 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 $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is exothermic, its equilibrium constant decreases with increasing temperature, and optimum yields of $NH_3(g)$ 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 $NH_3(g)$ is reasonably favourable. The yield of $NH_3(g)$ can be improved further by running the reaction at high pressures. Typical reaction conditions for the industrial synthesis of ammonia are 400 – 500 °C and 130 – 300 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 being 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:

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$$

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.

$$NaCl(s) \rightarrow Na^{+}(aq) + Cl^{-}(aq)$$

Acids and bases are also electrolytes. Some acids, like hydrochloric acid (HCl) and nitric acid (HNO_3), 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:

$$HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$$

or we write the reaction as:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^{+}(aq) + Cl^{-}(aq)$$

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

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^{-}(aq) + H^{+}(aq)$$

or we write the reaction as:

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

We can see that the → (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 $H_3O^+(aq)$ and $Cl^-(aq)$ ions. In the case of acetic acid, a ⇌ (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 $CH_3COO^-(aq)$ and $H^+(aq)$ ions. As time goes on, some of the $CH_3COO^-(aq)$ and $H^+(aq)$ 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,* $H_3O^+(aq)$. It has to be noted that the use of $H^+(aq)$ and $H_3O^+(aq)$ 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 “*acidusî* 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:

$HX\ (aq) \rightarrow H^+(aq) + X^-\ (aq)$
or
$HX\ (aq) + H_2O(l) \rightarrow H_3O^+(aq) + X^-\ (aq)$

Similarly, a base molecule like MOH(aq) ionizes in aqueous solution according to the equation:
$MOH(aq) \rightarrow M^+(aq) + OH^-(aq)$

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 Brönsted -Lowry definition of acids and bases

The Danish chemist, Johannes Brönsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brönsted-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;

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

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 latters section dealing with *conjugate acid-base pairs*).

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

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 Brönsted-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,

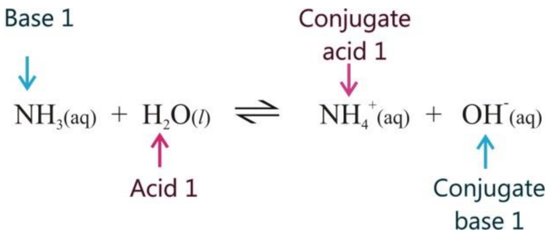
$$BF_3 + :NH_3 \rightarrow BF_3:NH_3$$

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

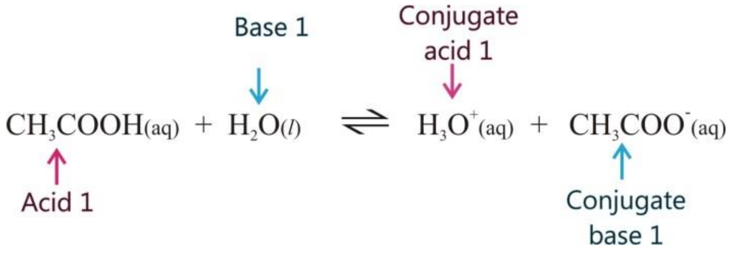
Brønsted definition of acids and bases can further be extended to the concept of the ***conjugate acid-base pair,*** which can be defined as *an acid and its conjugate base* or *a base and its conjugate acid.* The conjugate base of a Brønsted acid is the species that remains when one proton has been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

Consider the partial dissolution of $NH_3(aq)$ 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-Brönsted acid and base, respectively. In the reverse reaction, H^+ is transferred from $NH_4^+(aq)$ to $OH^-(aq)$. In this case, $NH_4^+(aq)$ acts as a Bronsted acid while OH^- acted as a Brönsted base. The acid-base pair that differs only by one proton is called a ***conjugate acid-base pair***. Therefore, $OH^-(aq)$ is called the conjugate base of an acid H_2O and $NH_4^+(aq)$ is called conjugate acid of the base $NH_3(aq)$. If Brönsted 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 $CH_3COOH(aq)$ in water. $CH_3COOH(aq)$ 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 $H_3O^+(aq)$ is produced when water accepts a proton from $CH_3COOH(aq)$. Therefore, $CH_3COO^-(aq)$ is a conjugate base of $CH_3COOH(aq)$ acid and $CH_3COOH(aq)$ is the conjugate acid of base $CH_3COO^-(aq)$. Similarly, H_2O is a conjugate base of the acid $H_3O^+(aq)$ and $H_3O^+(aq)$ 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 Brönsted 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 Brönsted bases: $NH_2^–$, NH_3 and $HCOO^–$.

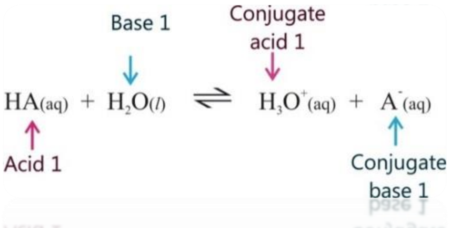
Answer

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), hyrdoiodic 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 $Ba(OH)_2$ 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 Brönsted-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 H_3O^+(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 $HA_{(aq)}$ is a stronger acid than $H_3O^+_{(aq)}$, and then $HA_{(aq)}$ will donate protons and not H_3O^+(aq), and the solution will mainly contain $A^-_{(aq)}$ and $H_3O^+_{(aq)}$ 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^-:

$$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$$

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:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

- 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:

$$O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$$

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:

$$\underset{\text{acid}}{H_2O(l)} + \underset{\text{base}}{H_2O(l)} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{H_3O^+(aq)} + \underset{\substack{\text{conjugate}\\\text{base}}}{OH^-(aq)}$$

The dissociation constant for the reaction is represented by,

$$K = \frac{[H_3O^+(aq)][OH^-(aq)]}{[H_2O(l)]^2}$$

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 g dm^{-3}/18 g mol^{-1} = 55.55 mol dm^{-3} is a constant) . Therefore, incorporation of $[H_2O(l)]$ into the equilibrium constant to give a new constant, K_w, which is called the ***ionic product of water***.

i.e, $K[H_2O(l)]^2 = K_w = [H_3O^+(aq)][OH^-(aq)]$

The concentrations of $H_3O^+(aq)$ and $OH^-(aq)$ have been found out experimentally as 1.0×10^{-7} mol dm^{-3} at 298 K. As dissociation of water produces equal number of $H_3O^+(aq)$ and $OH^-(aq)$ ions, the value of K_w at 298K is,

$$K_w = [H_3O^+(aq)]\big[[OH^-(aq)]\big] = (1 \times 10^{-7} \text{ mol dm}^{-3})^2 = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$$

It has to be noted that the K_w is temperature dependent and is an equilibrium constant. When $[H_3O^+(aq)] = [OH^-(aq)]$, the aqueous solution is said to be neutral. In an acidic solution there is an excess of hydronium ions and $[H_3O^+(aq)] > [OH^-(aq)]$. In a basic solution there is an excess of hydroxide ions, so $[H_3O^+(aq)] < [OH^-(aq)]$.

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 $(a_{H_3O^+(aq)})$ or $(a_{H^+(aq)})$ of the hydronium or hydrogen ion. In dilute solutions (< 0.01 mol dm^{-3}), activity of hydrogen ion is equal in magnitude to molarity represented by $[H_3O^+(aq)]$. It should be noted that activity has no units and is defined as:

$$(a_{H_3O^+(aq)}) \text{ or } (a_{H^+(aq)}) = [H_3O^+(aq)]/\ 1 \text{ mol dm}^{-3}$$

Therefore, from the definition of pH is

$$\text{pH} = -\log\ (a_{H_3O^+(aq)}) = -\log\ \{[\ H_3O^+(aq)]/\ 1\text{mol dm}^{-3}\}$$

As the $[H_3O^+(aq)]$ has units mol dm^{-3},

$\text{pH} = -\log\ \{[H_3O^+(aq)] \text{ mol dm}^{-3}/ \text{ mol dm}^{-3}\}$

$\text{pH} = -\log\ \{[H_3O^+(aq)]\ \}$

That is, pH value has no units.

Thus, an acidic solution of HCl (10^{-2} mol dm^{-3}) will have a pH = 2. Similarly, a basic solution of NaOH having $[OH^-] = 10^{-4}$ mol dm^{-3} and $[H_3O^+] = 10^{-10}$ mol dm^{-3} will have a pH = 10. At 25 °C, pure water has a concentration of hydronium or hydrogen ions, $[H_3O^+]$ or $[H^+] = 10^{-7}$ 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, $[H^+] > 10^{-7}$ mol dm^{-3}, while basic solutions possess a concentration of hydrogen ions, $[H^+] < 10^{-7}$ mol dm^{-3}. Thus, we can summarisethat

Acidic solution has pH < 7

Basic solution has pH > 7

Neutral solution has pH = 7

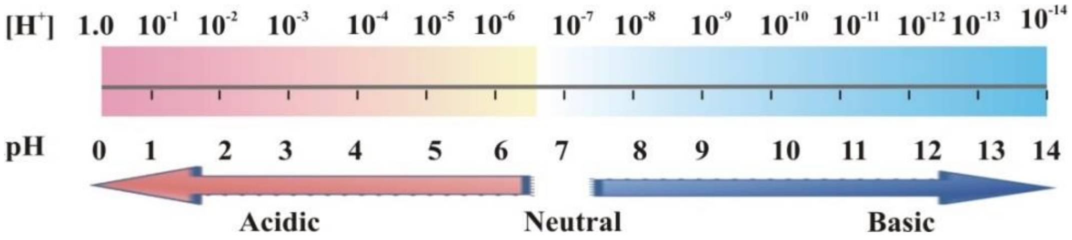


Figure 2.15 Simple visualization of the pH scale. At pH 7.0 solutions are said to be neutral. Proceeding to the lower pH values increases the acidity while the otherway increases the basisity of solutions.

$$K_w = [H_3O^+(aq)][OH^-(aq)]$$

Taking negative logarithm on both sides of equation, we obtain

$$-\log K_w = -\log\{[H_3O^+(aq)][OH^-(aq)]\}$$

$$pK_w = -\log[H_3O^+(aq)] - \log[OH^-(aq)]$$

$$pK_w = pH + pOH$$

or

$$pH + pOH = 14$$

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 $[H^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[H^+]$ 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 *p*H 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 1.0×10^{-4} mol dm^{-3} solution of HCl.

Answer

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

Example 2.14

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

Answer

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

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

or

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

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

Example 2.15

Calculate pH of a 1.0×10^{-8} mol dm^{-3} solution of HCl.

Answer

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

One should note that here the $[H^+]$ from HCl is less than that coming from the self-ionization of water (i.e. 1.0×10^{-7} mol dm^{-3}). Therefore, we should consider the $[H^+]$ generated from both HCl and water. That is, $[H^+]$ from the given HCl solution is 1.0×10^{-8} mol dm^{-3} and take that from water as x.
Therefore, $[OH^-] = x$ and $[H_3O^+] = 10^{-8} + x$
$K_w = [H_3O^+(aq)][OH^-(aq)] = 10^{-14} = (10^{-8} + x)\,x$
$x^2 + 10^{-8}x - 10^{-14} = 0$

Solving the above quadratic equation, we get
$[OH^-] = 9.5 \times 10^{-8}$ mol dm^{-3} and hence pOH = 7.02
Therefore, pH = 6.98

In the above calculations in examples, it was easy to decide the concentration of $[H^+]$ and $[OH^-]$ 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 equlibria.

2.2.6 Weak acids and their ionization (dissociation) constant

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

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

The equilibrium expression for this ionization is

$$K = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)][H_2O(l)]}$$

We can write,

$$K[H_2O(l)] = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

Taking $K[H_2O(l)] = K_a$, as a constant, because $[H_2O(l)]$ is a constant, we can write

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

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 $[H_3O^+(aq)]$ or $[H^+(aq)]$ 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 $\boldsymbol{c}$ and its extent of ionization (or degree of ionization) is $\boldsymbol{\alpha}$, we can express the equilibrium as,

	$HA(aq) + H_2O(l)$	$\rightleftharpoons$ $H_3O^+(aq)$	+ $A^-(aq)$
Initial concentration/ mol dm^{-3}	c	0	0
Concentration change/ mol dm^{-3}	$-c\alpha$	$+c\alpha$	$+c\alpha$
∴ Equilibrium concentration/ mol dm^{-3}	$c(1-\alpha)$	$c\alpha$	$c\alpha$

$$\therefore K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]} = \frac{c\alpha . c\alpha}{c(1-\alpha)} = \frac{c\alpha^2}{(1-\alpha)}$$

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

As the ionization of a weak acid is very small, we can assume that α **is very small or** $(\mathbf{1}-\alpha)\sim \mathbf{1}$. **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_3COOH)	1.74×10^{-5}
Benzoic Acid (C_6H_5COOH)	6.50×10^{-5}
Hypochlorous Acid (HClO)	3.00×10^{-8}
Hydrocyanic Acid (HCN)	4.90×10^{-10}
Phenol (C_6H_5OH)	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:

$$\mathbf{p}K_\mathbf{a} = -\log (K_\mathbf{a})$$

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 pH = – log[H_3O^+] or calculate [H_3O^+] once pH is known using **[H_3O^+]= 10^{-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:

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq) \text{ -------------- } (1)$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \text{ ----------- } (2)$$

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

	HF(aq) +	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$F^-(aq)$
Initial concentration/ mol dm^{-3}	0.2			0		0
Concentration hacnge/ mol dm^{-3}	-0.2α			$+0.2\alpha$		$+0.2\alpha$
∴ Equilibrium concentration/ mol dm^{-3}	$0.2(1-\alpha)$			$+0.2\alpha$		$+0.2\alpha$

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

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

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

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

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

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

$[H_3O^+] = [F^-] = c\alpha = 0.2$ mol dm^{-3} $\times 0.04 = 8.0 \times 10^{-3}$ mol dm^{-3}

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

Hence, pH = – log[H_3O^+] = –log(8.0×10^{-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 accepts 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:

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

$$HF(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^-(aq)$$

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

	$HF(aq)$ +	$H_2O(l)$	$\rightleftharpoons$	$H_3O^+(aq)$	+	$F^-(aq)$
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:

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

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

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

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

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

And we have

$[H_3O^+] = [F^-] = x = 8.0 \times 10^{-3}$ mol dm^{-3}

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

Hence, $pH = -\log[H_3O^+] = -\log(8.0 \times 10^{-3}) = 2.10$

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 $\boldsymbol{K_a}$ and **p**$\boldsymbol{K_a}$ of the monobasic acid.

Answer

$pH = -\log [H_3O^+]$

Therefore, $[H_3O^+] = 10^{-pH} = 10^{-4.50} = 3.16 \times 10^{-5}$

$[H_3O^+] = [A^-] = 3.16 \times 10^{-5}$ mol dm^{-3}

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

We can summarize these as follows

	$HA(aq)$ + $H_2O(l)$ ⇌	$H_3O^+(aq)$ +	$A^-(aq)$
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}
∴ Equilibrium concentration/ mol dm^{-3}	$(0.10 - 3.16 \times 10^{-5})$	3.16×10^{-5}	3.16×10^{-5}
∴ Equilibrium concentration/ mol dm^{-3}	0.10	3.16×10^{-5}	3.16×10^{-5}

Thus, $\boldsymbol{K_a} = \dfrac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$

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

$pK_a = -\log(10^{-8}) = 8$

2.2.7 Weak bases and base ionization constant

The ionization of base MOH can be represented by equation:

$$BOH(aq) \rightleftharpoons B^+(aq) + OH^-(aq)$$

We can write this reaction as,

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

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

$$K = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)][H_2O(l)]}$$

Similar to treatment in weak acids,

$$K[H_2O(l)] = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

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

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

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

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 $[OH^-(aq)] > [H^+(aq)]$ and therefore 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, $(CH_3)_2NH$	5.40×10^{-4}
Triethylamine, $(C_2H_5)_3N$	6.45×10^{-5}
Ammonia, NH_3 or NH_4OH	1.77×10^{-5}
Pyridine, C_5H_5N)	1.77×10^{-9}
Aniline, $C_6H_5NH_2$	4.27×10^{-10}
Urea, $CO(NH_2)_2$	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 $[OH^-(aq)]$ first rather than $[H^+(aq)]$ 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 × 10^{-5}

Answer

The following equilibrium reaction exists and let x be the equilibrium concentration of $NH_4^+(aq)$ and $OH^-(aq)$ ions in mold m^{-3}, we summarize:

	$NH_3(aq) + H_2O(l\ )$	$\rightleftharpoons$	$NH_4^+(aq)$ +	$OH^-(aq)$
Initial concentration/ mol dm^{-3}	0.4		0	0
Concentration change/ mol dm^{-3}	$-x$		$+x$	$+x$
$\therefore$ Equilibrium concentration/ mol dm^{-3}	$(0.4-x)$		$+x$	$+x$

$$K_b = \frac{[NH_4{}^+(aq)][OH^-(aq)]}{[NH_3(aq)]} = 1.80 \times 10^{-5}$$

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

Applying the approximation 0.40 – x ~ 0.40, we obtain

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

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

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

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

Applying the relationship pH + pOH = 14.00, we get

pH = 14.00 – 2.57 = 11.43

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

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

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

The conjugate base, $CH_3COO^-(aq)$, reacts with water according to the equation

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq)$$

The base ionization constant for the reaction,

$$K_b = \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

Consider the product of these two ionization constants.

$$K_a \times K_b = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} \times \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

$$K_a \times K_b = [H_3O^+(aq)][OH^-(aq)]$$

$$i.e.\quad \boldsymbol{K_a \times K_b = K_w}$$

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

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq) \quad ----- \quad K_a$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + CH_3COOH(aq) \quad ----- \quad K_b$$

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \quad ----- \quad K_w$$

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 $\boldsymbol{K_a\ K_b = K_w}$ 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;

$$NaNO_3(s) \rightarrow Na^+(aq) + NO_3^-(aq)$$

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.: CH_3COONH_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.

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

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

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

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). $K_{b(CH_3COO^-)} = 5.6 \times 10^{-10}$

Answer

As CH_3COONa completely ionizes into $CH_3COO^-(aq)$ and $Na^+(aq)$ in solution, $CH_3COO^-(aq)$ ion undergoes hydrolysis.

	$CH_3COO^-(aq)$ + $H_2O(l)$	$\rightleftharpoons$ $CH_3COOH(aq)$	+ $OH^-(aq)$
Initial concentration/ mol dm^{-3}	0.10	0	0
Concentration change/ mol dm^{-3}	$-x$	$+x$	$+x$
∴ 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.

$$K_b = \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

Substituting above values at equilibrium,

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

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

$$\frac{x^2}{0.10} \sim 5.6 \times 10^{-10}$$

$$x^2 = 5.6 \times 10^{-11}$$

$$x = [OH^-(aq)] = 7.5 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\therefore \text{pOH} = 5.13$$

$$\text{pH} = 14.00 - 5.13 = 8.87$$

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

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

Ammonium ions undergo hydrolysis with water to form $NH_4OH(aq)$ and $H^+(aq)$ ions

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH\,(aq) + H^+(aq)$$

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 CH_3COONH_4 salt formed from a weak acid and a weak base. The ions formed undergo hydrolysis as follow:

$$CH_3COO^-(aq) + NH_4^+(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + NH_4OH(aq)$$

CH_3COOH and NH_4OH, also remain in partially dissociated form:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

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

$$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$$

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.

- ***$K_b > K_a$ ($pK_b < pK_a$); 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.***
- ***$K_b < K_a$ ($pK_b > pK_a$); 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.***
- ***$K_a \sim K_b$ ($pK_b \sim pK_a$); 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 $CH_3COONa(aq)$ dissociates completely while $CH_3COOH(aq)$ undergoes partial dissociation.

$$CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

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

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.

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

We can write,

$$[H_3O^+(aq)] = K_a \frac{[HA(aq)]}{[A^-(aq)]}$$

Taking -log on both sides,

$$-\log [H_3O^+(aq)] = -\log K_a - \log \frac{[HA(aq)]}{[A^-(aq)]}$$

$$-\log \left[H_3O^+(aq)\right] = -\log K_a + \log \frac{[A^-(aq)]}{[HA(aq)]}$$

We can write,

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

or

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

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

If we know $\boldsymbol{K_a}$ 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 $A^-(aq)$ ion is generally very small. Moreover, the presence of common ion $A^-(aq)$ from the salt NaA further suppresses the ionization of HA and the presence of unionized HA further suppresses the hydrolysis of $A^-(aq)$. Thus we can use the starting concentrations as the equilibrium concentrations in the Henderson-Hasselbalch equation.

Example 2.20

(i) Calculate the pH of a solution containing 0.20 mol dm^{-3} CH_3COOH and 0.40 mol dm^{-3} CH_3COONa.

(ii) What would be the pH of a 0.20 mol dm^{-3} CH_3COOH solution if no salt was present? $K_{a(CH_3COOH)} = 1.8 \times 10^{-5}$

Answer

(i) $CH_3COONa(s)$ is a strong electrolyte and hence it dissociates completely giving $[CH_3COO^-(aq)]$ as 0.40 mol dm^{-3} and we can neglect the $[CH_3COO^-(aq)]$ from the CH_3COOH acid as its dissociation is suppressed. Therefore, we can take $[CH_3COO^-(aq)]$ as 0.40 mol dm^{-3} and $[CH_3COOH(aq)]$ as 0.20 mol dm^{-3}.

$$CH_3COONa(s) \rightarrow CH_3COO^-(aq) + Na^+(aq)$$

$$\underset{0.20\ \text{mol dm}^{-3}}{CH_3COOH(aq)} + H_2O(l) \rightleftharpoons \underset{0.40\ \text{mol dm}^{-3}}{CH_3COO^-(aq)} + H_3O^+(aq)$$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 1.8 \times 10^{-5}$$

$$[H_3O^+(aq)] = \frac{(0.20)}{(0.40)} \times 1.8 \times 10^{-5} = 9.0 \times 10^{-6}\ \text{mol dm}^{-3}$$

$$\text{pH} = -\log[H_3O^+(aq)] = 5.04$$

or we can use

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

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

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

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

$$\text{pH} = 5.04$$

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

	$CH_3COOH(aq) + H_2O(l)$	$\rightleftharpoons CH_3COO^-(aq)$	$+ H_3O^+(aq)$
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 $0.20 - x \sim 0.20$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 1.8 \times 10^{-5}$$

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

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

$$\therefore [H_3O^+(aq)] = 2 \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{pH} = 2.70$$

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 dm^3 solution made by adding 0.10 mol of acetic acid and 0.10 mol of sodium acetate.

Answer

In this case the $[CH_3COO^-(aq)]$ is the concentration of CH_3COONa because it ionizes completely and therefore we can write:

	$CH_3COOH(aq) + H_2O(l)$	$\rightleftharpoons CH_3COO^-(aq)$	$+ H_3O^+(aq)$
Initial concentration/ mol dm^{-3}	0.10	0	0.10
Change in concentration/ mol dm^{-3}	$-x$	$+x$	$+x$
∴ Equilibrium concentration/ mol dm^{-3}	$0.10 - x$	$+x$	$0.10 + x$

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 1.8 \times 10^{-5}$$

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

As x is small, we can write,

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

$$x = \left[H_3O^+(aq)\right] = 1.8 \times 10^{-5}\ \text{mol dm}^{-3}$$

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

$$\textbf{i.e. pH} = \mathbf{pK_a}$$

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

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

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

Here, $NH_4^+(aq)$ is predominant over $NH_3(aq)$ as it comes from the complete ionization of NH_4Cl and hence the equilibrium $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$ is suppressed. Therefore, in this solution, pH is mainly controlled by the equilibrium

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

We can write,

$$K_a = \frac{[H_3O^+(aq)]\,[NH_3(aq)]}{[NH_4^+(aq)]}$$

$$\left[H_3O^+(aq)\right] = \frac{K_a\left[NH_4^+(aq)\right]}{[NH_3(aq)]}$$

$$-\log\,[H_3O^+(aq)] = -\log K_a - \log\frac{\left[NH_4^+(aq)\right]}{[NH_3(aq)]}$$

$$-\log\,[H_3O^+(aq)] = -\log K_a + \log\frac{[NH_3(aq)]}{\left[NH_4^+(aq)\right]}$$

We can write

$$\text{pH} = \text{pK}_a + \log\frac{[NH_3(aq)]}{\left[NH_4^+(aq)\right]}$$

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

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.

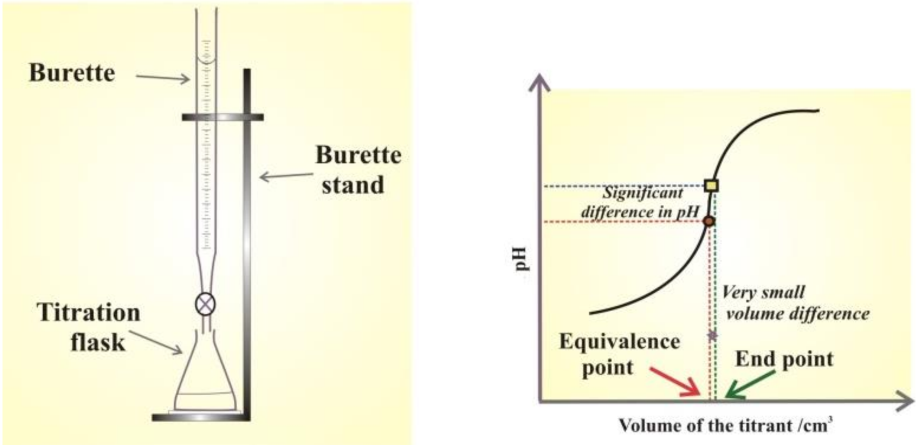
2.2.11 Volumetric titrations

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.



(a) (b)

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 tirant 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 (~ 0.05 cm^3) to observe the colour change in the indicator. In the case of equivalnce point it is the point at which stoichiometric amounts are exacatly 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:

(i) a strong acid and a strong base,
(ii) a weak acid and a strong base,
(iii) a strong acid and a weak base, and
(iv) a weak acid and a weak base .

Titrations 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 mol dm^{-3} HCl with 0.100 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,

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$$

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

$$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \rightarrow Na^+(aq) + Cl^-(aq) + H_2O(l)$$

We can see that the pH of the solution depends on the relative concentrations of $H^+(aq)$ and $OH^-(aq)$ 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 $C_aV_a = C_bV_b$
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

$$0.100 \times 25.00 = 0.100 \times V_b$$
$$\therefore V_b = 25.00 \text{ cm}^3$$

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

$$pH = -\log[H_3O^+] = -\log[HCl] = -\log(0.100) = 1.00$$

(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.

Initial amount of HCl (in moles) $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 2.50 \times 10^{-3}$ mol

Amount of NaOH added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 10.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 1.0 \times 10^{-3}$ mol

∴ Amount of HCl reacted $= 1.0 \times 10^{-3}$ mol

∴ Amount of HCl remaining $= (2.50 \times 10^{-3} - 1.00 \times 10^{-3})$ mol

$= 1.50 \times 10^{-3}$ mol

∴ Concentration of HCl (H_3O^+) remaining $= \frac{1.5\times10^{-3}\ \text{mol}}{35.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$

$= 0.043$ mol dm^{-3}

∴ pH = -log (0.043) = 1.37

(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,

$$H_3O^+(aq) + OH^-(aq) \rightleftharpoons 2H_2O(l)$$

At the equivalence point, $[H^+(aq)]=[OH^-(aq)]$ *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.

Initial amount of HCl (in moles) $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 2.50 \times 10^{-3}$ mol

Amount of NaOH added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 35.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 3.50 \times 10^{-3}$ mol

∴ Amount of HCl reacted $= 2.5 \times 10^{-3}$ mol

∴ Amount of NaOH remaining $= (3.50 \times 10^{-3} - 2.50 \times 10^{-3})$ mol

$= 1.0 \times 10^{-3}$ mol

∴ Concentration of NaOH (OH^-) remaining $= \frac{1.0\times10^{-3}\ \text{mol}}{60.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$

$= 0.017$ mol dm^{-3}

∴ pOH = -log (0.017) = 1.77

∴ pH = 14.00 - 1.77 = 12.23

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

Addition of 24.90 cm^3 of NaOH:

After adding 24.90 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.

Initial amount of HCl (in moles) $= \frac{0.100\text{ mol}}{1.0\text{ dm}^3} \times 25.00\text{ cm}^3 \times \frac{1.0\text{ dm}^3}{1000\text{ cm}^3}$

$= 2.50 \times 10^{-3}\text{ mol}$

Amount of NaOH added $= \frac{0.100\text{ mol}}{1.0\text{ dm}^3} \times 24.90\text{ cm}^3 \times \frac{1.0\text{ dm}^3}{1000\text{ cm}^3}$

$= 2.49 \times 10^{-3}\text{ mol}$

∴ Amount of HCl reacted $= 2.49 \times 10^{-3}\text{ mol}$

∴ Amount of HCl remaining $= (2.50 \times 10^{-3} - 2.49 \times 10^{-3})\text{ mol}$

$= 1.00 \times 10^{-5}\text{ mol}$

∴ Concentration of HCl (H_3O^+) remaining $= \frac{1.00\times10^{-5}\text{ mol}}{49.90\text{ cm}^3} \times \frac{1000\text{ cm}^3}{1.0\text{ dm}^3}$

$= 2.00 \times 10^{-4}\text{ mol dm}^{-3}$

∴ $\text{pH} = -\log(2.00 \times 10^{-4}) = 3.7$

Addition of 25.10 cm^3 of NaOH:

Initial amount of HCl (in moles) $= \frac{0.100\text{ mol}}{1.0\text{ dm}^3} \times 25.00\text{ cm}^3 \times \frac{1.0\text{ dm}^3}{1000\text{ cm}^3}$

$= 2.50 \times 10^{-3}\text{ mol}$

Amount of NaOH added $= \frac{0.100\text{ mol}}{1.0\text{ dm}^3} \times 25.10\text{ cm}^3 \times \frac{1.0\text{ dm}^3}{1000\text{ cm}^3}$

$= 2.51 \times 10^{-3}\text{ mol}$

∴ Amount of HCl reacted $= 2.50 \times 10^{-3}\text{ mol}$

∴ Amount of NaOH remaining $= (2.51 \times 10^{-3} - 2.50 \times 10^{-3})\text{ mol}$

$= 1.0 \times 10^{-5}\text{ mol}$

∴ Concentration of NaOH (OH^-) remaining $= \frac{1.0\times10^{-5}\text{ mol}}{50.10\text{ cm}^3} \times \frac{1000\text{ cm}^3}{1.0\text{ dm}^3}$

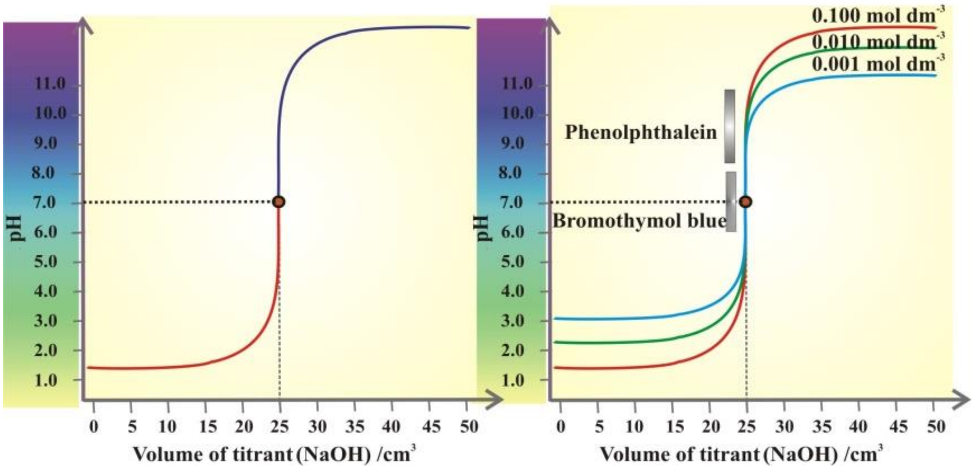
$= 2.00 \times 10^{-4}\text{ mol dm}^{-3}$

∴ $\text{pOH} = -\log(2.00 \times 10^{-4}) = 3.7$

∴ $\text{pH} = 14.00 - 3.70 = 10.30$

After addition of NaOH volumes higher than 25.00 cm^3, 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 cm^3 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.



(a) (b)

Figure 2.17 **(a)** Titration curve for the titration of 25.00 cm^3 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 cm^3 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):

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

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

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$$

As we have discussed earlier, the CH_3COO^- (aq) undergoes hydrolysis and the reaction will determine the pH at the equivalence point of the titration.

The acetate ion undergoes hydrolysis as follows:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

Therefore, at the equivalence point, where we have only sodium acetate, the pH will be greater than 7 as a result of the excess OH^-(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 mol dm*$^{-3}$ $CH_3COOH(aq)$ *with 0.100 mol dm*$^{-3}$ *NaOH.* $K_a(CH_3COOH) = 1.80 \times 10^{-5}$

We can see that the pH of the solution depends on the relative concentrations of the undissociated $CH_3COOH(aq)$ acid and $CH_3COO^-(aq)$ ions (formed as $CH_3COONa(aq)$) 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 $C_aV_a = C_bV_b$
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 mol dm^{-3} in CH_3COOH. Since CH_3COOH is a weak acid, $[H_3O^+]$ will be determined by its partial ionization, i.e

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

$[H_3O^+]$ is calculated from $\boldsymbol{K_a}$ as,

	$CH_3COOH(aq) + H_2O(l) \rightleftharpoons$	$CH_3COO^-(aq)$	$+ H_3O^+(aq)$
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 $(0.10 - x) \sim 0.1$)

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = \frac{x^2}{(0.1)} = 1.80 \times 10^{-5}$$

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

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

$$pH = -\log[H_3O^+] = -\log[1.34 \times 10^{-3}] = 2.87$$

Or $$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

$$K_a = \frac{\left[H_3O^+(aq)\right]^2}{C_0},$$

where initail concentration of the acid is C_0

$$\left[H_3O^+(aq)\right] = (K_a\, C_0)^{1/2}$$

$$-\log\left[H_3O^+(aq)\right] = -\log(K_a)^{\frac{1}{2}} - \log(\,C_0)^{\frac{1}{2}}$$

$$-\log\left[H_3O^+(aq)\right] = -\frac{1}{2}\log(K_a) \quad -\frac{1}{2}\log(\,C_0)$$

$$pH = -\frac{1}{2}pK_a - \frac{1}{2}\log(C_0)$$

(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 mol dm^{-3} NaOH.

$$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$$

Initial amount of CH_3COOH $= \frac{0.100\text{ mol}}{1.0\text{ dm}^3} \times 25.00\text{ cm}^3 \times \frac{1.0\text{ dm}^3}{1000\text{ cm}^3}$
$= 2.50 \times 10^{-3}$ mol

Amount of NaOH added $= \frac{0.100\text{ mol}}{1.0\text{ dm}^3} \times 10.00\text{ cm}^3 \times \frac{1.0\text{ dm}^3}{1000\text{ cm}^3}$
$= 1.0 \times 10^{-3}$ mol

∴ Amount of CH_3COOH reacted $= 1.0 \times 10^{-3}$ mol
∴ Amount of CH_3COOH remaining $= (2.50 \times 10^{-3} - 1.00 \times 10^{-3})$ mol
$= 1.50 \times 10^{-3}$ mol

∴ Concentration of CH_3COOH remaining $= \frac{1.5\times10^{-3}\text{ mol}}{35.00\text{ cm}^3} \times \frac{1000\text{ cm}^3}{1.0\text{ dm}^3}$
$= 0.043\text{ mol dm}^{-3}$

Amount of CH_3COONa formed = Amount of NaOH added $=1.0 \times 10^{-3}$ mol

Concentration of CH_3COONa formed $= \frac{1.0\times10^{-3}\text{ mol}}{35.00\text{ cm}^3} \times \frac{1000\text{ cm}^3}{1.0\text{ dm}^3}$
$= 0.029\text{ mol dm}^{-3}$

Substituting these values in,

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

$$pH = 4.74 + \log\frac{(0.029)}{(0.043)}$$

$$pH = 4.57$$

(iv) At the equivalence point (after addition of 25.00 cm^3 of NaOH) all the CH_3COOH and NaOH are consumed. The salt CH_3COONa present undergoes hydrolysis as,

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq)$$

According to the reaction, $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + H_2O(l)$

The amount of CH_3COONa ($CH_3COO^-(aq)$) formed $= 2.50 \times 10^{-3}$ mol

∴ The concentration of the salt $= \frac{2.5\times10^{-3}\ \text{mol}}{50.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$

$= 0.05\ \text{mol dm}^{-3}$

	$CH_3COO^-(aq) + H_2O(l)$	$\rightleftharpoons CH_3COOH(aq)$	$+ OH^-(aq)$
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 $(0.05 - x) \sim 0.05$)

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

$$K_b = \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]} = \frac{x^2}{(0.05)} = \frac{K_w}{K_a} = 5.6 \times 10^{-10}$$

$$x = [OH^-(aq)] = 5.3 \times 10^{-6}\ \text{mol dm}^{-3}$$

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

$$\therefore \text{pH} = 14.00 - 5.28$$

$$\therefore \text{pH} = 8.72$$

Or,

$$\boldsymbol{K_b} = \frac{[OH^-(aq)][CH_3COOH(aq)]}{[CH_3COO^-(aq)]}$$

$$\boldsymbol{K_b} = \frac{[OH^-(aq)]^2}{\boldsymbol{S}},$$

where S is the concentration of the salt

$$[OH^-(aq)] = (\boldsymbol{K_b\, S})^{1/2}$$

$$-\log[OH^-(aq)] = -\log(K_b)^{\frac{1}{2}} - \log(S)^{\frac{1}{2}}$$

$$-\log[OH^-(aq)] = -\frac{1}{2}\log(K_b) - \frac{1}{2}\log S$$

$$\textbf{pOH} = -\frac{1}{2}\text{p}K_b - \frac{1}{2}\log S$$

Substituting, $\quad \text{pH} + \text{pOH} = \text{p}K_w$ ***and*** $\text{p}K_a + \text{p}K_b = \text{p}K_w$

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

$$\therefore \text{pH} = \frac{1}{2}\text{p}K_a + \frac{1}{2}\text{p}K_w + \frac{1}{2}\log S$$

(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 $[OH^-(aq)]$.

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.

Initial amount of CH_3COOH $= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 25.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3}$

$= 2.50 \times 10^{-3}$ mol

Amount of NaOH added $= \frac{0.100 \text{ mol}}{1.0 \text{ dm}^3} \times 35.00 \text{ cm}^3 \times \frac{1.0 \text{ dm}^3}{1000 \text{ cm}^3}$

$= 3.50 \times 10^{-3}$ mol

∴ Amount of CH_3COOH reacted $= 2.5 \times 10^{-3}$ mol

∴ Amount of NaOH remaining $= (3.50 \times 10^{-3} - 2.50 \times 10^{-3})$ mol

$= 1.0 \times 10^{-3}$ mol

∴ Concentration of NaOH (OH^-) remaining $= \frac{1.0 \times 10^{-3} \text{ mol}}{60.00 \text{ cm}^3} \times \frac{1000 \text{ cm}^3}{1.0 \text{ dm}^3}$

$= 0.017 \text{ mol dm}^{-3}$

∴ pOH = -log (0.017) = 1.77

∴ pH = 14.00 - 1.77 = 12.23

Or, After the equivalence point, $[H_3O^+(aq)] = \frac{K_w}{[OH^-(aq)]}$

$[OH^-(aq)]$ ***is the excess concentration of the strong base***

And taking excess $[OH^-(aq)] = B'$

$$[H_3O^+(aq)] = \frac{K_w}{B'}$$

$$-\log[H_3O^+(aq)] = -\log(K_w) - (-\log B')$$

$$\mathbf{pH} = \mathbf{p}K_w + \log(B')$$

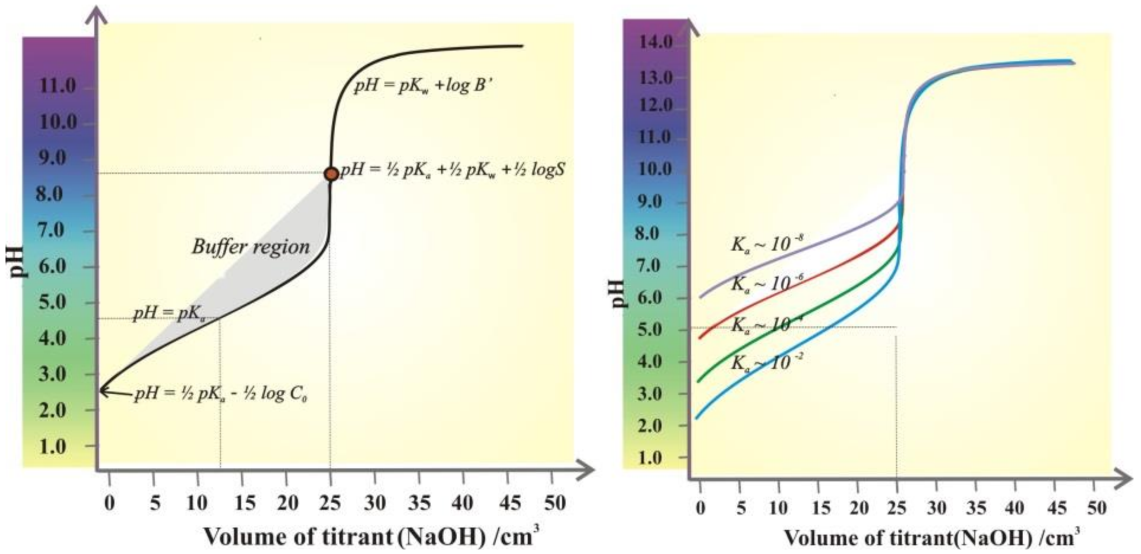
At the half-equivalence point:

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

Concentrations of the acid and the conjugate base are equal.

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

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



(a) (b)

Figure 2.18 **(a)** Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} CH_3COOH with 0.100 mol dm^{-3} NaOH. Equivalnvce 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). Charateristics 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 NH_3, a weak base and HCl, a strong acid: the reaction taking place is;

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

or simply

$$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$$

We can see that the pH at the equivalence point is *less than 7* due to the hydrolysis of the $NH_4^+(aq)$

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

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 mol dm^{-3} NH_3, a weak base be titrated with 0.10 mol dm^{-3} 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 $C_aV_a = C_bV_b$

(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 mol dm^{-3} in NH_3. Since NH_3 is a weak base, $[OH^-]$ will be determined considering its partial ionization, i.e

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

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

	$NH_3(aq) + H_2O(l)$ ⇌	$NH_4^+(aq)$ +	OH^- (aq)
Initial concentration/ mol dm^{-3}	0.1	0	0
Change in concentration/ mol dm^{-3}	$-x$	$+x$	$+x$
∴Equilibrium concentration/ mol dm^{-3}	$(0.10 - x)$	$+x$	$+x$
∴Equilibrium concentration/ mol dm^{-3} (with the assumption $(0.10 - x) \sim 0.1$)	0.10	$+x$	$+x$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]} = \frac{x^2}{(0.1)} = 1.80 \times 10^{-5}$$
$$x^2 = 1.80 \times 10^{-6}$$
$$x = 1.34 \times 10^{-3}$$

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

$\therefore pH = 14.00 - 2.87 = 11.13$

(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 mol dm^{-3} HCl.

$$HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$$

Initial amount of NH_3 $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 25.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 2.50 \times 10^{-3}$ mol

Amount of HCl added $= \frac{0.100\ \text{mol}}{1.0\ \text{dm}^3} \times 10.00\ \text{cm}^3 \times \frac{1.0\ \text{dm}^3}{1000\ \text{cm}^3}$

$= 1.0 \times 10^{-3}$ mol

∴ Amount of NH_3 reacted $= 1.0 \times 10^{-3}$ mol

∴ Amount of NH_3 remaining $= (2.50 \times 10^{-3} - 1.00 \times 10^{-3})$ mol

$= 1.50 \times 10^{-3}$ mol

∴ Concentration of NH_3 remaining $= \frac{1.5\times10^{-3}\ \text{mol}}{35.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3}$

$= 0.043$ mol dm^{-3}

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

Concentration of NH_4Cl formed $= \frac{1.0\times10^{-3}\ \text{mol}}{35.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3} = 0.029\ \text{mol dm}^{-3}$

Substituting these values in,

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\text{pOH} = 4.74 + \log\frac{(0.029)}{(0.043)}$$

$$\text{pOH} = 4.57$$

$$\therefore \text{pH} = 14.00 - 4.57 = 9.43$$

(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,

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

According to the reaction, $HCl(aq) + NH_3(aq) \rightarrow NH_4Cl(aq)$

The amount of NH_4Cl (NH_4^+ (aq)) formed $= 2.50 \times 10^{-3}$ mol

∴ The concentration of the salt $= \frac{2.5\times10^{-3}\ \text{mol}}{50.00\ \text{cm}^3} \times \frac{1000\ \text{cm}^3}{1.0\ \text{dm}^3} = 0.05\ \text{mol dm}^{-3}$

	$NH_4^+(aq) + H_2O(l)$	$\rightleftharpoons$ $NH_3(aq)$	$+ H_3O^+(aq)$
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 $(0.05 - x) \sim 0.05$)

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

$$K_\mathrm{b} = \frac{[\mathrm{NH_3(aq)}][\mathrm{H_3O^+(aq)}]}{[\mathrm{NH_4{}^+(aq)}]}$$

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

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

$$x = [\mathrm{H_3O^+(aq)}] = 5.3 \times 10^{-6}$$

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

(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 $[H_3O^+(aq)]$.

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.

Initial amount of NH_3 $= \frac{0.100\ \mathrm{mol}}{1.0\ \mathrm{dm^3}} \times 25.00\ \mathrm{cm^3} \times \frac{1.0\ \mathrm{dm^3}}{1000\ \mathrm{cm^3}}$

$= 2.50 \times 10^{-3}$ mol

Amount of HCl added $= \frac{0.100\ \mathrm{mol}}{1.0\ \mathrm{dm^3}} \times 35.00\ \mathrm{cm^3} \times \frac{1.0\ \mathrm{dm^3}}{1000\ \mathrm{cm^3}}$

$= 3.50 \times 10^{-3}$ mol

∴ Amount of NH_3 reacted $= 2.5 \times 10^{-3}$ mol

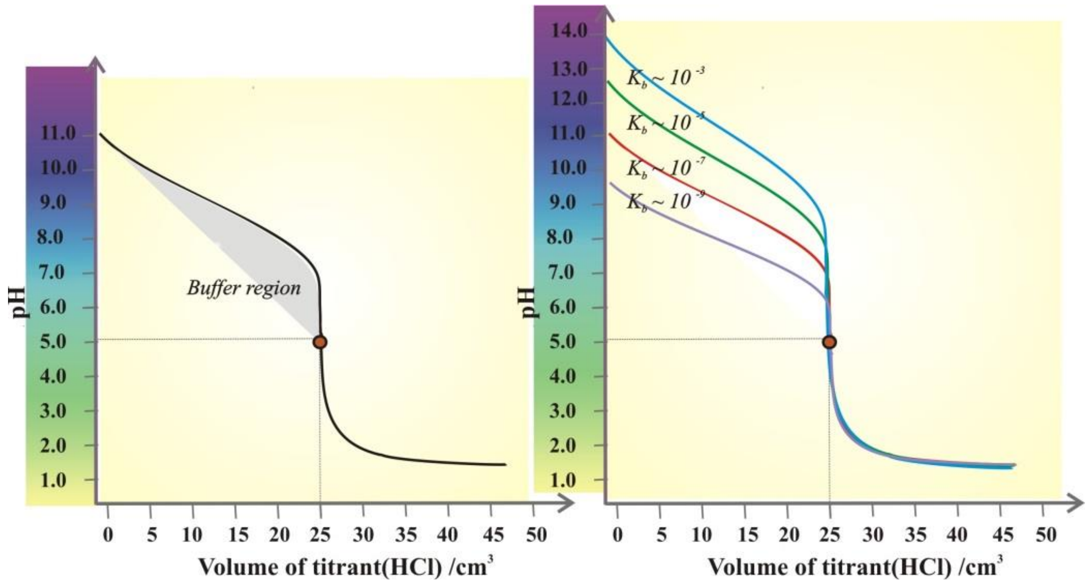
∴ Amount of HCl remaining $= (3.50 \times 10^{-3} - 2.50 \times 10^{-3})$ mol

$= 1.0 \times 10^{-3}$ mol

∴ Concentration of HCl ($H_3O^+(aq)$) remaining $= \frac{1.0\times10^{-3}\ \mathrm{mol}}{60.00\ \mathrm{cm^3}} \times \frac{1000\ \mathrm{cm^3}}{1.0\ \mathrm{dm^3}}$

$= 0.017\ \mathrm{mol\ dm^{-3}}$

∴ pH = -log (0.017) = 1.77



(a) (b)

Figure 2.19 (a) Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} NH_3 with 0.100 mol dm^{-3} HCl. Equivalnvce 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,

$$CH_3COOH(aq) + NH_3(aq) \rightarrow NH_4^+(aq) + CH_3COO^-(aq)$$

Now we can see that the products contain the base CH_3COO^- and the acid NH_4^+. Therefore, the pH at the equivalence point id determined by the strength of the hydrolysis of these. We can write,

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \ : \boldsymbol{K_a}$$

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \ : \boldsymbol{K_b}$$

From these reactions, we see that H_3O^+ and OH^- ions are formed and they undergo neutralization. Though neutralization occurs, still we may not have equal amount of H_3O^+ and OH^- and hence pH ≠ 7 at the equivalence point. It depends on the relative strengths of $\boldsymbol{K_a}$ and $\boldsymbol{K_b}$***: if*** $\boldsymbol{K_a > K_b}$***, the solution is acidic and if*** $\boldsymbol{K_a < K_b}$***, 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* p*K values of the acid and the base using the mathematical formula,*

$$pH = 7 + \frac{1}{2}(pK_a - pK_b)$$

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.*

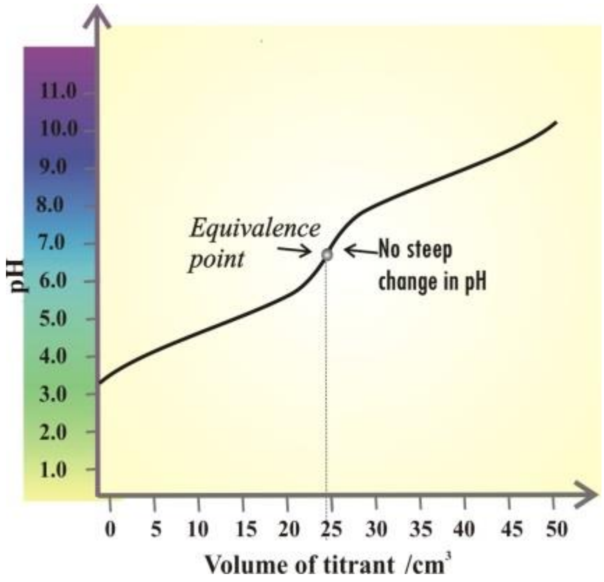


Figure 2.20 Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} CH_3COOH with 0.100 mol dm^{-3} NH_3. It is difficult to judge to location of the equivalence point as it depends on the relative strengths of the acid and the base. There is no steep change in pH in these types of systems.

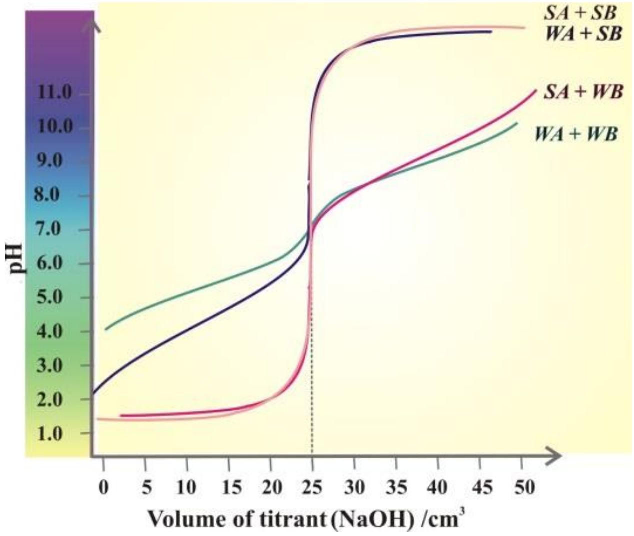


Figure 2.21 Summary of the four types of titrations with 0.100 mol dm^{-3} acid (mono basic) and 0.100 mol dm^{-3} base (mono acidic) discussed above. (SA-strong acid, SB-strong base, WA-Weak acid and WB-Weak base)

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

Some of the acids like oxalic acid ($H_2C_2O_4$), 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:

$$H_2A(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HA^-(aq)$$

$$HA^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^{2-}(aq)$$

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

$$K_{a_1} = \frac{[H_3O^+(aq)][HA^-(aq)]}{[H_2A(aq)]}$$

$$K_{a_2} = \frac{[H_3O^+(aq)][A^{2-}(aq)]}{[HA^-(aq)]}$$

Likewise, the ionization reactions of a *diacidic base* B_2^- are represented by the equations:

$$B^{2-}(aq) + H_2O(l) \rightleftharpoons H\,B^-(aq) + OH^-(aq)$$

$$HB^-(aq) + H_2O(l) \rightleftharpoons H_2B(aq) + OH^-(aq)$$

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

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

$$K_{b_2} = \frac{[H_2B(aq)][OH^-(aq)]}{[HB^-(aq)]}$$

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 HCl(aq) (titrant) to Na_2CO_3(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 Na^+(aq) and CO_3^{2-} (aq) ions.

$$Na_2CO_3(aq) \rightarrow Na^+(aq) + CO_3^{2-}(aq)$$

Therefore, the major entities in the mixture are Na^+(aq), CO_3^{2-}(aq) and H_2O(l). At the beginning of the titration, H^+(aq) ions from HCl(aq) react with CO_3^{2-}(aq) ions since carbonate ions are the strongest bases present in the initial mixture.

$$H^+(aq) + CO_3^{2-}(aq) \rightarrow HCO_3^-(aq)$$

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

$$H^+(aq) + HCO_3^-(aq) \rightarrow H_2CO_3(aq)$$

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 $HCO_3^-(aq)$ ions.

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3\,(aq) + OH^-\,(aq)$$

At the second equivalence point following equilibrium exists in the mixture and therefore the pH is determined by the hydrolysis (first ionization) of H_2CO_3 (aq) acid.

$$H_2CO_3\,(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq)$$

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 mol dm^{-3} $Na_2CO_3(aq)$ solution with 0.10 mol dm^{-3} HCl(aq) acid. Acid dissociation constants for the carbonic acid, H_2CO_3 are $K_{a_1} = 4.3 \times 10^{-7}$ mol dm^{-3} and $K_{a_2} = 4.7 \times 10^{-11}$ 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:

$$H_2CO_3\,(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) : K_{a_1}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons CO_3^{2-}(aq) + H_3O^+(aq) : K_{a_2}$$

Therefore,

$$K_{a_1} = \frac{[H_3O^+(aq)][HCO_3^-(aq)]}{[H_2CO_3(aq)]} = 4.3 \times 10^{-7}\ \text{mol dm}^{-3}$$

$$K_{a_2} = \frac{[H_3O^+(aq)][CO_3^{2-}(aq)]}{[HCO_3^-(aq)]} = 4.7 \times 10^{-11}\ \text{mol dm}^{-3}$$

Initial pH (at 0.00 cm^3 of HCl):
At this point as no acid has been added, and only 0.10 mol dm^{-3} $Na_2CO_3(aq)$ sodium carbonate solution is present. The pH is determined by the extent of carbonate ion reaction with water to give $HCO_3^-(aq)$ and $OH^-(aq)$.

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

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

$$K' = \frac{[HCO_3^-(aq)][OH^-(aq)]}{[CO_3^{2-}(aq)]}$$

Consider; $\frac{K_w}{K_{a_2}} = \frac{[H_3O^+(aq)][OH^-(aq)]}{\frac{[H_3O^+(aq)][CO_3^{2-}(aq)]}{[HCO_3^-(aq)]}} = \frac{[HCO_3^-(aq)][OH^-(aq)]}{[CO_3^{2-}(aq)]} = K' = K_{b_1}$

$$\therefore K_{b_1} = \frac{1.0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}}{4.7 \times 10^{-11}\ \text{mol dm}^{-3}} = 2.13 \times 10^{-4}\ \text{mol dm}^{-3}$$

$$\therefore K_{b_1} = \frac{[OH^-(aq)]^2}{[CO_3^{2-}(aq)]} \quad (\text{as } [HCO_3^-(aq)] = [OH^-(aq)])$$

$$[OH^-(aq)]^2 = K_{b_1}[CO_3^{2-}(aq)] = 2.13 \times 10^{-4}\ \text{mol dm}^{-3} \times 0.10\ \text{mol dm}^{-3}$$
$$= 2.13 \times 10^{-5}\ \text{mol dm}^{-3}$$

$$\therefore [OH^-(aq)] = 4.61 \times 10^{-3}\ \text{mol dm}^{-3}$$
$$[H_3O^+(aq)] = 2.2 \times 10^{-12}\ \text{mol dm}^{-3}$$

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

First equivalence point S (at 25.00 cm^3 of HCl):
As previously explained, at the first equivalence point equilibrium existing is;

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \quad \ldots\ldots\ldots\ (1)$$

For the above equilibrium we can write,

$$K = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]}$$

This K has a direct relationship with the K_{a_1} of carbonic acid as,

$$K = \frac{K_w}{K_{a_1}} = \frac{[H_3O^+(aq)][OH^-(aq)]}{\frac{[H_3O^+(aq)][HCO_3^-(aq)]}{[H_2CO_3(aq)]}} = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]} = K_{b_2}$$

K_{b_2} is the second ionization constant of $CO_3^{2-}(aq)$ as we can write,

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \ : K_{b_1}$$

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq) \ : K_{b_2}$$

$$\therefore K_{b_2} = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]} = \frac{1.0 \times 10^{-14}\ \text{mol}^2\ \text{dm}^{-6}}{4.3 \times 10^{-7}\ \text{mol dm}^{-3}} = 2.33 \times 10^{-8}\ \text{mol dm}^{-3}$$

For the reaction (1),

$$HCO_3^-(aq) + H_2O(l) \rightleftharpoons H_2CO_3(aq) + OH^-(aq)$$

$$K_{b_2} = \frac{[H_2CO_3(aq)][OH^-(aq)]}{[HCO_3^-(aq)]}$$

At equilibrium:

$$K_{b_2} = \frac{[OH^-(aq)]^2}{[HCO_3^-(aq)]} \quad (\text{as } [H_2CO_3(aq)] = [OH^-(aq)])$$

As the first equivalence point occurs at 25.00 cm^3 of HCl;

$$[HCO_3^-(aq)] = \frac{0.10\ \text{mol dm}^{-3} \times 25.00 \times 10^{-3}\ \text{dm}^3}{50.00 \times 10^{-3}\ \text{dm}^3} = 0.05\ \text{mol dm}^{-3}$$

$$\therefore [OH^-(aq)]^2 = K_{b_2}[HCO_3^-(aq)] = 2.33 \times 10^{-8}\ \text{mol dm}^{-3} \times 0.05\ \text{mol dm}^{-3}$$

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

$$[H_3O^+(aq)] = 2.9 \times 10^{-10}\ \text{mol dm}^{-3}$$

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

Second equivalence point (at 50.00 cm^3 of HCl):

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

$$H_2CO_3(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + H_3O^+(aq) \quad \text{.............. (2)}$$

For the above equilibrium we can write;

$$K' = \frac{[HCO_3^-(aq)][H_3O^+(aq)]}{[H_2CO_3(aq)]} = K_{a_1} = \frac{[H_3O^+(aq)]^2}{[H_2CO_3(aq)]}$$

$$(\text{as } [H_2CO_3(aq)] = [H_3O^+(aq)])$$

To reach the second equivalence point after the first equivalence point another 25.00 cm^3 of HCl is needed. Therefore, $[H_2CO_3(aq)]$ at the second equivalence point can be calculated as follows.

$$[H_2CO_3(aq)] = \frac{0.10\ \text{mol dm}^{-3} \times 25.00 \times 10^{-3}\ \text{dm}^3}{75.00 \times 10^{-3}\ \text{dm}^3} = 0.03\ \text{mol dm}^{-3}$$

$$[H_3O^+(aq)]^2 = K_{a_1}[H_2CO_3(aq)]$$

$$[H_3O^+(aq)]^2 = 4.3 \times 10^{-7}\ \text{mol dm}^{-3} \times 0.03\ \text{mol dm}^{-3} = 1.3 \times 10^{-8}\ \text{mol}^2\ \text{dm}^{-6}$$

$$[H_3O^+(aq)] = 1.14 \times 10^{-4}\ \text{mol dm}^{-3}$$

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

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 indictor while methyl orange is suitable to detect the second equivalence point. Figure 2.22 shows the variation of pH during the titration.

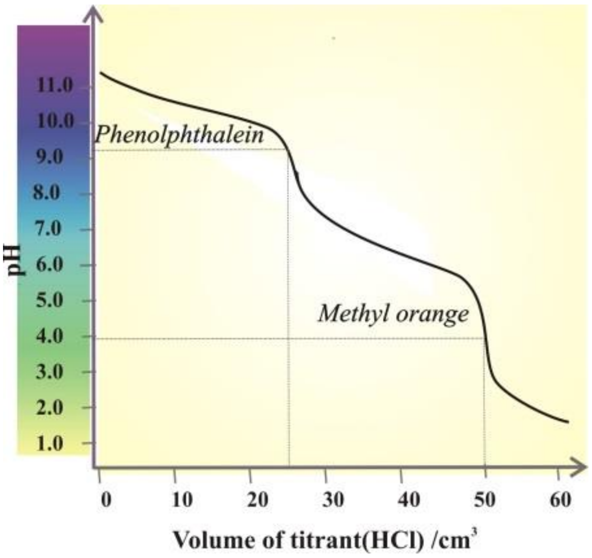


Figure 2.22 Titration curve for the titration of 25.00 cm^3 of 0.100 mol dm^{-3} Na_2CO_3 with 0.100 mol dm^{-3} HCl. There are two equivalence points: first is due to the reaction of CO_3^{2-} with HCl to form HCO_3^- and the second one is due to the conversion of HCO_3^- to H_2CO_3.

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.

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

for which the equilibrium constant is,

$$K_{In} = \frac{[H_3O^+(aq)][In^-(aq)]}{[HIn(aq)]}$$

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

$$-\log[H_3O^+(aq)] = -\log K_{In} + \log\frac{[In^-(aq)]}{[HIn(aq)]}$$

$$pH = pK_{In} + \log\frac{[In^-(aq)]}{[HIn(aq)]}$$

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 **p*K*In**. The equivalence point and the end point coincide, therefore, if an indicator is selected whose **p*K*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 **pH**s 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,

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

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

∴ color of *HIn* acid predominates

When,

$$\frac{[\mathrm{In}^-(\mathrm{aq})]}{[\mathrm{HIn}(\mathrm{aq})]} \geq 10$$
$$\mathrm{pH} = \mathrm{p}K_{\mathrm{In}} + \log\frac{10}{1}$$
$$\mathrm{pH} = \mathrm{p}K_{\mathrm{In}} + 1$$

color of In^- conjugate base predominates

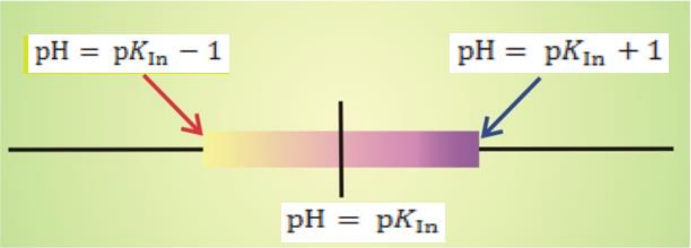


Figure 2.23 Behaviour of an indicator: $HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$

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 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 (~ 0.05 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

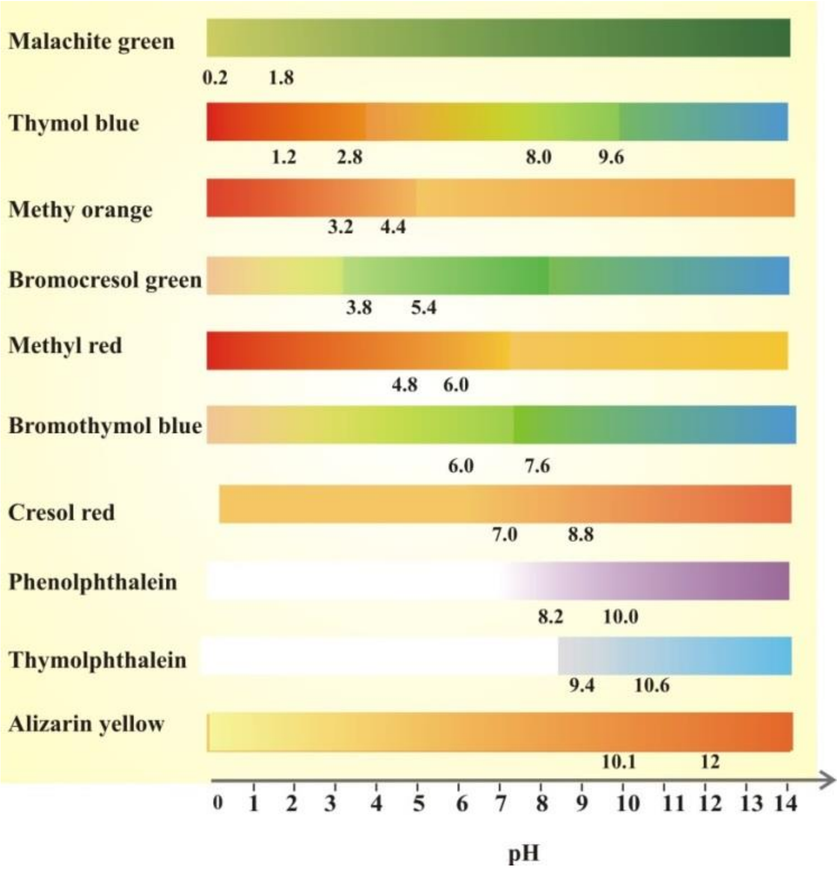
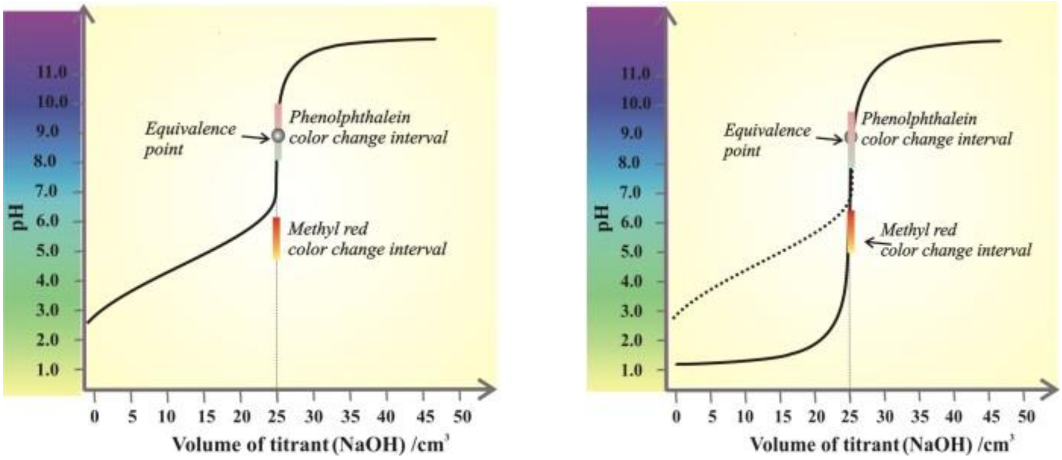


Figure 2.24 Colour changing pH ranges for some indicators

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.



(a) (b)

Figure 2.25 Selection of an appropriate indicator for a given titration. In the case of weak acid-strong base titration phenolphthalein is a sutable 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 $\mathbf{p}\boldsymbol{K}_\mathbf{a}$ of the acid or $\mathbf{p}\boldsymbol{K}_\mathbf{b}$ 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:

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

If an acid is added, the H^+ ions will be consumed by the conjugate base in the buffer, CH_3COO^-, according to the equation:

$$CH_3COO^-(aq) + H^+(aq) \rightleftharpoons CH_3COOH(aq)$$

If a base is added to the buffer system, the OH^- ions will be neutralized by the acid in the buffer:

$$CH_3COOH(aq) + OH^-(aq) \rightleftharpoons CH_3COO^-(aq) + H_2O(l)$$

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:

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

If an acid is added, the H^+ ions will be consumed by the base in the buffer, NH_3, according to the equation:

$$NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$

If a base is added, the OH^- ions will be consumed by the conjugate acid in the buffer, NH_4^+, according to the equation:

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

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.

$$NaA(aq) \rightarrow Na^+(aq) + A^-(aq)$$

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Here we can take $[A^-(aq)]$ as the concentration of $A^-(aq)$ from NaA and assume that the dissociation of HA is suppressed due to the presence of $A^-(aq)$ as the common ion. Substituting these terms in the K_a expression of a weak acid we have,

$$K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

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,

$$[H_3O^+(aq)] = K_a \frac{[HA(aq)]}{[A^-(aq)]}$$

and finally we get the equation,

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

or

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

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 to1.0 dm^3 of 0.10 mol dm^{-3} NH_3 solution to prepare a buffer solution with pH 9.0. $K_b\,(NH_3) = 1.8 \times 10^{-5}$.

Answer

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

First, we need to estimate the $[NH_4^+(aq)]$

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]} = 1.8 \times 10^{-5}$$

As we know the pH of the solution, $[OH^-(aq)]$ can be calculated.

pOH = 14 – pH = 5.0 and hence $[OH^-(aq)] = 1.0 \times 10^{-5}\ \text{mol dm}^{-3}$

$$[NH_4^+(aq)] = K_b \frac{[NH_3(aq)]}{[OH^-(aq)]}$$

$$= 1.8 \times 10^{-5}\ \text{mol dm}^{-3} \times \frac{0.10\ \text{mol dm}^{-3}}{1.0 \times 10^{-5}\ \text{mol dm}^{-3}}$$

$$= 0.18\ \text{mol dm}^{-3}$$

$\therefore$ Number of moles of NH_4^+ $= 0.18\ \text{mol dm}^{-3} \times 1.0\ \text{dm}^3$

$= 0.18\ \text{mol}$

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.

$K_a(CH_3COOH) = 1.8 \times 10^{-5}$ mol dm^{-3}

Answer

Due to the presence of common ion of CH_3COO^- from $CH_3COONa(aq)$, we can neglect the ionization of CH_3COOH and hydrolysis of the CH_3COO^- ion. Therefore,

$[CH_3COOH(aq)] = 1.0$ mol dm^{-3} and $[CH_3COO^-(aq)] = 2.0$ mol dm^{-3}

$$K_a = \frac{[H_3O^+(aq)][CH_3COO^-(aq)]}{[CH_3COOH(aq)]} = 1.8 \times 10^{-5}$$

$$[H_3O^+(aq)] = \frac{[\ 1.0]}{[2.0]} \times 1.8 \times 10^{-5}$$

$$[H_3O^+(aq)] = 9.0 \times 10^{-6}$$

$$pH = 5.05$$

After the addition of 0.2 mol of HCl to 1.0 dm^3 of the buffer solution (i.e. $[H^+(aq)]= 0.10$ mol dm^{-3}), complete ionization of HCl acid occurs:

$$\begin{array}{lcll} HCl(aq) & \rightarrow & H^+(aq) + Cl^-(aq) & \\ 0.10 & & 0.10 \quad\quad 0.10 & mol\ dm^{-3} \end{array}$$

Then the H^+ from HCl is neutralized by the 2.0 mol dm^{-3} CH_3COONa as

$$\begin{array}{lcll} H^+(aq) + CH_3COO^-(aq) & \rightleftharpoons & CH_3COOH(aq) & \\ 0.10 \quad\quad 0.10 & & 0.10 & mol\ dm^{-3} \end{array}$$

(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)

∴ The number of moles of acetic acid and the number of moles of acetate ions present in 1.0 dm^3 solution are,

$CH_3COOH(aq) = 1.10$ mol or $[CH_3COOH(aq)] = 1.10$ moldm^{-3}

$CH_3COO^-(aq) = 1.90$ mol or $[CH_3COO^-(aq)] = 1.90$ moldm^{-3}

Substituting these values in $\boldsymbol{K_a}$ expression,

$$[H_3O^+(aq)] = \frac{1.1}{1.9} \times 1.8 \times 10^{-5}$$

$$[H_3O^+(aq)] = 1.04 \times 10^{-5}\ mol\ dm^{-3}$$

$$pH = 4.98$$

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*

$$[H_3O^+(aq)] = \frac{1.0}{1.0} \times 1.8 \times 10^{-5}$$
$$[H_3O^+(aq)] = 1.8 \times 10^{-5}$$
$$pH = 4.74$$

i.e. pH = pK_a

This can be easily understood by, applying the equation,

$$pH = pK_a + \log\frac{[A^-(aq)]}{[HA(aq)]}$$
$$pH = pK_a + \log\frac{1.0}{1.0}$$
$$\therefore pH = pK_a$$

Example 2.24

Calculate the pH of a buffer that is 0.020 mol dm^{-3} in NH_3 and 0.030 mol dm^{-3} in NH_4Cl. What is the *p*H 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 5.70×10^{-10} mol dm^{-3}

Answer

We can directly use,

$$pH = pK_a + \log\frac{[NH_3(aq)]}{[NH_4{}^+(aq)]}$$
$$pH = 9.24 + \log\frac{(0.02)}{(0.03)}$$
$$pH = 9.06$$

Adding NaOH converts a portion of the NH_4^+ to NH_3 due to the following reaction

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

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

$$[NH_4^+(aq)] = \frac{\text{moles of initial } NH_4^+ - \text{moles of } OH^- \text{ added}}{\text{total volume}}$$

$[NH_4^+(aq)] = \frac{(0.03)\times(0.1)\ -(0.1)\times(1.0\times10^{-3})}{(0.101)} = 0.029\ \text{mol dm}^{-3}$

and

$[NH_3\ (aq)] = \frac{\text{moles of initial } NH_3 + \text{ moles of } OH^- \text{ added}}{\text{total volume}}$

$[NH_3\ (aq)] = \frac{(0.02)\times(0.1)+(0.1)\times(1.0\times10^{-3})}{(0.101)} = 0.021\ \text{mol dm}^{-3}$

Substituting these in the equation, we get

$$\text{pH} = \text{p}K_a + \log\frac{[NH_3(aq)]}{[NH_4^+(aq)]}$$

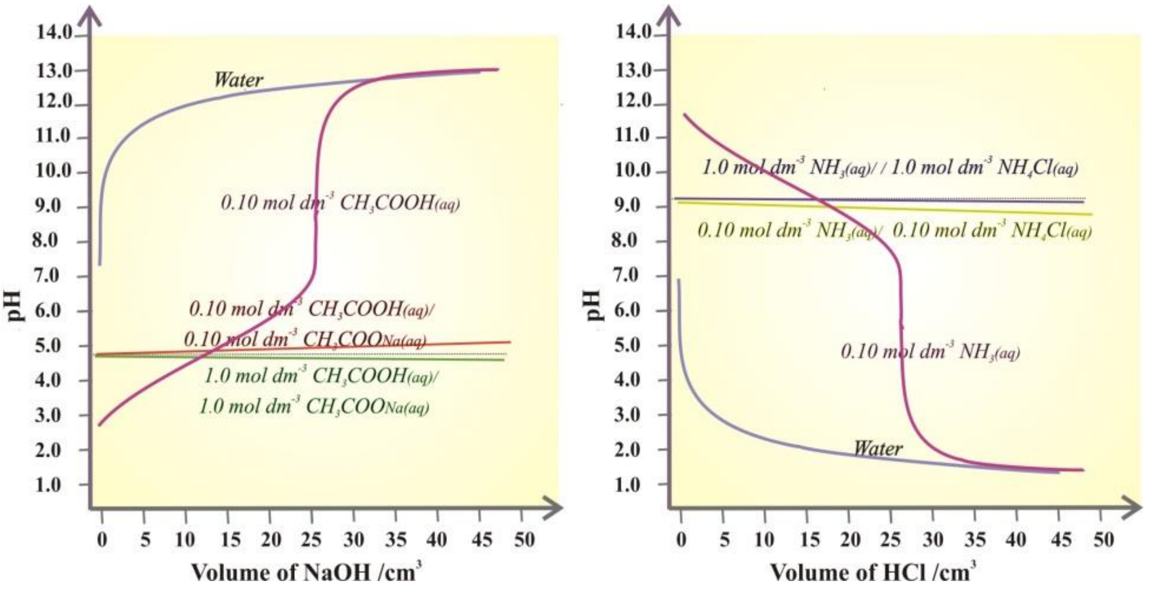
$$\text{pH} = 9.24 + \log\frac{(0.021)}{(0.029)}$$

$$\text{pH} = 9.10$$

From the above examples we can see that the addition of a little amount of acid or base does not afftect 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 charateristics of buffer solutions.

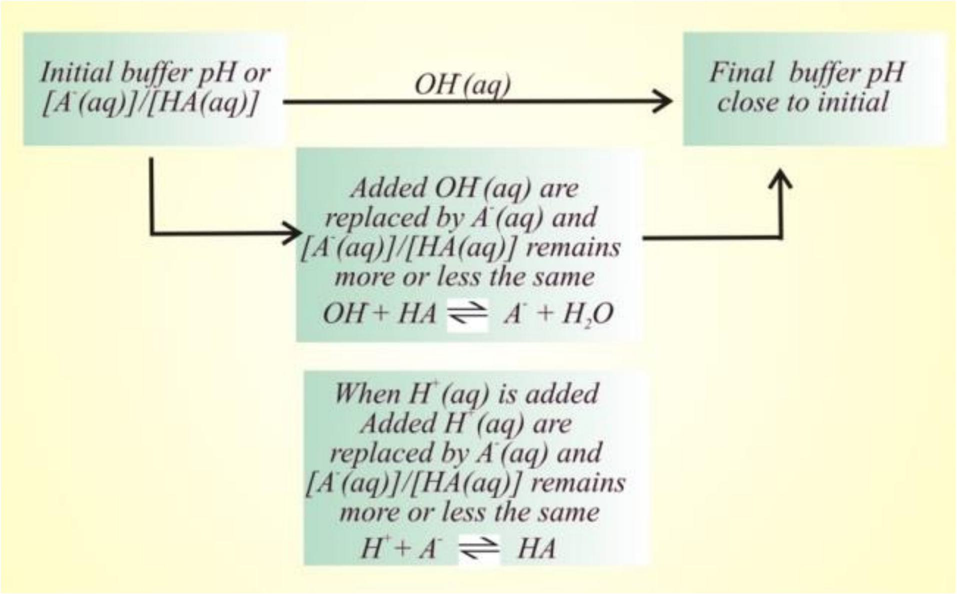
(i) Contain relatively large concentrations of a weak acid (base) and its conjugate base (acid).
(ii) When acid is added, it reacts with the conjugate base.
(iii) When base is added, it reacts with the conjugate acid.
(iv) pH is determined by the ratio of the base and acid.

These characteristics are depicted in Figure 2.26 and Figure 2.27.



(a) (b)

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 varaiation 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.



Initial buffer pH or $[A^-(aq)]/[HA(aq)]$

$OH^-(aq)$

Final buffer pH close to initial

Added $OH^-(aq)$ are replaced by $A^-(aq)$ and $[A^-(aq)]/[HA(aq)]$ remains more or less the same

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

When $H^+(aq)$ is added Added $H^+(aq)$ are replaced by $A^-(aq)$ and $[A^-(aq)]/[HA(aq)]$ remains more or less the same

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

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:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{1}{10} = \mathrm{p}K_\mathrm{a} - 1$$

and

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{10}{1} = \mathrm{p}K_\mathrm{a} + 1$$

Thus it is seen that acid–base buffer exists within the range of $\mathbf{pH = p}\boldsymbol{K}_\mathbf{a} \pm \mathbf{1}$

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 important 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 he 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 $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ 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.

Ionic compounds: $NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

Covalent compounds: $C_6H_{12}O_6(s) \rightarrow : C_6H_{12}O_6(aq)$

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 mol dm^{-3}
Category II : Slightly soluble - 0.01 mol dm^{-3} $<$ Solubility $<$ 0.10 mol dm^{-3}
Category III : Sparingly soluble - Solubility < 0.01 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 mol dm^{-3} $Na^+(aq)$ and 0.10 mol dm^{-3} $Cl^-(aq)$ ions showing complete dissociation.

$$\begin{array}{lllll} NaCl(s) + Water \rightarrow & NaCl(aq) \rightarrow & Na^+(aq) + & Cl^-(aq) & \\ & 0.10 & 0.10 & 0.10 & mol\ dm^{-3} \end{array}$$

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.

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

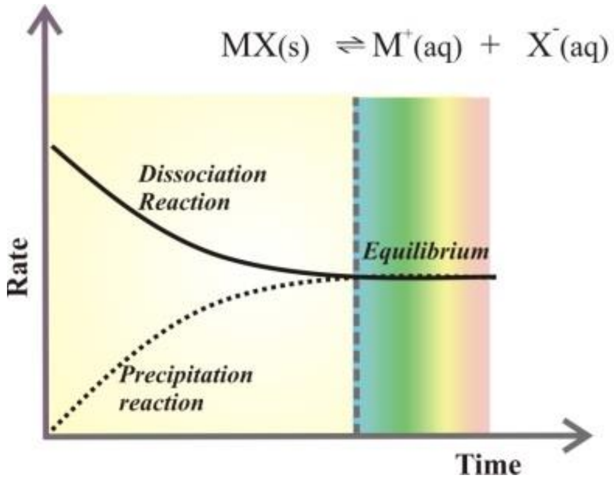


Figure 2.28 In saturated solutions dynamic equilibrium exists between undissolved solids and ionic species in the solution. Hence solid continues to dissolve and ion-pairs continue to form the solid and the rate of dissolution is equal to the rate of precipitation.

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 dm^3 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 = 1.8×10^{-3} g / 143.4 g mol^{-1} = 1.26×10^{-5} mol

Since molar solubility is expressed in units of mol dm^{-3}:

Molar solubility = 1.26×10^{-5} mol/ 1.00 dm^3 = 1.26×10^{-5} mol dm^{-3}

We can express solubility in other units as 1.8×10^{-3} 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:

$$MX(s) \rightleftharpoons M^+(aq) + X^-(aq)$$

The equilibrium constant K is given by the equation:

$$K = \frac{[M^+(aq)][X^-(aq)]}{[MX(s)]}$$

For a pure solid substance the concentration remains constant and we can write;

$$K\,[MX(s)] = [M^+(aq)][X^-(aq)]$$
$$\therefore K_{sp} = [M^+(aq)][X^-(aq)]$$

In general, if we have an equilibrium;

$$M_mX_n(s) \rightleftharpoons mM^{n+}(aq) + nX^{m-}(aq)$$

Solubility product,

$$K_{sp} = [M^{n+}(aq)]^m[X^{m-}(aq)]^n$$

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;

$$\mathrm{M_mX_n(s)} \rightleftharpoons \mathrm{mM^{n+}(aq)} + \mathrm{nX^{m-}(aq)}$$

Solubility product,

$$K_{sp} = [\mathrm{M^{n+}(aq)}]^m[\mathrm{X^{m-}(aq)}]^n$$

Units:

$$(\mathrm{mol^m dm^{-3m}})\ (\mathrm{mol^n dm^{-3n}})$$

$$\mathbf{mol^{(m+n)}\ dm^{-3(m+n)}}$$

Simply for the equilibrium: $\mathrm{MX(s)} \rightleftharpoons \mathrm{M^+(aq)} + \mathrm{X^-(aq)}$

$$K_{sp} = [\mathrm{M^+(aq)}][\mathrm{X^-(aq)}]\ \mathrm{mol^2\ dm^{-6}}$$

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,

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)} : K_{sp} = [\mathrm{Ag^+(aq)}][\mathrm{Cl^-(aq)}]$$

$$\text{At 298 K},\quad K_{sp} = 1.60 \times 10^{-10}\ \mathrm{mol^2\ dm^{-6}}$$

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 $\boldsymbol{s}$, then

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag^+(aq)} + \mathrm{Cl^-(aq)}$$

At the equilibrium: s s mold m^{-3}

$$\text{At 298 K},\quad K_{sp} = 1.60 \times 10^{-10}\ \mathrm{mol^2\ dm^{-6}} = \boldsymbol{s} \times \boldsymbol{s} = \boldsymbol{s^2}$$

$$\therefore\ \boldsymbol{s} = 1.26 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$$

Thus, at 298 K, molar solubility of silver chloride will be equal to $1.26 \times 10^{-5}\ \mathrm{mol\ dm^{-3}}$.

A solid salt of the general formula

$$\mathrm{M_mX_n(s)} \rightleftharpoons \mathrm{mM^{n+}(aq)} + \mathrm{nX^{m-}(aq)}$$

Molar solubility S in equilibrium $m\,\boldsymbol{s}$ $n\,\boldsymbol{s}$

$K_{sp} = [\mathrm{M^{n+}(aq)}]^m[\mathrm{X^{m-}(aq)}]^n$

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

$$Zr_3(PO_4)_4\,(s) \rightleftharpoons 3Zr^{4+}(aq) + 4PO_4^{3-}(aq)$$

At equilibrium: 3*s* 4*s*

$K_{sp} = [Zr^{4+}(aq)]^3[PO_4^{3-}(aq)]^4 = (3s)^3(4s)^4 = 6912\,(s)^7$

$$\therefore s = \left[\frac{K_{sp}}{6912}\right]^{1/7}$$

In this example we can notice that $K_{sp} = [Zr^{4+}(aq)]^3[PO_4^{3-}(aq)]^4$ has units $(mol dm^{-3})^7$.

And the units of ***s*** is $[(\text{mol dm}^{-3})^7]^{\frac{1}{7}} = \text{mol dm}^{-3}$

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 5.60×10^{-2} g $PbI_2(s)$. Calculate K_{sp}.

Answer

First we need the molar solubility of PbI_2:

Moles of PbI_2 $= 5.60 \times 10^{-2}$ g /461 g mol^{-1} $= 1.21 \times 10^{-4}$ mol

Molar solubility of PbI_2 $= 1.21 \times 10^{-4}$ mol/ 0.100 dm^3

$= 1.21 \times 10^{-3}$ mol dm^{-3}

Next calculate the concentration of the ions and substitute in the *Ksp* expression:

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq)$$

At equilibrium : $[Pb^{2+}{}_{(aq)}] = 1.21 \times 10^{-3}$ mol dm^{-3} and

$[I^-{}_{(aq)}] = 2 \times 1.21 \times 10^{-3}$ mol dm^{-3} $= 2.42 \times 10^{-3}$ 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 2.0×10^{-15} mol^3 dm^{-9} and 6×10^{-17} mol^2 dm^{-6} respectively. Which salt is more soluble?

Answer

Consider the equilibrium,

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

If the solubility is x,

At equilibrium : x $2x$

$K_{sp} = [\,Ni^{2+}(aq)]\,[OH^{-}(aq)]^2 = 4x^3$

$4x^3 = 2.0 \times 10^{-15}$ mol^3 dm^{-9}

$x = 7.94 \times 10^{-5}$ mol dm^{-3}

Similarly,

$$AgCN(s) \rightleftharpoons Ag^{+}(aq) + CN^{-}(aq)$$

If the solubility is y,

At equilibrium : y y

$K_{sp} = [\,Ag^{+}(aq)]\,[CN^{-}(aq)] = y^2$

$y^2 = 6 \times 10^{-17}$ mol^2 dm^{-6}

$y = 7.8 \times 10^{-9}$ mol dm^{-3}

we can notice that; $x > y$

Therefore, $Ni(OH)_2(s)$ is more soluble than AgCN(s).

(It is also possible to predict this comparing K_{sp} values; Since K_{sp} ($Ni(OH)_2(s)$) > K_{sp} (AgCN(s)), solubility of $Ni(OH)_2(s)$ is higher than that of AgCN(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) = 8.1×10^{-12} mol^3 dm^{-9}

Answer

First, consider the equilibrium, and if ***x*** is the molar solubility, we can write

$$Ag_2CO_{3(s)} \rightleftharpoons 2\,Ag^+_{(aq)} + CO_3^{2-}{}_{(aq)}$$

At equilibrium: $2x$ x mol dm^{-3}

$K_{sp} = [\,Ag^+_{(aq)}]^2\,[CO_3^{2-}{}_{(aq)}]$

$= (2x)^2(x) = 4x^3$

$\therefore\ 4x^3 = 8.1 \times 10^{-12}$ mol^3 dm^{-9}

We get

$x = (8.1 \times 10^{-12}\ \text{mol}^3\ \text{dm}^{-9})^{1/3}$

$x = 1.26 \times 10^{-4}$ mol dm^{-3}

$\therefore\ [Ag^+_{(aq)}] = 2x = 2 \times 1.26 \times 10^{-4}$ mol dm^{-3} = 2.53×10^{-4} 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? $K_{sp}(AgCl) = 1.8 \times 10^{-10}$ mol^2 dm^{-6} and $K_{sp}(Ag_2CO_3) = 8.1 \times 10^{-12}$ mol^3 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_2CO_3
From previous examples:		
$[Ag^+_{(aq)}]$	1.34×10^{-5} mol dm^{-3}	2.53×10^{-4} 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} cocentrations.

However, the situation with very dilute solutions (concentrations < 0.10 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 *vise 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 5.0×10^{-3} mol dm^{-3} $Mg(NO_3)_2$ and 50.00 cm^3 of 1.0×10^{-2} mol dm^{-3} K_2CO_3 are mixed?

$K_{sp(MgCO_3)} = 3.5 \times 10^{-8}$ $mol^2\ dm^{-6}$

Answer

First write the reaction between $Mg(NO_3)_2$ and K_2CO_3

$$Mg(NO_3)_2(aq) + K_2CO_3(aq) \rightarrow 2KNO_3(aq) + MgCO_3(s)$$

As two solutions are being mixed, dilution occurs.

Therefore the concentrations of the solutions are different when mixed.

$[Mg(NO_3)_2(aq)] = (5.0 \times 10^{-3}\ mol\ dm^{-3} \times 50 \times 10^{-3}\ dm^3) / 100 \times 10^{-3}\ dm^3$
$= 2.5 \times 10^{-3}\ mol\ dm^{-3}$

$[K_2CO_3(aq)] = (1.0 \times 10^{-2}\ mol\ dm^{-3} \times 50 \times 10^{-3}\ dm^3) / 100 \times 10^{-3}\ dm^3$
$= 5.0 \times 10^{-3}\ mol\ dm^{-3}$

As $Mg(NO_3)_2(aq)$ and $K_2CO_3(aq)$ dissociate completely, we can write:

$Mg(NO_3)_2(aq) \rightarrow Mg^{2+}(aq) + 2NO_3^-(aq)$
2.5×10^{-3} 2.5×10^{-3} mol dm^{-3}

$K_2CO_3(aq) \rightarrow 2K^+(aq) + CO_3^{2-}(aq)$
5.0×10^{-3} 5.0×10^{-3} mol dm^{-3}

As the precipitate formed is $MgCO_3$:

$$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$$

$K_{sp} = [Mg^{2+}(aq)][CO_3^{2-}(aq)]$

Ion Product $= [Mg^{2+}(aq)][CO_3^{2-}(aq)] = (2.5 \times 10^{-3})(5.0 \times 10^{-3})\ mol^2 dm^{-6}$
$= 12.5 \times 10^{-6}\ mol^2\ dm^{-6}$

$IP\ (12.5 \times 10^{-6}\ mol^2\ dm^{-6}) > K_{sp(MgCO_3)}\ (3.5 \times 10^{-8}\ mol^2\ dm^{-6})$

Therefore a precipitate of $MgCO_3$ will form.

Example 2.32

Will a precipitate form if 50.00 cm^3 of 1.0×10^{-3} mol dm^{-3} $CaCl_2$ solution is added to 50.00 cm^3 of 1.0×10^{-2} mol dm^{-3} Na_2SO_4 solution? $K_{sp}(CaSO_4) = 2.4 \times 10^{-5}$ mol^2 dm^{-6}

Answer

First write the reaction between $Mg(NO_3)_2$ and K_2CO_3.

$$CaCl_2(aq) + Na_2SO_4(aq) \rightarrow 2NaCl(aq) + CaSO_4(s)$$

As two solutions are mixed, dilution occurrs

Therefore the concentrations of the solutions are different when mixed.

$[CaCl_2(aq)] = (1.0 \times 10^{-3}\ mol\ dm^{-3} \times 50 \times 10^{-3}\ dm^3) / 100 \times 10^{-3}\ dm^3$

$= 5.0 \times 10^{-4}\ mol\ dm^{-3}$

$[Na_2SO_4\ (aq)] = (1.0 \times 10^{-2}\ mol\ dm^{-3} \times 50 \times 10^{-3}\ dm^3) / 100 \times 10^{-3}\ dm^3$

$= 5.0 \times 10^{-3}\ mol\ dm^{-3}$

$CaCl_2(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$

5.0×10^{-4} 5.0×10^{-4} mol dm^{-3}

$Na_2SO_4(aq) \rightarrow 2Na^+(aq) + SO_4^{2-}(aq)$

5.0×10^{-3} 5.0×10^{-3} mol dm^{-3}

As the precipitate formed is $CaSO_4$:

$$CaSO_4\ (s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(\ aq)$$

$K_{sp} = [Ca^{2+}(aq)][\ SO_4^{2-}(aq)]$

Ion Product $= [Ca^{2+}(aq)][\ SO_4^{2-}(aq)] = (5.0 \times 10^{-4})\ (5.0 \times 10^{-3})\ mol^2\ dm^{-6}$

$= 2.5 \times 10^{-6}\ mol^2\ dm^{-6}$

$IP\ (2.5 \times 10^{-6}\ mol^2\ dm^{-6}) < K_{sp}(CaSO_4) = 2.4 \times 10^{-5}\ mol^2\ dm^{-6}$

Therefore a precipitate of $CaSO_4$ will not be formed.

Example 2.33

What is the maximum $[Sr^{2+}(aq)]$ that can exist in a 0.020 mol dm^{-3} solution of K_2SO_4 without forming a precipitate of $SrSO_4$? $K_{sp(SrSO_4)} = 3.2 \times 10^{-7}$ mol^2 dm^{-6}

Answer

$$\begin{array}{llll} K_2SO_4(aq) & \rightarrow\ 2K^+(aq)\ + & SO_4^{2-}(aq) & \\ 2.0 \times 10^{-2} & & 2.0 \times 10^{-2} & mol\ dm^{-3} \end{array}$$

$SrSO_4\ (s) \rightleftharpoons Sr^{2+}(aq) + SO_4^{2-}(aq)$

$K_{sp} = [Sr^{2+}(aq)][SO_4^{2-}(aq)]$

$\therefore\ 3.2 \times 10^{-7}\ mol^2\ dm^{-6} = [Sr^{2+}(aq)](\ 2.0 \times 10^{-2}\ mol\ dm^{-3})$

$[Sr^{2+}(aq)] = 1.6 \times 10^{-5} mol\ dm^{-3}$

Example 2.34

XA(s) and YA(s) are two sparingly water soluble salts.

At 298 K, $K_{sp}(XA) = 1.80 \times 10^{-10}\ mol^2\ dm^{-6}$ and $K_{sp}(YA) = 1.80 \times 10^{-7}\ mol^2\ dm^{-6}$. A completely water soluble salt of NaA is added slowly to a 1.00 dm^3 solution containing 0.100 moles of $X^+(aq)$ and $Y^+(aq)$.

(i) Predict which of the salts precipitates first.

(ii) 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

$K_{sp} = [X^+(aq)]\ [A^-(aq)]$

$[A^-(aq)] = K_{sp}/\ [X^+(aq)] = (1.80 \times 10^{-10}/\ 0.100)\ mol\ dm^{-3} = 1.80 \times 10^{-9}\ mol\ dm^{-3}$

For YA

$K_{sp} = [Y^+(aq)]\ [A(aq)]$

$[A^-(aq)] = K_{sp}[Y^+(aq)] = (1.80 \times 10^{-7}\ /\ 0.100)\ mol\ dm^{-3} = 1.80 \times 10^{-6}\ mol\ dm^{-3}$

$[A^-(aq)]$ necessary to precipitate XA is less than that needed to precipitate YA.

$\therefore$ XA precipitates first.

(ii) $K_{sp(XA)} = [X^+(aq)]\ [A^-(aq)]$

at this stage $[A^-(aq)]$ is the $[A^-(aq)]$ needed to start precipitation of YA.

$[X^+(aq)]$ left in the solution $= (1.80 \times 10^{-10}\ /\ 1.80 \times 10^{-6})\ mol\ dm^{-3}$

$= 1.\ 0 \times 10^{-4}\ mol\ dm^{-3}$

Example 2.35

Consider a solution of 0.10 mol dm^{-3} $A^{2+}(aq)$ and 0.20 mol dm^{-3} $B^{3+}(aq)$.

$K_{sp}(AI_2) = 9.0\times10^{-9}$ and $K_{sp}(BI_3) = 1.6\times10^{-18}$

(i) What are the minimum concentration of $I^-(aq)$ needed to start precipitation of the $A^{2+}(aq)$ and $B^{3+}(aq)$?

(ii) What range of concentrations of $I^-(aq)$ can be used to precipitate only $B^{3+}(aq)$?

Answer

(i) For AI_2

$K_{sp} = [A^{2+}(aq)]\,[I^-(aq)]^2$

$$[I^-(aq)] = \sqrt[2]{\frac{K_{sp}}{[A^{2+}(aq)]}}$$

$$= \sqrt[2]{\frac{9.0\times10^{-9}}{0.10}}$$

$= 3.0 \times 10^{-4}$ mol dm^{-3}

For BI_3

$K_{sp} = [B^{3+}(aq)]\,[I^-(aq)]^3$

$$[I^-(aq)] = \sqrt[3]{\frac{K_{sp}}{[B^{3+}(aq)]}}$$

$$= \sqrt[3]{\frac{1.6\times10^{-18}}{0.20}}$$

$= 2.0 \times 10^{-6}$ mol dm^{-3}

(ii) 2.0×10^{-6} mol dm^{-3} < $[I^-(aq)]$ < 3.0×10^{-4} 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.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

If $[Ag^+(aq)]$ 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 $[Ag^+(aq)]$ 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 mol dm^{-3} NaOH.

$K_{sp}(Ni(OH)_2) = 2.0\times10^{-15}$ mol^3 dm^{-9}

Answer

Let the solubility of $Ni(OH)_2$ as ***s***.

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

At equilibrium : $\quad s \quad\quad 2s + 0.10$

$K_{sp} = [\ Ni^{2+}(aq)]\ [OH^{-}(aq)]^2$

$= s\ (2s + 0.10)^2$

As K_{sp} is small, $(2\boldsymbol{s} << 0.10)$

$\therefore\ (2\boldsymbol{s} + 0.10) \approx 0.10$

2.0×10^{-15} mol^3 $dm^{-9} = \boldsymbol{s}\ (0.10)^2$

$s\ = 2.0\ \times 10^{-13}$ mol dm^{-3}

If we do not have a common ion solubility is 7.94 × 10^{-6} mol dm^{-3}.

Example 2.37

Calculate the molar solubility of $BaCrO_4$ in (i) 0.100 mol dm^{-3} and (ii)1.00×10^{-3} mol dm^{-3} $BaCl_2$ solutions at 298 K. $K_{sp}(BaCrO_4) = 1.2 \times 10^{-10}$ mol^2 dm^{-6}.

Answer

(i) $$BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq)$$

At equilibrium : $\quad s + 0.100 \quad\quad s$

$K_{sp} = [\ Ba^{2+}(aq)]\ [CrO_4^{2-}\ (aq)] = (s + 0.10)\ s$

As K_{sp} is small, $(\boldsymbol{s} << 0.100)$

$\therefore\ (s + 0.100) \approx 0.100$

1.2×10^{-10} mol^2 $dm^{-6} = s\ (0.100)$

$\boldsymbol{s\ = 1.2\ \times 10^{-9}}$ **mol dm^{-3}**

(ii) $$BaCrO_4(s) \rightleftharpoons Ba^{2+}(aq) + CrO_4^{2-}(aq)$$

At equilibrium : $\quad s + 0.001 \quad\quad s$

$K_{sp} = [\ Ba^{2+}(aq)]\ [CrO_4^{2-}\ (aq)] = (s + 0.001)\ s$

As K_{sp} is small, $(\boldsymbol{s} << 0.001)$

$\therefore\ (s + 0.001) \approx 0.001$

1.2×10^{-10} mol^2 $dm^{-6} = s\ (0.001)$

$\boldsymbol{s\ = 1.2\ \times 10^{-7}}$ **mol dm^{-3}**

These results indicate that the solubility of $BaCrO_4(s)$ 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:

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

The solubility of the $PbCl_2(s)$ can be increased by decreasing either $[Pb^{2+}(aq)]$ or $[Cl^{-}(aq)]$.
The $[Pb^{2+}(aq)]$ 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 $[Pb^{2+}(aq)]$.

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 1.4×10^{-8} mol^3 dm^{-9} while K_{sp} of $PbCl_2$ is 1.8×10^{-5} mol^3 dm^{-9}. Similarly, $AgNO_3$ can be added to decrease the $[Cl^{-}(aq)]$ which precipitates as AgCl.

Example 2.38
Compare the relative solubility of $CaC_2O_4(s)$ in 0.10 mol dm^{-3}solutions of (i)NaOH, (ii)KCl and (iii) $Ca(NO_3)_2$

Answer
As $CaC_2O_4(s)$ is a spairingly soluble salt we can write,

$$CaC_2O_4(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$

(i) In NaOH(aq) : $NaOH(aq) \rightarrow Na^{+}(aq) + OH^{-}(aq)$
$OH^{-}(aq)$ will precipitate $Ca^{2+}(aq)$ as $Ca(OH)_2(s)$
Thus, $[Ca^{2+}(aq)]$ decreases, causing a shift to right, so the solubility of $CaC_2O_4(s)$ increases.

(ii) In KCl(aq): $KCl(aq) \rightarrow K^{+}(aq) + Cl^{-}(aq)$
$K^{+}(aq)$ and $Cl^{-}(aq)$ will not affect the equilibrium.

(iii)In $Ca(NO_3)_2$ (aq): $Ca(NO_3)_2(aq) \rightarrow Ca^{2+}(aq) + 2NO_3^{-}(aq)$
$Ca^{2+}(aq)$ is a common ion, so $[Ca^{2+}(aq)]$ increases, causing a shift to left, forming more $CaC_2O_4(s)$. 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:

$$MA(s) \rightleftharpoons M^+(aq) + A^-(aq) \quad : \quad K_{sp} = [\,M^+(aq)][\,A^-(aq)] \;\ldots\ldots\; (1)$$

The anion can also react with water in a hydrolysis reaction:

$$A^-(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + HA(aq) \;\ldots\ldots(2)$$

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:

$$Ag_3PO_4(s) \rightleftharpoons 3Ag^+(aq) + PO_4^{3-}(aq)$$

If HNO_3 is added, the following reaction occurs:

$$H_3O^+(aq) + PO_4^{3-}(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$$

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:

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

- 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 $Cu^{2+}{}_{(aq)}$ concentration in a saturated solution of $Cu(OH)_2$ at 298 K, (i) when pH =10.0 and (ii) when pH = 5.0. $K_{sp(Cu(OH)_2)} = 2.2 \times 10^{-20}$ mol^{3}dm^{-9}.

Answer

(i) when pH = 10.00

$[H^+(aq)] = 1.0\times10^{-10}$ and $[OH^-(aq)] = 1.0\times10^{-4}$ mol dm^{-3}

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

At equilibrium: x 1.0×10^{-4} mol dm^{-3}

$K_{sp} = [Cu^{2+}(aq)][OH^-(aq)]^2 = 2.2 \times 10^{-20}$ mol^{3}dm^{-9}

$x\,(1.0\times10^{-4}\text{ mol dm}^{-3})^2 = 2.2 \times 10^{-20}$

$\therefore x = [Cu^{2+}(aq)] = \mathbf{2.2 \times 10^{-12}\ mol\ dm^{-3}}$

(ii) when pH = 5.00

$[H^+(aq)] = 1.0\times10^{-5}$ and $[OH^-(aq)] = 1.0\times10^{-9}$ mol dm^{-3}

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

At equilibrium : x 1.0×10^{-9}

$K_{sp} = [Cu^{2+}(aq)][OH^-(aq)]^2 = 2.2 \times 10^{-20}$

$x\,(1.0\times10^{-9}\text{ mol dm}^{-3})^2 = 2.2 \times 10^{-20}$ mol^{3}dm^{-9}

$\therefore x = [Cu^{2+}(aq)] = \mathbf{2.2 \times 10^{-2}\ mol\ dm^{-3}}$

We can note that decreasing pH increases the solubility of such metal hydroxides.

In the above example, the anion $OH^-(aq)$ is derived from water and thus we could consider the effect of $H^+(aq)$ 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.

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)\ ; \quad K_{sp} = 3.45 \times 10^{-11}$$

When strong acid is added to a saturated solution of CaF_2, the following reaction occurs.

$$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq)$$

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

$$CaF_2(s) + 2H^+(aq) \rightarrow Ca^{2+}(aq) + 2HF(aq)$$

In another case of metal carbonates: $MCO_3(s)$

$$MCO_3(s) \rightleftharpoons M^{2+}(aq) + CO_3^{2-}(aq)$$

$$H^+(aq) + CO_3^{2-}(aq) \rightleftharpoons HCO_3^-(aq)$$

The overall reaction is thus,

$$MCO_3(s) + H^+(aq) \rightarrow M^{2+}(aq) + HCO_3^-(aq)$$

i.e. More $MCO_3(s)$ 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 4.8×10^{-10} mol^{2}dm^{-6}, 9.8×10^{-9} mol^{3}dm^{-9} and 2.5×10^{-5} mol^2 dm^{-6}, respectively at 298 K. Compare their relative solubilities when a strong acid is added to saturated solutions of them.

We can write:

$$PbC_2O_4(s) \rightleftharpoons Pb^{2+}(aq) + C_2O_4^{2-}(aq) \,;\ K_{sp} = 4.8 \times 10^{-10}\ \text{mol}^2\,\text{dm}^{-6}$$

$$PbI_2(s) \rightleftharpoons Pb^{2+}(aq) + 2I^-(aq) \,;\ K_{sp} = 9.8 \times 10^{-9}\ \text{mol}^3\,\text{dm}^{-9}$$

$$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq) \,;\ K_{sp} = 2.5 \times 10^{-5}\ \text{mol}^2\,\text{dm}^{-6}$$

The anions $C_2O_4^{2-}$, I^-, and SO_4^{2-} formed in the above equilibria are all conjugate bases of acids $H_2C_2O_4$, 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 $H^+(aq)$ and the corresponding anion.

$C_2O_4^{2-}(aq)$ has high affinity for one proton and low affinity for a second proton. Therefore, addition of a strong acid to a saturated solution of $PbC_2O_4(s)$ will result in the following reactions:

$$C_2O_4^{2-}(aq) + H^+(aq) \rightleftharpoons HC_2O_4^-(aq)$$

and

$$HC_2O_4^-(aq) + H^+(aq) \rightleftharpoons H_2C_2O_4(aq)$$

These reactions will decrease [$C_2O_4^{2-}$(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.

$$SO_4^{2-}(aq) + H^+(aq) \rightleftharpoons HSO_4^-(aq)$$

The pK_a of HSO_4^-(aq) (1.99) << pK_{a2} of oxalic acid, so the reverse reaction in the above equilibrium is largely favored. In other words, basicity of oxalic acid >>> 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 3.0×10^{-6} mol dm^{-3} of M^{3+}(aq) in an acidic solution. To what pH must the solution be adjusted to begin precipitation of M^{3+} as $M(OH)_3$?

$Ksp = 2.4 \times 10^{-20}$ mol^4 dm^{-12}

Answer

K_{sp} = [M^{3+}(aq)] [OH^-(aq)]^3= 2.4×10^{-20} mol^4 dm^{-12}

$$[OH^- (aq)] = \sqrt[3]{\frac{2.4 \times 10^{-20}}{3.0 \times 10^{-6}}} = 2.0 \times 10^{-5}\ \text{mol dm}^{-3}$$

∴ pOH = **4.7**

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+}, Sn^{4+}/ 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:

$$Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$$
$$Hg_2^{2+}(aq) + 2Cl^-(aq) \rightarrow Hg_2Cl_2(s)$$
$$Pb^{2+}(aq) + 2Cl^-(aq) \rightarrow PbCl_2(s)$$

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, HS^-(aq), and sulfide ions, S^{2-}(aq) and we can consider the following equilibria.

Three equilibria are involved:

$$H_2S(g) \rightleftharpoons H_2S(aq)$$

$$H_2S(aq) \rightleftharpoons H^+(aq) + HS^-(aq); \quad K_1 = \frac{[H^+(aq)]\,[HS^-(aq)]}{[H_2S(aq)]} = 9.1 \times 10^{-8}\ \text{mol dm}^{-3}$$

$$HS^-(aq) \rightleftharpoons H^+(aq) + S^{2-}(aq); \quad K_2 = \frac{[H^+(aq)]\,[S^{2-}(aq)]}{[HS^-(aq)]} = 1.0 \times 10^{-19}\ \text{mol dm}^{-3}$$

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:

$$M^{2+}(aq) + H_2S(aq) \rightleftharpoons MS(s) + 2H^+(aq)$$

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 H^+(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} (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 H_2S(g) into the filtrate from group I separation.

The reactions involved in the precipitation of Group II cations are as follows.

$$Cu^{2+}(aq) + H_2S(aq) \rightarrow CuS(s) + 2H^+(aq)$$
$$Cd^{2+}(aq) + H_2S(aq) \rightarrow CdS(s) + 2H^+(aq)$$
$$Hg^{2+}(aq) + H_2S(aq) \rightarrow HgS(s) + 2H^+(aq)$$
$$2Bi^{3+}(aq) + 3H_2S(aq) \rightarrow Bi_2S_3(s) + 6H^+(aq)$$
$$2As^{3+}(aq) + 3H_2S(aq) \rightarrow As_2S_3(s) + 6H^+(aq)$$

$$2Sb^{3+}(aq) + 3H_2S(aq) \rightarrow Sb_2S_3(s) + 6H^+(aq)$$
$$Sn^{4+}(aq) + 2H_2S(aq) \rightarrow SnS_2(s) + 4H^+(aq)$$

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 1×10^{-5} mol dm^{-3}) an ammonia-ammonium chloride (NH_3 / NH_4Cl) buffer is used. In the ammonia solution the following ionization equilibrium prevails:

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

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

If 0.10 mol dm^{-3} NH_3 solution is used, the hydroxide ion concentration will be 1.3×10^{-3} 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 $[OH^-(aq)]$ of about 1×10^{-5} 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 : $K_{sp(Al(OH)_3)} = 1.8 \times 10^{-33}$ mol^4 dm^{-12}, $K_{sp(Cr(OH)_3)} = 3.0 \times 10^{-29}$ mol^4 dm^{-12}, $K_{sp(Fe(OH)_3)} = 1.4 \times 10^{-28}$ mol^{4}dm^{-12} and $K_{sp(Mg(OH)_2)} = 1.8\times 10^{-11}$ mol^{3}dm^{-9}.

The equations for the precipitation of the ions of Group III are:

$$Al^{3+}(aq) + 3H_2O(aq) + 3NH_3(aq) \rightarrow Al(OH)_3(s) + 3NH_4^+(aq)$$
$$Cr^{3+}(aq) + 3H_2O(aq) + 3NH_3(aq) \rightarrow Cr(OH)_3(s) + 3NH_4^+(aq)$$
$$Fe^{3+}(aq) + 3H_2O(aq) + 3NH_3(aq) \rightarrow Fe(OH)_3(s) + 3NH_4^+(aq)$$

At this stage, if the $[OH^-_{(aq)}]$ is high enough to precipitate $Mg(OH)_2$

$$Mg^{2+}(aq) + OH^-(aq) \rightarrow Mg(OH)_2(s)$$

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.

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

In the presence of $OH^-(aq)$ ions, the $H^+(aq)$ ions are neutralized and therefore the solution contains fairly high concentration of $S^{2-}(aq)$ 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:

$$Zn^{2+}(aq) + H_2S(aq) \rightarrow ZnS(s) + 2H^+(aq)$$
$$Ni^{2+}(aq) + H_2S(aq) \rightarrow NiS(s) + 2H^+(aq)$$
$$Co^{2+}(aq) + H_2S(aq) \rightarrow CoS(s) + 2H^+(aq)$$
$$Mn^{2+}(aq) + H_2S(aq) \rightarrow MnS(s) + 2H^+(aq)$$

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 $H_2S_{(aq)}$ in filtrate from group IV by boiling and adding NH_4Cl/ NH_4OH in excess. Adding $(NH_4)_2CO_3$ solution will enable the precipitation of group V cations. The equations for the precipitation of the ions of Group V are:

$$Ca^{2+}(aq) + CO_3^{2-}(aq) \rightarrow CaCO_3(s)$$
$$Sr^{2+}(aq) + CO_3^{2-}(aq) \rightarrow SrCO_3(s)$$
$$Ba^{2+}(aq) + CO_3^{2-}(aq) \rightarrow BaCO_3(s)$$

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 mol dm^{-3} Zn^{2+} and 0.1 mol dm^{-3} Fe^{2+} ions. What should be the *p*H of the solution, if they are to be separated by passing H_2S gas through the solution?

Given that K_{sp} for ZnS = 1.6×10^{-24} $mol^2\ dm^{-6}$ and K_{sp} for FeS= 6.3×10^{-18} mol^2dm^{-6}. In a solution $H_2S(aq)$ has a concentration of 0.10 mol dm^{-3}.

Answer

When $H_2S(g)$ is passed through a solution following equilibria exist.

$$H_2S(g) \rightleftharpoons H_2S(aq)$$

$$H_2S(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HS^-(aq);\ K_{a_1} = \frac{[H_3O^+(aq)]\,[HS^-(aq)]}{[H_2S(aq)]}$$

$$= 9.1 \times 10^{-8}\ \text{mol dm}^{-3}$$

$$HS^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + S^{2-}(aq);\ K_{a_2} = \frac{[H_3O^+(aq)]\,[S^{2-}(aq)]}{[HS^-(aq)]}$$

$$= 1.0 \times 10^{-19}\ \text{mol dm}^{-3}$$

From these two equations we can write

$$K_{a_1}\,K_{a_2}\,[H_2S(aq)] = [H_3O^+(aq)]^2\,[S^{2-}(aq)]$$

Substituting the given, we get,

$$[H_3O^+(aq)]^2\,[S^{2-}(aq)] = (9.1 \times 10^{-8})\,(1.0 \times 10^{-19})\,(0.1)\ \text{mol}^3\ \text{dm}^{-9}$$

$$= 9.1 \times 10^{-28}\ \text{mol}^3\ \text{dm}^{-9}$$

From the given data, we have,

$K_{sp}(ZnS) = [Zn^{2+}(aq)][S^{2-}(aq)] = 1.6 \times 10^{-24}$ $mol^2\ dm^{-6}$ and

$K_{sp}(FeS) = [Fe^{2+}(aq)][S^{2-}(aq)] = 6.3 \times 10^{-18}$ $mol^2\ dm^{-6}$

In case when $[Zn^{2+}(aq)] = 0.1$ mol dm^{-3}, minimum $[S^{2-}(aq)]$ required for precipitating ZnS can be calculated as,

$$[S^{2-}(aq)] = \frac{1.6 \times 10^{-24}}{0.1} = 1.6 \times 10^{-23}\ \text{mol dm}^{-3}$$

Corresponding to this minimum concentration of S^{2-} ions we can calculate the maximum H_3O^+ concentration by using the following equation

$$[H_3O^+(aq)]^2\,[S^{2-}(aq)] = 9.1 \times 10^{-28}\ \text{mol}^3\ \text{dm}^{-9}$$

$$\therefore [H_3O^+(aq)]^2 = \frac{9.1 \times 10^{-28}}{1.6 \times 10^{-23}} = 5.7 \times 10^{-5}\ \text{mol}^2\ \text{dm}^{-6}$$

$$\therefore [H_3O^+(aq)] = 7.6 \times 10^{-3}\ \text{mol dm}^{-3}$$

$$\therefore \text{pH} = -\log[H_3O^+(aq)] = 2.1$$

∴ The minimum pH required for precipitation of ZnS= 2.1

Likewise in case when $[Fe^{2+}(aq)] = 0.1$ mol dm^{-3}
Minimum $[S^{2-}(aq)]$ required for precipitating FeS is,

$$[S^{2-}(aq)] = \frac{6.3 \times 10^{-18}}{0.1} = 6.3 \times 10^{-17} \text{ mol dm}^{-3}$$

And the maximum $[H_3O^+(aq)]$ required is given by,

$$\therefore [H_3O^+(aq)]^2 = \frac{9.1 \times 10^{-28}}{6.3 \times 10^{-17}} = 1.4 \times 10^{-11} \text{ mol}^2 \text{ dm}^{-6}$$

$$\therefore [H_3O^+(aq)] = 3.7 \times 10^{-6} \text{ mol dm}^{-3}$$

$$\therefore \text{pH} = -\log[H_3O^+(aq)] = 5.4$$

Therefore, the minimum pH at which FeS precipitates = 5.4
It is seen that if the H_3O^+ ion concentration is higher than $10^{-5.4}$ mol dm^{-3} (3.7×10^{-6} 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.*

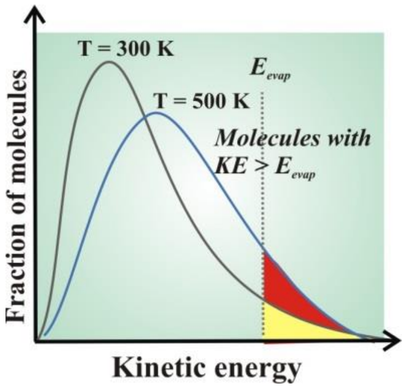


Figure 2.29 The distribution of the kinetic energies of the molecules of a liquid at two temperatures of 300 K and 400 K. Increasing the temperature shifts the peak to a higher energy and broadens the curve. Only molecules with a kinetic energy greater than E_{evap} can escape from the liquid to enter 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.

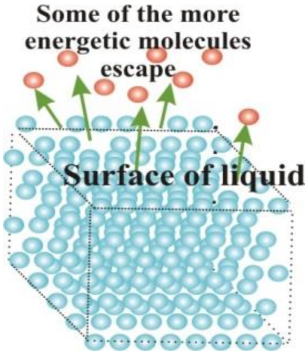


Figure 2.30 Patter of evaporation of a liquid in an open container at a given temperature. Most of the molecules with high energy that escape into the vapour phase will not collide with the surface of the liquid again and return to the liquid phase. Instead, they will diffuse through the gas phase away 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.

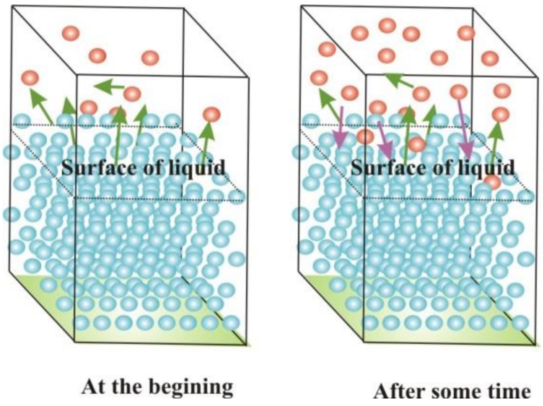


Figure 2.31 Macroscopic view of the molecular interpretation of vapour pressure. When a liquid is placed in a closed container at a given temperature, few molecules start to evaporate at the beginning and none of them can come back and re-enter into the liquid. After some time the density of the molecules 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.

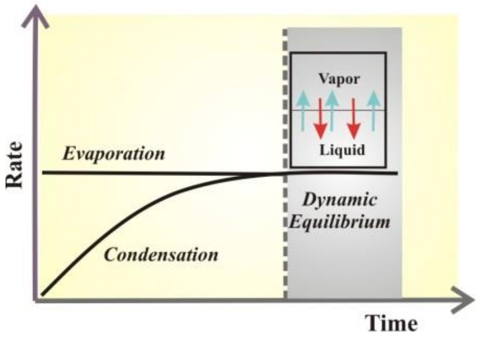


Figure 2.32 Variation of the rates of evaporation and condensation over the time for a liquid in a closed container at a given temperature. Rate of evaporations remains a constant while the rate of condensataion increases as the number of molecules in the vapour phase increases till the two rates become 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 measurd 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 mecury level gives a value for the saturated vapour pressure of the liquid at this temperature.

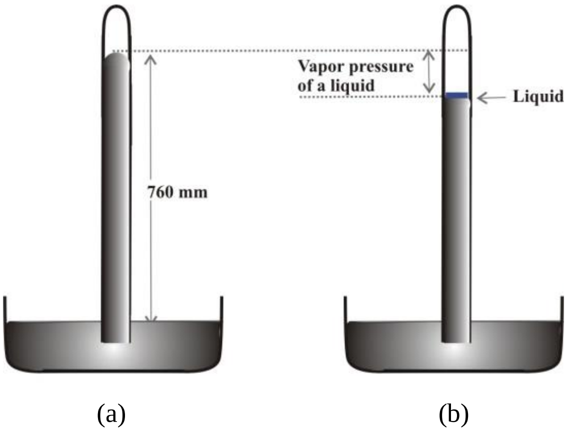


Figure 2.33 Measuring the saturated vapour pressure. **(a)** when a mecury barometer is just in air, the reading is 760 mmHg. **(b)** when a liquid is introduced into the tube, it goes on to the top of the mecury in a barometer and the level of Hg falls down. The difference is the saturated vapour pressure 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.

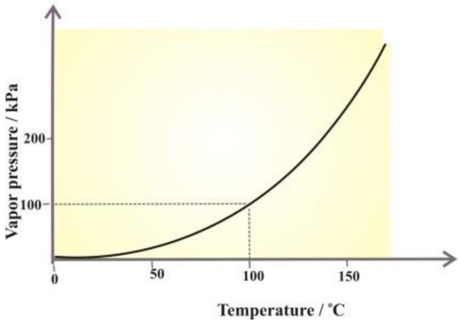


Figure 2.34 Variation of the saturated vapour pressure of water with temperature.

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.

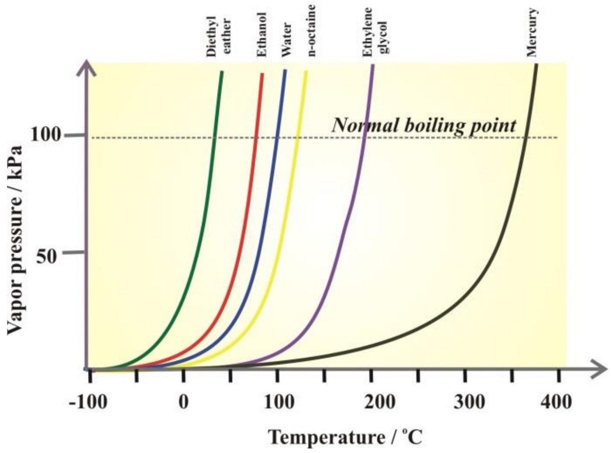


Figure 2.35 The vapour pressures of several liquids as a function of temperature. The point at which the vapour pressure curve crosses the P = 100 kPa line (dotted) is the normal boiling point of the liquid.

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 (1atm) 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.*

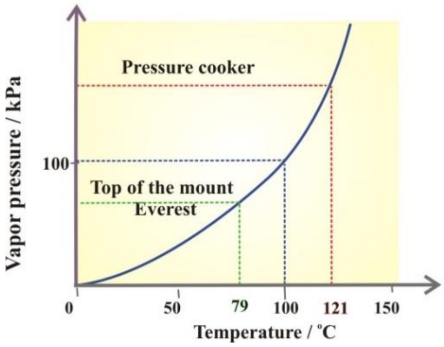


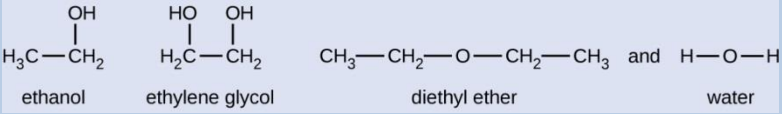
Figure 2.36 Change in boiling point of water with the pressure: water boils at normal boling point of 100 °C at atmospheric pressure of 100 kPa, boiling of water occurs at around 79 °C at mountain top and the boiling temperature increses to around 121 °C when it boils inside a pressure cooker.

Example 2.42

Compare the variation in relative vapour pressures of ethanol, ethelene glycol, diethyl eather 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 −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 eather > ethanol > water > ethelene 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.

$P_{methanol} > P_{ethanol} > P_{propanol} > P_{butanol}$

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:

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H_{vap} = 44.01 \text{ kJ mol}^{-1}$$

As described in the chapter on thermochemistry, the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$H_2O(g) \rightarrow H_2O(l) \qquad \Delta H_{con} = -44.01 \text{ kJ mol}^{-1}$$

Example 2.44

At normal body temperature, how much heat is required when 1.5 dm^3 of water (as sweat) is evaporated from the body? $\Delta H_{vap} = 43.46 \text{ kJ mol}^{-1}$ at 37 °C.

Answer

Weight of 1.5 dm^3 of water $= 1.5 \text{ dm}^3 \times 1000 \text{ g dm}^{-3} = 1.5 \times 10^3$ g

$\therefore$ Amount of moles of water evaporated $= 1.5 \times 10^3 \text{ g} / (18 \text{ g mol}^{-1}) = 83.333$ mol

$\therefore$ Heat required $= 43.46 \text{ kJ mol}^{-1} \times 83.333 \text{ mol} = 3621$ 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 heatd, 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:

$$\textbf{Solid} \quad \underset{\text{freezing}}{\overset{\text{melting}}{\rightleftharpoons}} \quad \textbf{Liquid}$$

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*, $\Delta \boldsymbol{H}_{\mathbf{fus}}$ of the substance. The enthalpy of fusion (melting) of ice is 6.0 kJ mol^{-1} at 0 °C and is an endothermic process:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta H_{\text{fus}} = 6.0 \text{ kJ mol}^{-1}$$

The opposite process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ mol^{-1} at 0 °C:

$$H_2O(l) \rightarrow H_2O(s) \quad \Delta H_{\text{fus}} = -\ 6.0 \text{ kJ mol}^{-1}$$

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) use in fire extingushers sublimes (disappear) 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:

$$CO_2(s) \rightarrow CO_2(g) \qquad \Delta H_{sub} = 26.1 \text{ kJ mol}^{-1}$$

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$CO_2(g) \rightarrow CO_2(s) \qquad \Delta \mathrm{H}_{sub} = -26.1 \text{ kJ mol}^{-1}$$

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.

$$\text{solid} \rightarrow \text{liquid:} \quad \Delta H_{fus} \quad \text{and} \quad \text{liquid} \rightarrow \text{gas:} \quad \Delta H_{vap}$$

Therefore by applying Hess's law we can write,

$$\text{solid} \rightarrow \text{gas:} \quad \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

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.

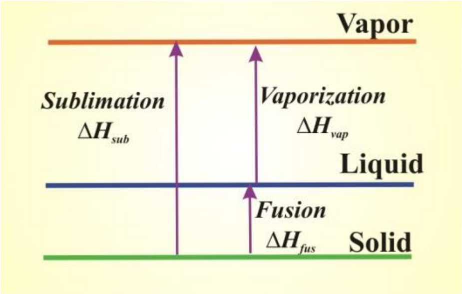


Figure 2.37 For a given substance, the sum of its enthalpy of fusion and enthalpy of vapourization is approximately equal to its enthalpy of sublimation.

The processes of phase transiations described above can be experimentally observed by constructing either heating or cooling curves. When a substance for example ice ($H_2O(s)$)

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.

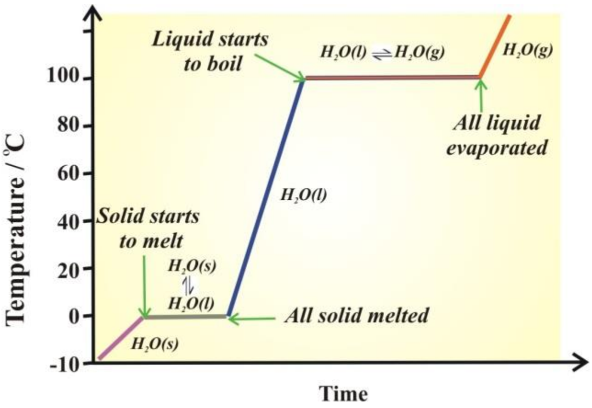


Figure 2.38 A typical heating curve for water depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the water undergoes phase transitions. Longer plateau for the equilibrium of $H_2O(l) \rightleftharpoons H_2O(g)$ compared to that of $H_2O(s) \rightleftharpoons H_2O(l)$ is due to $\Delta H_{fus} < \Delta H_{vap}$.

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 J g^{-1} $°C^{-1}$

$$\therefore q_1 = ms(\Delta t) = 180 \text{ g} \times 2.09 \text{ J g}^{-1} \text{°C}^{-1} \times 15 \text{ °C} = 5643 \text{ J} = 5.6 \text{ kJ}$$

Then, the heat needed to induce a phase change of ice to liquid water is a given $q_2 = n \times \Delta H_{fus}$.

$$\therefore q_2 = 10 \text{ mol} \times 6.0 \text{ kJ mol}^{-1} = 60 \text{ kJ}$$

$\therefore$ Total heat required = $q_1 + q_2$ = 65.6 kJ

2.5.6 Phase diagrams of pure substances

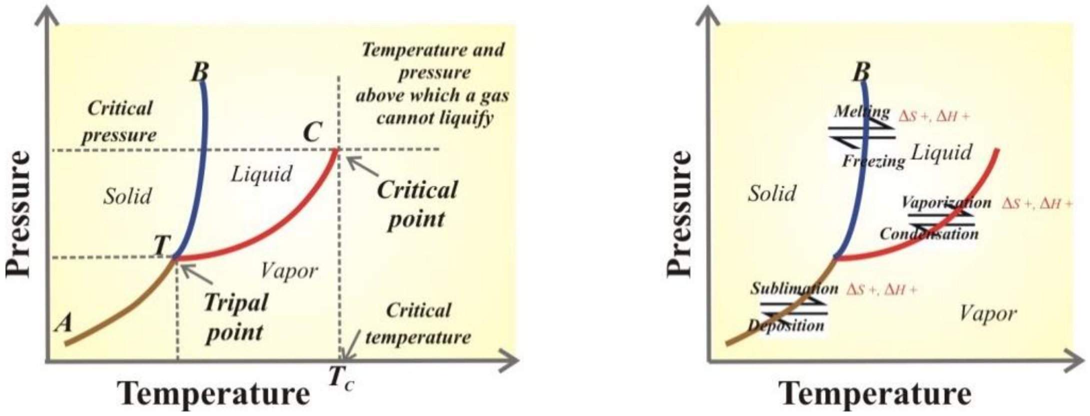
As we know, a phase is simply a physical state of a substance present under given conditions such as at a given temperature and pressure. That is, a phase is another meaning for solid, liquid or gas. If we consider some ice floating in water, there are two phases of a solid present and a liquid. If there 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 skeptual 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.



(a) (b)

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 Δ*S* and Δ*H*.

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 digram 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, thre is no any 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 bevaviour 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 repeate 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 solid $\rightleftharpoons$ 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

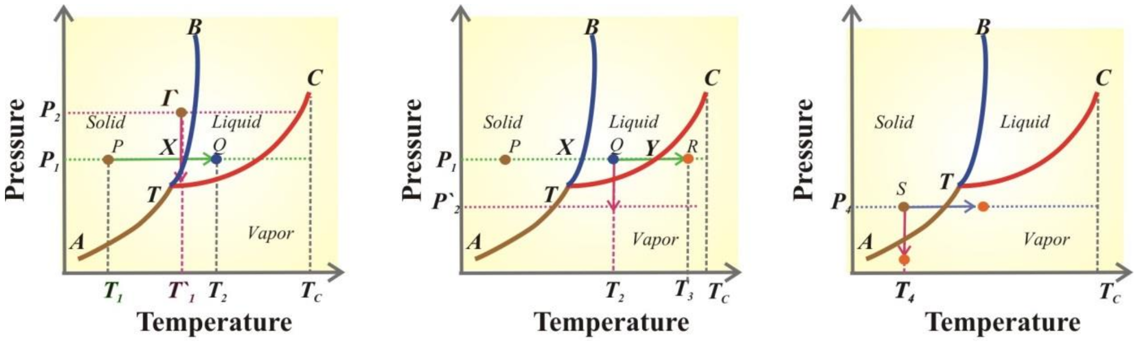
If we continue heating at the same pressure (P_1), along line PR, the liquid will meet the TC curve at point Y at which there is equilibrium between liquid and vapour and then turns into a pure vapour at the temperature T_3 (point R). In other words, it vapourizes. i.e., the liquid will change into a 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 $\mathbf{P_2}$**`** 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 exists 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.



(a) (b) (c)

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.

Deatailed 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;

$$\text{Ice} \rightleftharpoons \text{Water}$$

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.

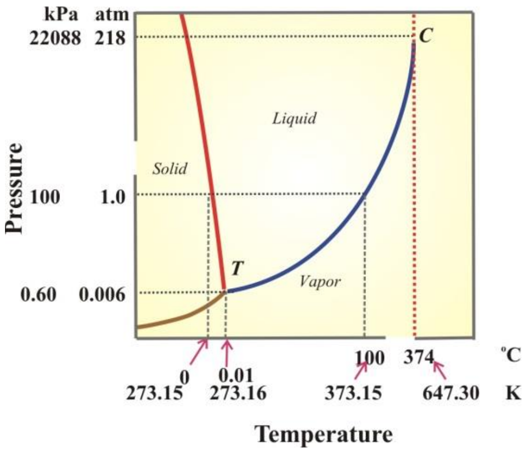


Figure 2.41 Phase diagram of water

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 g cm^{-3} = 55.6 mol dm^{-3}

Density of gaseous water = 2.7×10^{-4} 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 CO_2 is shown in the Figure 2.42.

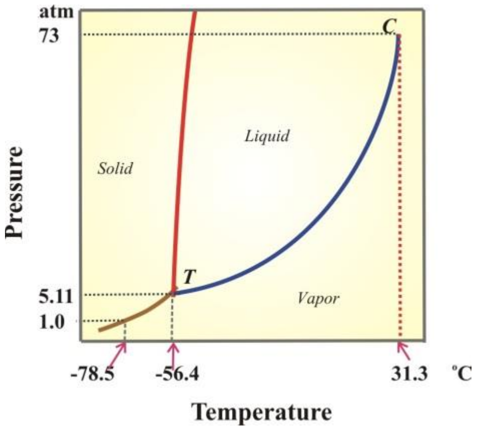


Figure 2.42 Phase diagram of CO_2

Compared to the phase diagram of water, the only thing special about the the phase diagram of CO_2 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 CO_2 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

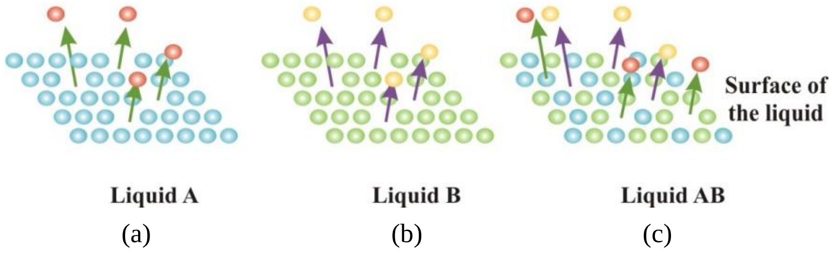
In this section, characteristics of the mixtures of two volatile liquids will be discussed wth the help of therotical concepts first. In the first part the discussion is made on the cases where the two liquids are entirely miscible in all proportions to give a single liquid. To understand the behaviour of these solutions, a concpt 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 completly 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 discuused 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.



(a) (b) (c)

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 tthey 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 attarctions occur. Energy is needed to break the interactions while energy is released during the formation of new attarctions. 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* $f_{A\text{-}A}$, $f_{B\text{-}B}$ *and* $f_{A\text{-}B}$ *are equal* ($f_{A\text{-}A} = f_{B\text{-}B} = f_{A\text{-}B}$) *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 and ideal binary liquid solution (mixture) made by mixing of liquids **A** and **B** in a closed container with a vaccum 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 pont can be testified with the consistency of the ***total vapour pressure*** and the ***composition of the vapour phase*** at a constant temperature. According to Dolton 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 buid up the higher partial pressure. That is, concentration of a component in the vapour phase is proportional to its partial pressure ($[A(g)] \alpha\, p_A$) and in a mixture the concentration of a component is proportional to its mole fraction ($[A(l)] \alpha\, x_A$).

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:

$$\mathrm{A(l)} \underset{r_c}{\overset{r_v}{\rightleftharpoons}} \mathrm{A(g)} \quad \ldots\ldots..(1) \qquad\qquad \mathrm{B(l)} \underset{r_c'}{\overset{r_v'}{\rightleftharpoons}} \mathrm{B(g)} \quad \ldots\ldots\ldots(2)$$

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;

$$r_v = k\,[\mathrm{A(l)}] \;=\; k_1\,x_\mathrm{A}$$

X_A is the mole fraction of A in solution.

Likewise,

$$r_v' \;=\; k\,'[\mathrm{A(g)}] \;=\; k_2\,p_\mathrm{A}$$

P_A is the partial pressure of A in vapour phase.

At equilibrium,

$$r_v = r_v'$$

$$k_2\,p_\mathrm{A} \;=\; k_1\,x_\mathrm{A}$$

$$\therefore\; p_\mathrm{A} \;=\; \frac{k_1}{k_2}x_\mathrm{A} \;\text{ or }\; \therefore\; p_\mathrm{A} \;=\; k\,x_\mathrm{A}$$

$$when\; x_\mathrm{A} = 1,\; p_\mathrm{A} = \mathrm{p}_\mathrm{A}^0 = saturated\ vapor\ pressure\ of\ A$$

$$\therefore\;\; k = \mathrm{p}_\mathrm{A}^0$$

$$\therefore\qquad p_\mathrm{A} = p_\mathrm{A}^0\,x_\mathrm{A}$$

$$\text{and}\quad p_\mathrm{B} \;=\; p_\mathrm{B}^0\,x_\mathrm{B}$$

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 ∴ $p_\mathrm{A} < p_\mathrm{A}^0$ and $p_\mathrm{B} < p_\mathrm{B}^0$

Therefore, decrease or lowering in the vapor pressure of A

$= \; p_\mathrm{A}^0 - p_\mathrm{A} = p_\mathrm{A}^0 \;-\; p_\mathrm{A}^0 x_\mathrm{A} = \;\; p_\mathrm{A}^0(1 - x_\mathrm{A})$

$= \; p_\mathrm{A}^0\,x_\mathrm{B}$

$$\therefore\;\; \frac{p_\mathrm{A}^0 - p_\mathrm{A}}{p_\mathrm{A}^0} \;=\; x_\mathrm{B} \;\text{ and }\; \frac{p_\mathrm{B}^0 - p_\mathrm{B}}{p_\mathrm{B}^0} \;=\; x_\mathrm{A}$$

The above is an alternative form of Roult 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 Roult law with Dolton law of partial pressures, it is possible to determine the composition in the vapour phase. If $\boldsymbol{p}$ is the total vapour pressure and $\boldsymbol{y_A}$ and $\boldsymbol{y_B}$ are the mole fractions of A and B in the vapor phase, respectively, from Dolton law:

$$p_A = py_A = (p_A + p_B)y_A$$

$$p_A^0 x_A = (p_A^0 x_A + p_B^0 x_B)y_A$$

$$\therefore\ Y_A = \frac{p_A^0 x_A}{(\ p_A^0 x_A + \ \ p_B^0 x_B\ )} \text{ and } y_B = \frac{p_B^0 x_B}{(p_A^0 x_A + p_B^0 x_B)}$$

Roult law is only applied for ideal mixtures or ideal mixtures follow Roult 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.

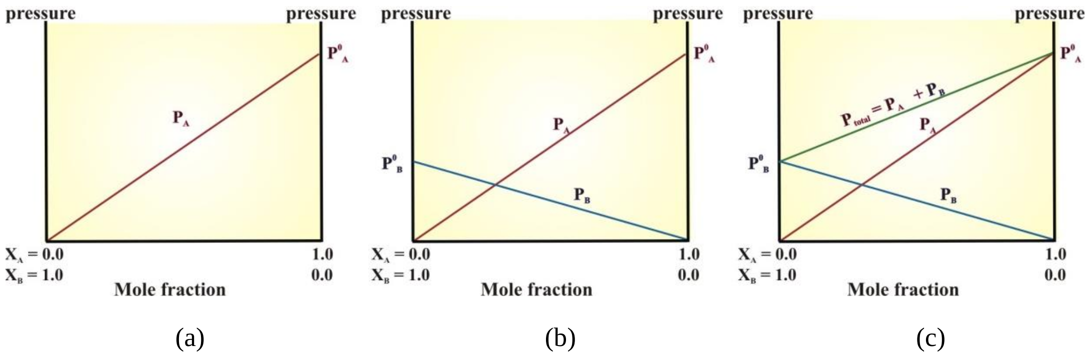


Figure 2.44 Vapour pressure – composition diagrams for an ideal mixture AB which obeys the Roult law at constant temperature. **(a)** Variation of vapour pressure of component A; **(b)** variation of vapour pressure of component B included and **(c)** variation in total vapour pressure of the mixture.

Temperature (Boliling 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 thaught 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 $p_{\mathrm{A}}^{0} > p_{\mathrm{B}}^{0}$ at constant pressure $T_{\mathrm{b(A)}} < T_{\mathrm{b(B)}}$ 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).

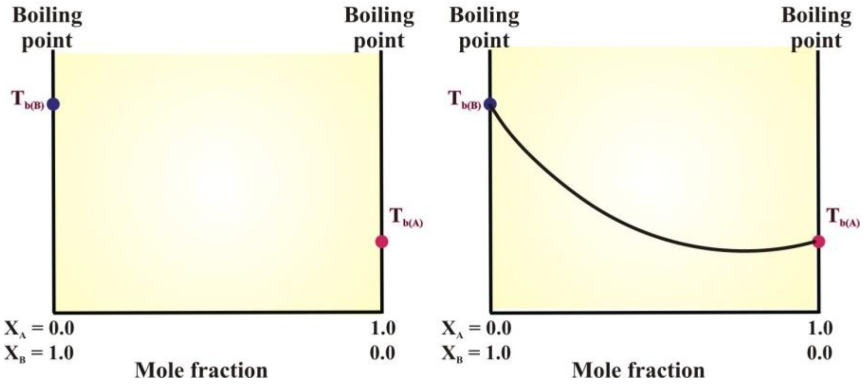
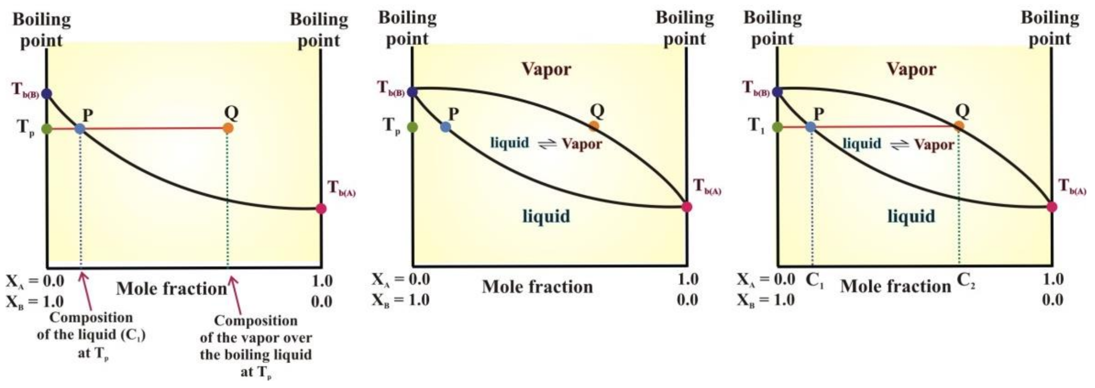


Figure 2.45 Boiling point (temperature) – composition diagrams for an ideal mixture AB at constant pressure. **(a)** Boiling points of components A and B; **(b)** variation of boiling point of the mixture.

First we can mark the boiling points on the respective axes with $T_{\mathrm{b(A)}} < T_{\mathrm{b(B)}}$ 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.



(a) (b) (c)

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 ⇌ vapor exists. (c) Finds the composition of the liquid corresponds to the point Q as C_2.

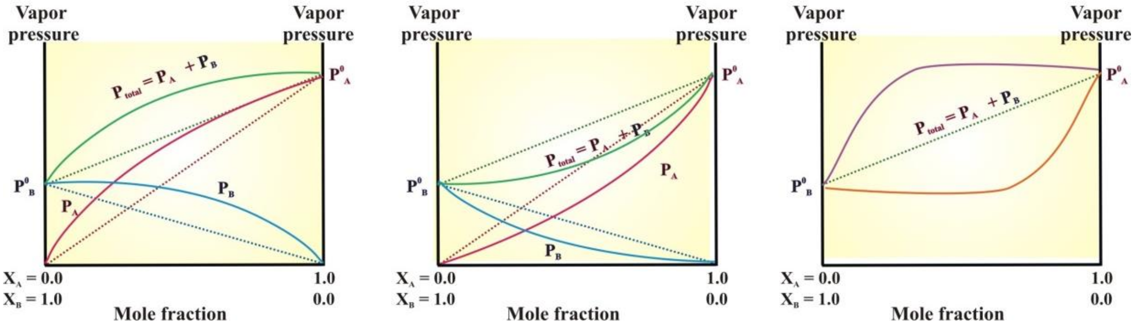
As described in Figure 2.46 (b), by boiling a liquid mixture we can find the temperature at which it boils, and the composition of the vapour over the boiling liquid. For example, in the Figure 2.46 (c), a liquid mixture of composition C_1 boils at a temperature T_1 and the vapour over the top of the boiling liquid will have the composition C_2. Likewise we can repeat this for other compositions and from the liquid composition curve the boling point can be determind. 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 discus that application it is worth seeing the characteristics of systems of liquid mixtures showing some devistions from the Roult law.

Non-ideal mixtures of liquids

A liquid mixture which does not obey Roult 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-idael mixture with components A and B, $f_{A\text{-}A} \neq f_{B\text{-}B} \neq f_{A\text{-}B}$, 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 Roult 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 $p_A^0 > p_B^0$.



(a) (b) (c)

Figure 2.47 Vapour pressure – composition diagrams for non-ideal mixture AB at constant temperature. (a) Positive deviation from Roult law and (b) negative deviation from Roult law. (c) Shows mixtures having large positive and negative deviations from Roult law.

Positive deviations from Raoult law

Some mixtures are formed at constant temperature by components A and B where $f_{A\text{-}B} < f_{A\text{-}A}$ and $f_{B\text{-}B}$, 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, $p_{\mathrm{A}} > p_{\mathrm{A}}^0 x_{\mathrm{A}}$ and $p_{\mathrm{B}} > p_{\mathrm{B}}^0 x_{\mathrm{B}}$: this results;

$$p_{\mathrm{AB}} > (p_{\mathrm{A}}^0 x_{\mathrm{A}} + p_B^0 x_{\mathrm{B}})$$

This means that the total vapor pressure of the mixture is higher than that of an ideal mixture;

$$p_{\mathrm{AB}} > p_{(\mathrm{AB})_{\mathrm{ideal}}}$$

These type of mixtures/solutions are said to exhibit ***positive deviations*** from Roult 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 $p_{\mathrm{A}}^0 > p_{\mathrm{B}}^0$. 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 $f_{A\text{-}B} > f_{A\text{-}A}$ and $f_{B\text{-}B}$, 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;

$$p_{AB} < (p_A^0 x_A + p_B^0 x_B)$$

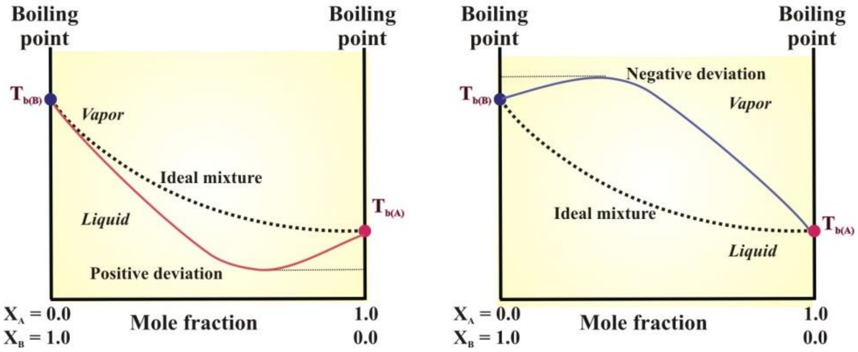
This means that the total vapor pressure of the mixture is lower than that of an ideal mixture;

$$p_{AB} < p_{(AB)_{ideal}}$$

These type of mixtures/solutions are said to exhibit ***negative deviations*** from Roult 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 mixd, 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 Roult 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.



(a) (b)

Figure 2.48 Boiling point – composition diagrams for non-ideal mixture AB at constant temperature. **(a)** Positive deviation from Roult law and **(b)** negative deviation from Roult law.

In the case of the mixtures with negative deviation from Roult 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 °C when the mixture contains 68% by mass of nitric acid. That can be compared with the boiling point of pure nitric acid (86 °C), and water (100 °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 relavent 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

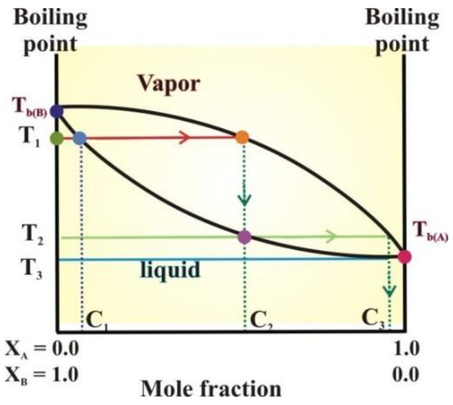


Figure 2.49 Concept of fractional distillation

If we continue the process of ocondensing 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.

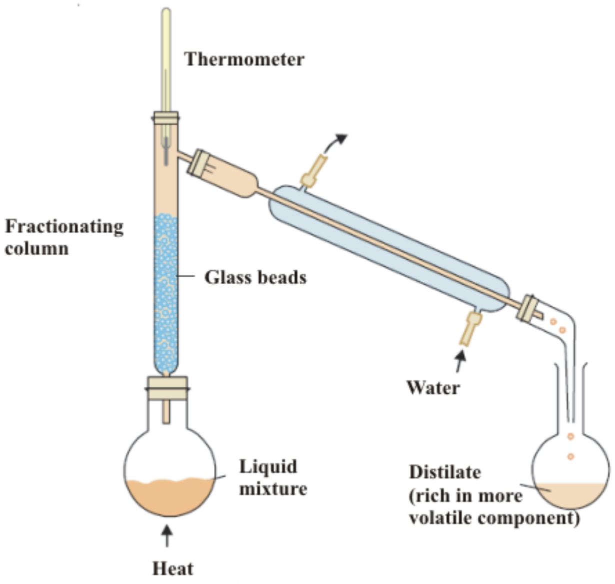


Figure 2.50 A sketch of the complete set up use for the fractional distillation with fractionating column

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 boling 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 boilng and condensastions 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 boling 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,

$$p_{\mathrm{T}} = p^{\circ}_{\mathrm{A}} + p^{\circ}_{\mathrm{B}}$$

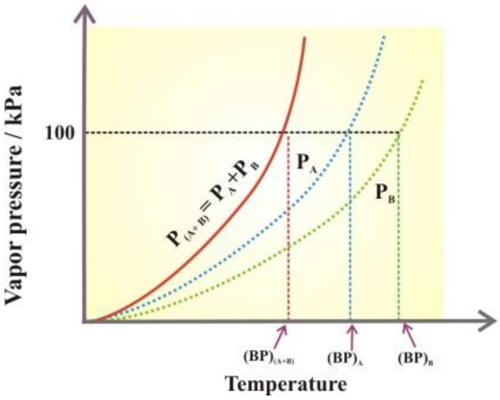


Figure 2.51 Variation of vapor pressure of totally immiscible liquid – liquid system

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 boling 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-boling compounds by the application of steam distillation. For example, phenylamine $C_6H_5NH_2$ oxidizes rapidly at its normal boiling temperature (184 °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 than 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 depeding 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.

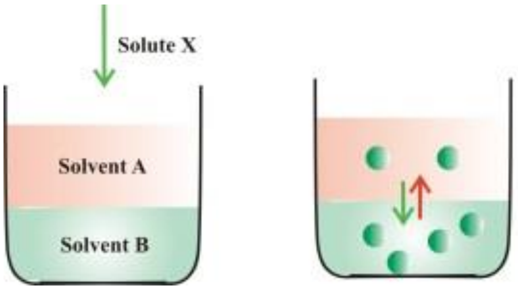


Figure 2.52 Skeptual diagram for the distribution of solute X in A and B solvents

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,

$$\frac{[\mathrm{X_A}]}{[\mathrm{X_B}]} = K_\mathrm{D}$$

The constant $\boldsymbol{K_\mathrm{D}}$ 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

$$\frac{[\mathrm{X_A}]}{[\mathrm{X_B}]} = \frac{S(\mathrm{X})_\mathrm{A}}{S(\mathrm{X})_\mathrm{B}} = K_\mathrm{D}$$

$S(\mathrm{X})_\mathrm{A}$ and $S(\mathrm{X})_\mathrm{B}$ are the solubilities of the solute in the two solvents. Hence knowing the value of the Distribution coefficient $\boldsymbol{K_\mathrm{D}}$ 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 $\mathrm{cm^3}$ of the benzene layer was found to contain 0.20 g of X and 100.00 $\mathrm{cm^3}$ of water layer cantained 0.40 g of X. X has its normal molecular weight in both solvents. Calculate the $\boldsymbol{K_D}$.

Answer

Concentration of X in benzene, $C_\mathrm{b} = \frac{0.20\ \mathrm{g}}{20.00\ \mathrm{cm^3}} = 1.0 \times 10^{-2}\ \mathrm{g\ cm^{-3}}$

Concentration of X in water, $C_\mathrm{w} = \frac{0.40\ \mathrm{g}}{100.00\ \mathrm{cm^3}} = 4.0 \times 10^{-3}\ \mathrm{g\ cm^{-3}}$

$$\therefore K_\mathrm{D} = \frac{C_\mathrm{b}}{C_\mathrm{w}} = \frac{1.0 \times 10^{-2}\ \mathrm{g\ cm^{-3}}}{4.0 \times 10^{-3}\ \mathrm{g\ cm^{-3}}} = 2.5$$

Note: *It is not necessary to find the concentration in mol dm*$^{-3}$ *always. As* K_D *is a dimentionless 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

$$K_D = \frac{C_{\mathrm{CCl_4}}}{C_{\mathrm{H_2O}}} = \frac{4.00\ \mathrm{g\ dm^{-3}}}{0.05\ \mathrm{g\ dm^{-3}}} = 80$$

$$\therefore \frac{(Solubility)_{\mathrm{CCl_4}}}{(Solubility)_{\mathrm{H_2O}}} = \frac{(Solubility)_{\mathrm{CCl_4}}}{0.40\ \mathrm{g\ dm^{-3}}} = 80$$

$$\therefore (Solubility)_{\mathrm{CCl_4}} = 32.00\ \mathrm{g\ dm^{-3}}$$

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.

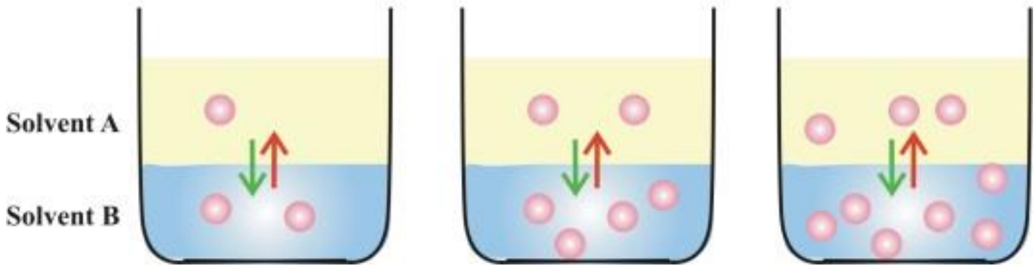


Figure 2.53 Distribution of X solute increases to keep the K_D constant at constant temperature

Thus we have,

$r_1 \alpha C_1$ and $r_2 \alpha C_2$

$\therefore r_1 = k_1 C_1$ and $r_2 = k_2 C_2$

k_1 and k_2 are rate constants.

At equilibrium,

$r_1 = r_2$ *therefore,* $k_1 C_1 = k_2 C_2$

$$\frac{C_1}{C_2} = \frac{k_2}{k_1} = K_D$$

Usually following conditions are necessary to apply this distribution law.

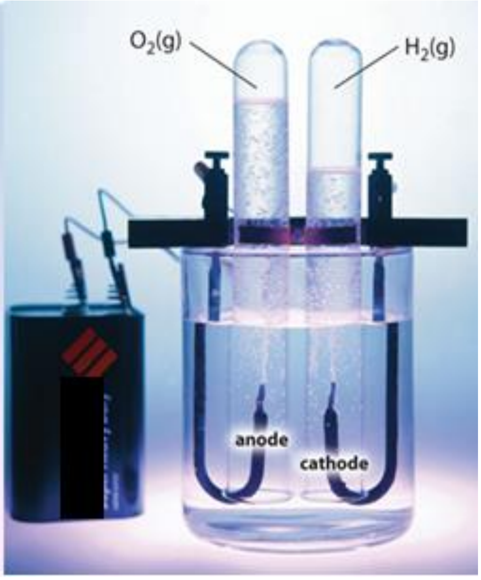
(i) Constant temperature: The temperature should be constant throughout the experiment.

(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 immiscibile.



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3. Electrochemistry

Content

Introduction

Electrochemistry, the study of the exchange between electrical and chemical energy, dealing with chemical reactions that produce electricity in which the energy released by a spontaneous reaction is converted to electricity and/ or electrical energy is used to cause a nonspontaneous reaction to occur. In these specific systems the reactions involve electron transfer, and so they are mainly a pair of reactions named oxidation-reduction (redox) reactions. An oxidation involves the loss of one or more electrons from a chemical species while a reduction involves the gain of one or more electrons by a chemical species. When an oxidation and a reduction are paired together in a redox reaction, electrons can flow from the oxidized species (the reducing agent or reductant) to the reduced species (the oxidizing agent or oxidant). That electron flow can either be spontaneously produced by the reaction and converted into electricity, as in a galvanic cell, or it can be imposed by an outside source to make a non-spontaneous reaction proceed, as in an electrolytic cell. The following descriptions on electrochemistry involve basics in redox reactions, galvanic cells, electrolytic cells, and the applications with electrolysis.

3.1 Conductivity

We encounter different materials in our day to day life such as paper, wood, glass, plastics, rubber, metals, and composite materials (i.e. mix of two different kind of materials). These materials have different properties thus differ in applications. One such important property is ability of a material to flow electricity through it. It is necessary to define a few terms before we consider the subject of conductance of electricity through electrolytic solutions. The electrical resistance is represented by the symbol *'R'* and it is measured in ohm (Ω) which in terms of SI base units is equal to (kg m^2). It can be measured with the help of a Wheatstone bridge. The electrical resistance of any object is directly proportional to its length, *l*, and inversely proportional to its area of cross section, *A*. That is,

$$R \propto l \quad \text{and} \quad R \propto \frac{1}{A}$$

Therefore, $$R \propto \frac{l}{A}$$

$$R = \rho \frac{l}{A}$$

The constant of proportionality, **ρ** (rho), is called **resistivity** (specific resistance). Its SI units are ohm metre (Ω m) and quite often, ohm centimetre (Ω cm) is also used. That is, physically, the resistivity for a substance is its resistance when it is one metre long and its area of cross section is one m^2. It can be seen that: 1 Ω m = 100 Ω cm.

The inverse of resistance, R, is called **conductance**, G, and we have the relation,

$$\textbf{Conductance } (\boldsymbol{G}) = \frac{\mathbf{1}}{\boldsymbol{R}}.$$

The SI unit of conductance is siemens, represented by the symbol ‘S’ and is equal to ohm^{-1} (also known as mho) or Ω^{-1}.

Further we can write,

$$\textbf{Conductance } (G) = \frac{1}{R} = \frac{A}{\rho\, l} = \kappa \frac{A}{l}$$

The inverse of resistivity, $\frac{1}{\rho} = \kappa$, called **conductivity** (specific conductance) is represented by the symbol, κ (Greek, kappa). The SI units of conductivity are S m^{-1} but quite often, κ is expressed in S cm^{-1}. Conductivity of a material in S m^{-1} is its conductance when it is 1 m long and its area of cross section is 1 m^2. It may be noted that 1 S cm^{-1} = 100 S m^{-1}. These definitions can be depicted by Figure 3.1 as given below.

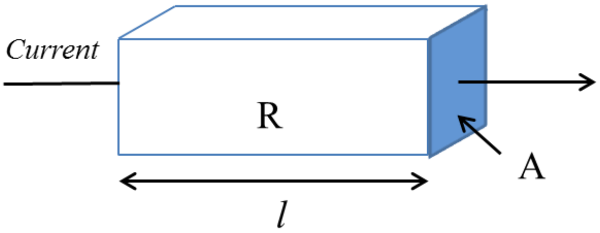


Figure 3.1 Resistance and resistivity

Conductivity and resistivity are constant for a particular substance (metal or an ionic solution with known concentration). However, it is important to provide the temperature at which conductivity or resistivity was measured as it varies with the temperature. In general, about 2% change in conductivity per one degree Celsius is observed for solutions.

Electricity can be conducted through materials (such as metals) as a flow of electrons in the metal. Such materials are known as **electrical conductors**. Electricity can also be conducted as a flow of ions in a solution or molten ionic compound. These are called **ionic conductors**. So, to conduct electricity through materials, it is essential to present electrons (or holes) which can move or ions in solid or liquid state when an electric field is applied.

Solutions can be categorized as **strong electrolytes, weak electrolytes and non-electrolytes (insulators)**. If a particular substance is fully ionized in solution, such as ionic solids and strong acids/ bases, it is called a **strong electrolyte**. Such solutions have concentration of ions proportional to the concentration of strong electrolytes used. Examples for strong electrolytes are aqueous solutions of NaCl, KNO_3, HCl. In the case where electrolytes added are partially ionized in aqueous solution, these are called **weak electrolytes**. Weak aqueous Bronsted acids and bases such as CH_3COOH, NH_3, H_2O are examples for weak electrolytes. The other extreme of electrolytes are the substances which do not produce ions in aqueous media. These are called ***non-electrolytes*** or insulators and these do not conduct electricity. Non polar organic compounds such as Benzene (C_6H_6) and Kerosene are examples for such non-electrolytes.

The conductivity and resistivity of an electrolyte solution can be measured using two oppositely charged metal electrodes placed in an imaginary cuboid shaped portion of a solution with dimensions, length (*l*) and area of cross section(A) as shown in Figure 3.2.

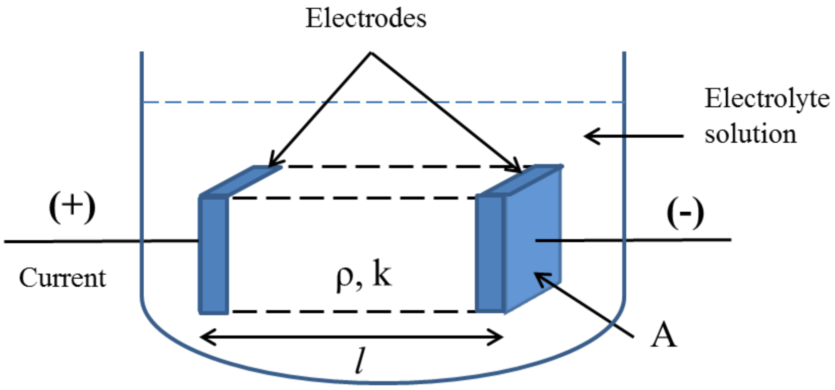


Figure 3.2 Conductivity and resistivity through a solution of electrolytes

3.1.1 Factors affecting conductivity of a solution

There are several factors which affect the conductivity of a solution. These are: **nature of the solute, concentration of the solute, and the temperature of the solution**. All of these factors affect conductivity because mobility of charge carriers is dependent on the above factors and as a result conductivity is dependent on the mobility of charge carriers.

The nature of the species plays important role as it determines presence of ions or mobile charge carriers. Aqueous solutions of strong electrolytes (e.g.: KCl, NaCl) can conduct electricity as these species produce ions due to complete dissociation. However, in the solid state these strong electrolytes do not conduct electricity due to absence of ions. If such a solid electrolyte is brought to the molten state, such as NaCl(l) then ions gain mobility thus conduct electricity. On the other hand, weak acids and bases are also able to conduct electricity as these will react with water to produce ionic species through partial dissociation.

Example 3.1

Which of the following substances once dissolved in water will conduct electricity?

(a) table salt (b) glucose (c) vinegar

Answer

(a) Chemical formula of table salt is NaCl. It is an electrolyte which fully dissolves in water to produce Na^+ and Cl^- ions. Since table salt is a substance that produces ions in water, it is capable of conducting electricity.

(b) Glucose is an organic compound with formula $C_6H_{12}O_6$. When glucose is dissolved in water it will not produce any ionic species. Therefore, a glucose solution cannot conduct electricity.

(c) Vinegar is mostly consists of acetic acid, CH_3COOH. Acetic acid is a weak acid which partially dissociates in water to produce H_3O^+ and CH_3COO^- ions. As a result vinegar solution is able to conduct electricity due to presence of ions.

Another important factor that affects the conductivity of a solution is concentration. When the concentration of dilute aqueous solution is decreased, the conductivity is also decreased. This is due to decreased amount and interactions of ions upon dilution. The Table 3.1 illustrates the effect of concentration on conductivity.

Table 3.1 Conductivities of various water samples and solutions at 298 K

Sample	Conductivity / µS cm^{-1}
Distilled water	1 – 2
0.01 mol dm^{-3} KCl solution	1,480
0.10 mol dm^{-3} KCl solution	12,400
1.0 mol dm^{-3} KCl solution	110,000
Well water	100 – 200
Pipe borne water	50 – 150
Sea water	40,000

µS: micro seimans

The temperature of the solution has a considerable influence on the conductivity values measured. When the temperature is increased, conductivity of the solution is also increased at a given concentration due to enhanced speed of ions. This effect is clearly demonstrated in the Table 3.2 below.

Table 3.2 Conductivities of KCl(aq) and solutions at different temperatures

Concentration / mol dm^{-3}	Conductivity / µS cm^{-1}		
	0 °C	13 °C	25 °C
1.00 KCl solution	6.5×10^4	9.8×10^4	1.1×10^5
0.10 KCl solution	7.2×10^3	1.1×10^4	1.3×10^4
0.01 KCl solution	7.8×10^2	1.2×10^3	1.4×10^3

Current carried by an ion at a given temperature and an electric field depends on the concentration of ions and their speed. The speed of an ion depends on it's charge, size, and potential gradient of the applied electric field. According to Table 3.3, H^+ and OH^- ions have the highest speeds due to relatively small size. Thus, these ions are major contributors for the conductance of an aqueous solution.

Table 3.3 Speeds of ions in an aqueous solution under the potential gradient 1 V cm^{-1} at 298 K

Ion	Speed/ mm min^{-1}	Ion	Speed/ mm min^{-1}
H^+	2.05	NO_3^-	0.40
OH^-	1.12	Cl^-	0.42
Na^+	0.29	SO_4^{2-}	0.88
K^+	0.42	Ca^{2+}	0.67

Conductivity of a solution plays an important role when analyzing ionic content of a water sample. In practice, conductivity meters are used to measure the conductivity of a solution. Such measurements can be used in evaluating salinity, calculating solubility products, and in many other applications.

3.2 Electrodes in equilibrium

3.2.1 Metal – metal ion electrode

Before discussing details about this *electrode equilibrium* it may be worth understanding the behaviour of reactivity of metals in solutions as that would be the basic concept of building up an electrode.

As we know, when metals react, they give away electrons and form positive ions. For example, $Mg^{2+}(aq)$, $Zn^{2+}(aq)$ or $Cu^{2+}(aq)$ ions are formed when the respective metals react in aqueous solutions of their ions and form positive and negative charges as shown by the following reaction.

$$Mg(s) \rightarrow Mg^{2+}(aq) + 2e$$

This occurs as follows; once a piece of solid magnesium is dipped in a beaker of Mg^{2+} solution there will be some tendency for the magnesium atoms to remove electrons and go into solution as Mg^{2+}(aq) ions. The electrons will be left behind on the magnesium as depicted in the Figure 3.3.

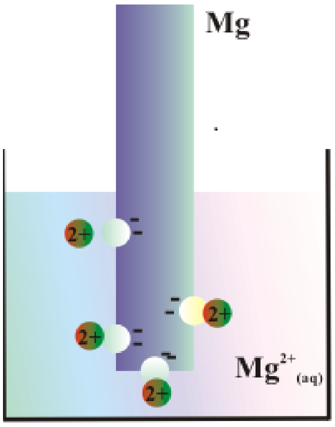


Figure 3.3 Behaviour of Mg metal in an aqueous solution of Mg^{2+}(aq) ions

Once the Mg rod is dipped in Mg^{2+} solution, there will be a quick build-up of electrons on the magnesium, and it will be surrounded in the solution by a layer of positive Mg^{2+} ions. These will tend to stay close because they are attracted to the negative charge on the piece of metal. Some of them will be attracted enough that they will reclaim their electrons and stick back on to the piece of metal. A dynamic equilibrium will be established when the rate at which ions are leaving the surface is exactly equal to the rate at which they are joining it again. At that point there will be a constant negative charge on the magnesium rod and a constant number of Mg^{2+}(aq) ions surround the rode. This dynamic equilibrium is shown in Figure 3.4 in which the negative charge on the Mg rod is balanced by the positive charges surrounded by it in the solution. Once this situation is achieved, we consider and define such a system as an electrode.

A system where a metal is in dynamic equilibrium with its ions can be defined as an ***electrode****.*

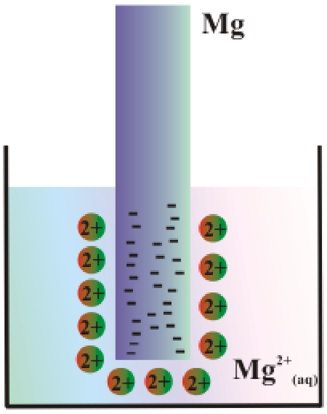


Figure 3.4 Behaviour of Mg metal in an aqueous solution at dynamic equilibrium

As with the above descriptions it is notable that the equilibrium exists in two ways; in one direction Mg solid is converted to $Mg^{2+}(aq)$ ions while in the other direction $Mg^{2+}(aq)$ ions in the solution are converted to Mg metal. In other words, Mg oxidizes in one direction and $Mg^{2+}(aq)$ reduces in the other direction indicating that the overall system exhibits an oxidation-reduction couple.

Accordingly, we can get the idea that a charge separation occurs at the interface between metal and the solution/water. The tendency of this charge separation depends on the activity of metal. For example if we use a rod of Cu metal, the charge separation will be less compared to that of Mg. This relates the activity of metals described in electrochemistry (detailed discussion of this will appear in a later section).

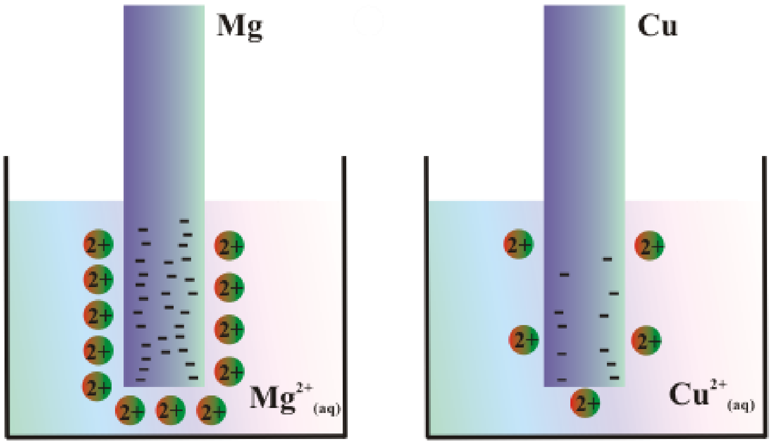


Figure 3.5 Behaviour of Mg and Cu metals in an aqueous solutions at dynamic equilibrium. As Cu is less reactive than Mg, Cu forms its Cu^{2+} ions less readily.

In general any ions which do break away are more likely to reclaim their electrons and stick back on to the metal again. The equilibrium position can still reachable, but there will be less charge on the metal, and fewer metal ions in solution as compared in Figure 3.5.

Once systems are in dynamic equilibrium, two reactions can be written as given below and it will also be possible to compare the positions of equilibrium of the two systems.

$$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s) \quad \ldots\ldots\ldots\ldots (1)$$

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s) \quad \ldots\ldots\ldots\ldots\ldots (2)$$

According to Figure 3.5, the position of the equilibrium (1) is further to the left than that of the equilibrium (2).

It has to be noted the way that the two equilibria are written. By convention, all these equilibria are usually written with the electrons on the left-hand side of the equation that is as a reduction reaction.

As the position of equilibrium is different in the above two cases, the ability to reach the equilibrium may be expressed by introducing some numbers and that can be directly related to the term **electrode potential** which is simply an attempt to attach some numbers to these differing positions of equilibria. In principle, that is quite easy to do. In the case of magnesium, there is a large difference between the negativeness of the metal and the positiveness of the solution around it. In the copper case, the difference is much less and this can be used to understand the potential which arises due to the charge separation at the interface of the particular electrode.

This **potential difference** can be recorded as a voltage meaning that the bigger the difference between the positiveness and the negativeness, the bigger the voltage. Unfortunately, that voltage is impossible to measure by connecting a device to the above mentioned systems.

Even though, it would be easy to connect a voltmeter to the piece of metal, the problem is how a connection is made to the solution. If any probe is put into the solution a similar sort of equilibrium would happen around it. Therefore, the best measure would be some sort of combination of the effects at the probe and the piece of metal of interest.

That means, it is not required to measure the absolute voltage between the metal and the solution. It is enough to compare the voltage with a standardized system called a **reference electrode** and the system used is called a *standard hydrogen electrode (SHE)* which is shown in Figure 3.6.

As we know from the unit 12 (Equilibrium), the position of any equilibrium can be changed by changing conditions. That means the conditions must be standardized so that you can make fair comparisons.

In the standard hydrogen electrode the following conditions are used: 101325 Pa ~100 kPa, 1 atm pressure of hydrogen gas, the temperature of 298 K (25 °C) and 1.0 mol dm^{-3} concentration of the hydrogen ions in the solution.

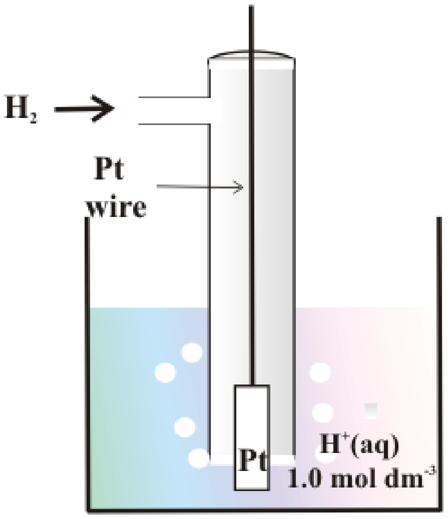


Figure 3.6 The standard hydrogen electrode

In this electrode, as the hydrogen gas flows over the porous platinum, an equilibrium is established between hydrogen molecules and hydrogen ions in solution which is catalyzed by platinum.

$$2H^+(aq) + 2e \rightleftharpoons H_2(g)$$

Now let us see how we would measure the potential of a given electrode. In this measurement, the standard hydrogen electrode is attached to the electrode system for example, a piece of magnesium in a solution containing magnesium ions as considered earlier; a conducting Pt wire is introduced to connect the voltmeter and a salt bridge is introduced as shown in Figure 3.7.

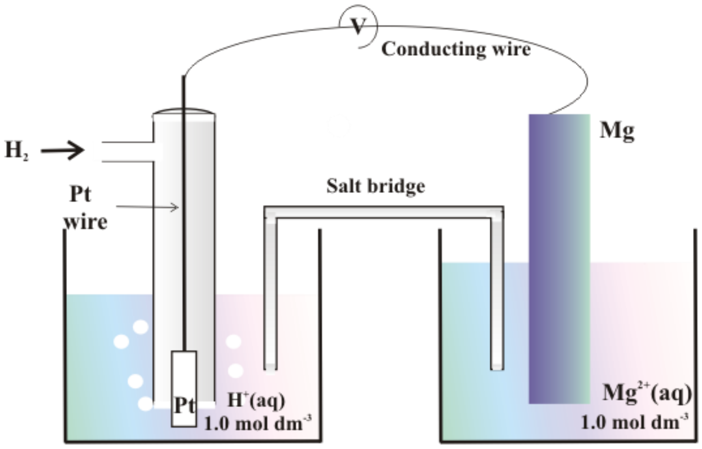


Figure 3.7 Measurement of electrode potential using the standard hydrogen electrode

The salt bridge is introduced to complete the electrical circuit making a liquid junction. It is just a glass tube filled with a solution of an electrolyte like potassium nitrate. The ends are "stoppered" by bits of cotton wool or sometimes with agar gel to prevent mixing of the contents in the salt bridge with the contents of the two beakers. Each electrode on one side is defined as a *half-cell*.

It has to be noted that the electrolyte in the salt bridge is chosen so that it doesn't react with the contents of either beaker.

Once the two electrodes are connected two equilibria are set up on the two electrodes as follows.

$$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$$

$$2H^{+}(aq) + 2e \rightleftharpoons H_2(g)$$

Magnesium has a much higher ability to form its ions than hydrogen does. Therefore, position of the Mg/Mg^{2+} equilibrium will be more to the left than that of the H_2/H^{+} equilibrium. This means that there is a much greater build-up of electrons on the piece of magnesium than on platinum. Therefore, there is a major difference between the charges on the two electrodes and hence a potential difference which can be measured with a voltmeter.

The value of potential mentioned above for $Mg^{2+}(aq) / Mg(s)$ is actually the standard electrode potential of the $Mg^{2+}(aq) / Mg(s)$ system.

The potential difference measured when a metal / metal ion electrode is coupled to a hydrogen electrode under standard conditions is known as the standard electrode potential of that metal / metal ion combination. This means that each $E°$ value shows whether the position of the equilibrium lies to the left or right of the hydrogen equilibrium. The difference in the positions of equilibrium causes the number of electrons built up on the metal electrode and the platinum of the hydrogen electrode to be different. Here, as a convention the number of electrons produced on the Pt surface is considered to be negligible. The standard cell potential $E^{\mathbf{0}}$ of the standard hydrogen electrode is taken as 0.00 V at room temperature. The potential difference produced is measured as a voltage having units of volts (V).

As we know that magnesium has the greater amount of negativeness, the voltage measured would be 2.37 V and the voltmeter would show magnesium as the negative electrode and the hydrogen electrode as positive. Therefore, the standard electrode potential of the $Mg^{2+}(aq)/ Mg(s)$ electrode is recorded as $E^{0} = -2.37$ V.

In the case when a similar measurement is done with the $Cu^{2+}(aq)/ Cu(s)$ electrode, copper forms its ions less readily than hydrogen does.

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$$

$$2H^{+}(aq) + 2e \rightleftharpoons H_2(g)$$

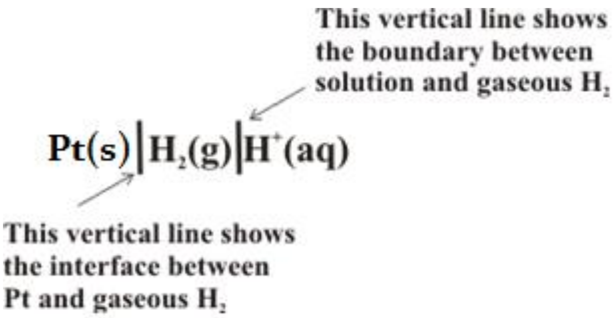
Therefore, the equilibrium in the hydrogen electrode lies further to the left. As a result there will be less build-up of electrons on copper than that is on the platinum of the hydrogen electrode. Therefore, there is less difference between the electrical charges on the two electrodes, so the voltage measured will be less (only +0.34 volts).

The other major change is that this time the copper is the more positive (less negative) electrode. The voltmeter will show the hydrogen electrode as the negative electrode and the copper electrode as the positive electrode and hence the electrode potential is recorded as + 0.34 V.

(If any current flows, the voltage measured drops. In order to make proper comparisons, it is important to measure the maximum possible voltage in any situation. This is called the ***electromotive force*** *or* ***e.m.f****. Details of this will be discussed in coming sections).*

Electrode notations

The hydrogen electrode is represented as below.



This vertical line shows the boundary between solution and gaseous H_2

This vertical line shows the interface between Pt and gaseous H_2

From the above descriptions we know that the standard electrode potential of a metal / metal ion combination is the potential difference measured when that metal / metal ion electrode is coupled to a hydrogen electrode under the standard conditions.

The measurement of electrode potentials allows us to determine the position of the metal/ metal ion equilibrium with respect to the equilibrium involving hydrogen.

A few typical standard electrode potentials are shown in the table below.

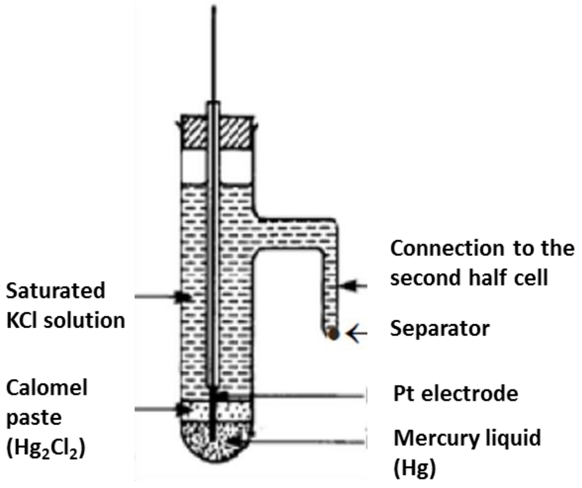
Metal / metal ion combination	*E*°/ V
Mg^{2+}(aq)/ Mg(s)	-2.37
Zn^{2+}(aq)/ Zn(s)	-0.76
Cu^{2+}(aq)/ Cu(s)	+0.34
Ag^{+}(aq)/ Ag(s)	+0.80

Comparing these with the *E*° values, it can be seen that the ones whose positions of equilibrium lie furthest to the left have the most negative *E*° values. That is because they form ions more readily leaving more electrons behind on the metal. Those which don't release electrons readily have positions of equilibrium further to the right. Their *E*° values get progressively more positive.

In addition to these metal-metal ion electrodes, there are other types of electrodes as discussed below.

3.2.2 Metal – insoluble salt electrode

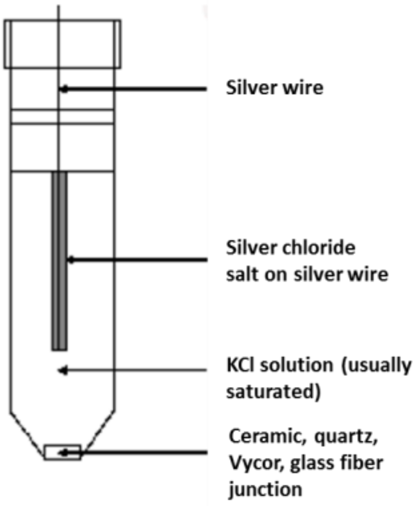
In order to define an electrode it is necessary to have oxidized and reduced species of the same element to be present. Accordingly, if a metal is in contact with the solid salt of the same metal, such electrodes are called **metal – insoluble salt type**. Examples for such electrodes are calomel electrode and silver-silver chloride electrode. Figure 3.8 shows details of the calomel electrode. A Pt wire is used to establish the electrical connection with an external circuit. A saturated solution of KCl is used for the electrical conductance.



$$Hg_2Cl_2(s) + 2e \longrightarrow 2Hg(l) + 2Cl^-(aq)$$

Figure 3.8 Calomel electrode

Silver – silver chloride is another example for metal-insoluble salt type of an electrode. The essential components of this electrode comprise a silver wire coated with AgCl which is in contact with the KCl electrolyte. An important part of silver – silver chloride electrode is the tip (ceramic, quartz, vycor tip, glass fibre) that connects electrode with the external solution. Figure 3.9 illustrates silver-silver chloride electrode.



$$AgCl(s) + e \longrightarrow Ag(s) + Cl^{-}(aq)$$

Figure 3.9 Silver – silver chloride electrode

In general, calomel electrode and silver – silver chloride electrode are also known as **reference electrodes** as potential of these electrodes remains almost constant during experiment time.

3.2.3 Gas electrodes

Hydrogen electrode

Standard Hydrogen Electrode is an example for a gas electrode. The standard conditions used here are 1.0 mol dm^{-3} H^{+} ion concentration, 1 atm pressure for H_2 gas, and temperature of the system is at 298 K. This hydrogen electrode is called the **standard electrode** as the potential of this electrode is defined as 0.00 V as described earlier.

$$2H^{+}_{(aq)} + 2e \rightleftharpoons H_2(g)$$

Chlorine electrode

Chlorine is well known as an oxidizing agent. Since the electrochemical series is about ranking substances according to their oxidizing or reducing ability, it makes some insights to the electrode reactions with gases like chlorine. Again, as has been done above, we can measure the position of this equilibrium relative to the hydrogen equilibrium.

$$Cl_2(g) + 2e \rightleftharpoons 2Cl^{-}(aq)$$

Note that as usual, the equilibrium is still written with the electrons on the left-hand side of the equation. That's why the chlorine gas has to appear on the left-hand side rather than on the right indicating the reduction during the reaction. For this chlorine electrode, a half-cell can be built as similar to the hydrogen electrode by bubbling chlorine gas over a platinum electrode, which is immersed in a solution containing chloride ions with a concentration of 1.0 mol dm^{-3}.

The notation of writing the cell looks like this.

$$Pt(s)|Cl_2(g)\ |\ Cl^-(aq)$$

It can be noted that the chloride ions are losing electrons and hence the cell has a positive potential difference.

3.2.4 Redox electrodes

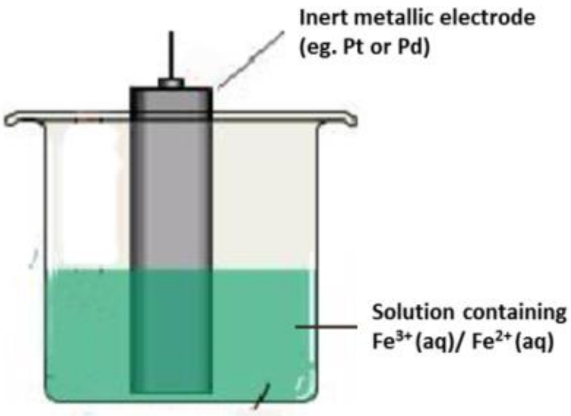
These types of electrodes are frequently observed in redox reactions. Both oxidized and the reduced species must be present in the solution when defining a particular redox electrode. A Pt wire can be used to establish the electrical connection with the external circuit. Such a redox type of electrode is given in Figure 3.10.

Fe^{2+}/ Fe^{3+} redox electrode system

Iron(II) ions can easily be oxidized to iron(III) ions, and iron(III) ions are fairly easily reduced to iron(II) ions. The equilibrium for this can be written as follows.

$$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$$

To measure the redox potential of this, a platinum electrode can be inserted into a beaker containing a solution of both iron(II) and iron(III) ions (1.0 mol dm^{-3} with respect to each), and couple this to a hydrogen electrode.



$$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$$

Figure 3.10 The Fe^{2+}/ Fe^{3+} redox electrode system

- When writing electrode in standard notation, phase boundaries are separated by a vertical line “|”

  E,g. Gas electrodes: $Pt(s)\vert O_2(g)\vert OH^-(aq)$
- Physical states must be included next to each chemical species and conditions should be included where possible.

  E.g. Redox electrodes: $Pt(s)\vert Fe^{2+}(aq,1\ mol/dm^3),\ Fe^{3+}(aq,1\ mol/dm^3)$

The following table summarizes the types of different electrodes with some examples.

Table 3.4 Summary of different types of electrodes

Type of electrode	Standard notation	Redox couple	Reduction half reaction
Metal – metal ion	**$M(s)\vert M^{n+}(aq)$**	**$M(s)/M^{n+}(aq)$**	**$M^{n+}(aq) + ne \rightarrow M(s)$**
	$Zn(s)\vert Zn^{2+}(aq)$	$Zn(s)/Zn^{2+}(aq)$	$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$
Metal – insoluble salt	**$M(s)\vert MX_n(s)\vert X^-(aq)$**	**$M(s)/MX_n(s)$**	**$MX(s) + ne \rightarrow nM(s) + X^-\ (aq)$**
	$Ag(s)\vert AgCl(s)\vert Cl^-(aq)$	$Ag(s)/Ag^+(aq)$	$AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$
	$Pt(s)\vert Hg(l)\vert Hg_2Cl_2(s)\vert Cl^-(aq)$	$Hg(l)/Hg_2Cl_2(s)$	$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$
Gas	**$Pt(s)\vert X_2(g)\vert X^+(aq)$**	**$X_2(g)/X^+(aq)$**	**$X^+(aq) + e \rightarrow \frac{1}{2}X_2(g)$**
	$Pt(s)\ \vert X_2(g)\ \vert X^-(aq)$	$X^-(aq)/X_2(g)$	$\frac{1}{2}X_2(g) + e \rightarrow X^-(aq)$
	$Pt(s)\vert H_2(g)\vert H^+(aq)$	$H_2(g)/H^+(aq)$	$H^+(aq) + e \rightarrow \frac{1}{2}H_2(g)$
	$Pt(s)\vert O_2(g)\vert OH^-(aq)$	$OH^-(aq)/O_2(g)\vert$	$2O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^-(aq)$
Redox	**$Pt(s)\vert M^+(aq),M^{2+}(aq)$**	**$M^+(aq)/M^{2+}(aq)$**	**$M^{2+}(aq) + e \rightarrow M^+(aq)$**
	$Pt(s)\vert Sn^{2+}(aq),Sn^{4+}(aq)$	$Sn^{2+}(aq)/Sn^{4+}(aq)$	$Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq)$

Note: *When writing any electrode reaction, a single arrow is used when there is a current passing through (not in equilibrium) and an equilibrium arrow is used when the electrode is isolated. Also, it is compulsory to mention the physical state of the chemical species whenever electrode reactions are written.*

As indicated in above examples it is necessary to note that the electrode potentials of half-cells are given as redox potentials (the potential of the redox reaction).

Therefore, by arranging various redox equilibria in the order of their standard electrode potentials (redox potentials) we can build up the **electrochemical series**. The most negative $E°$ values are placed at the top of the electrochemical series, and the most positive at the bottom as summarized in Table 3.5.

Table 3.5 Standard reduction potentials of selected electrodes at 298K

Reduction half reaction	**Standard reduction potential (E^{Θ} / V)**
$Li^+(aq) + e \rightarrow Li(s)$	-3.05
$K^+(aq) + e \rightarrow K(s)$	-2.93
$Ca^{2+}(aq) + 2e \rightarrow Ca(s)$	-2.87
$Na^+(aq) + e \rightarrow Na(s)$	-2.71
$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$	-2.36
$Al^{3+}(aq) + 3e \rightarrow Al(s)$	-1.66
$Mn^{2+}(aq) + 2e \rightarrow Mn(s)$	-1.18
$2H_2O\ (l) + 2e \rightarrow H_2\ (g) + 2OH^-\ (aq)$	-0.83
$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$	-0.76
$Fe^{2+}(aq) + 2e \rightarrow Fe(s)$	-0.44
$Ni^{2+}(aq) + 2e \rightarrow Ni(s)$	-0.23
$Sn^{2+}(aq) + 2e \rightarrow Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e \rightarrow Pb(s)$	-0.13
$H^+(aq) + e \rightarrow 1/2H_2(g)$	**0.0**
$Sn^{4+}(aq) + 2e \rightarrow Sn^{2+}(aq)$	+0.15
$AgCl(s) + e \rightarrow Ag(s) + Cl^-(aq)$	+0.22
$Hg_2Cl_2(s) + 2e \rightarrow 2Hg(l) + 2Cl^-(aq)$	+0.27
$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	+0.34
$O_2(g) + 2H_2O(l) + 4e \rightarrow 4OH^-(aq)$	+0.40
$I_2(s) + 2e \rightarrow 2I^-\ (aq)$	+0.54
$Fe^{3+}(aq) + e \rightarrow Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e \rightarrow Ag(s)$	+0.80
$Br_2(l) + 2e \rightarrow 2Br^-(aq)$	+1.09
$O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l)$	+1.23
$Cl_2(g) + 2e \rightarrow 2Cl^-(aq)$	+1.36
$Au^{3+}(aq) + 3e \rightarrow Au(s)$	+1.40
$S_2O_8^{2-}(aq) + 2e \rightarrow 2SO_4^{2-}(aq)$	+2.05
$F_2(g) + 2e \rightarrow 2F^-(aq)$	+2.87

Reducing agents and oxidizing agents

As we know, a **reducing agent** reduces some other chemical species. That means that a **reducing agent** gives electrons to another chemical species. Conversely, an **oxidizing agent** oxidizes something else by accepting electrons.

According to the above electrochemical series, magnesium is good at giving away electrons to form its ions. Hence Magnesium is a good reducing agent. On the other hand, copper doesn't form its ions very readily, and its ions easily pick up electrons to convert to metallic copper. Hence, copper(II) ions must be a good as an oxidizing agent.

It is with this idea we notice that the metals at the top of the series (with negative standard electrode potential) are good at giving away electrons hence act as good reducing agents. The reducing ability of the metal increases going up the series.

Metal ions at the bottom of the series are good at picking up electrons. These are good oxidizing agents. The oxidizing ability of the metal ions increases down the series.

In other words, the more negative the $E°$ value, the position of the equilibrium to the left and the tendency of the metal to lose electrons. Therefore, the more negative the value, a particular species is stronger reducing agent. The situation is opposite for the species at the bottom of the electrochemical series as these are good oxidizing agents. Therefore, metals such as Na, Mg, Zn, etc. with negative reduction potential prefer to be in ionic state rather elemental state and shows higher reactivity. The opposite is true for the species listed below the potential of standard hydrogen electrode. When two metals are in contact, metals with higher negative standard potential prefer to be in ionic state, thus can be used to reduce ions of the other metal in contact.

3.3 Electrochemical cells

3.3.1 Construction of an electrochemical cell

So far we have considered combinations of a hydrogen electrode with the different electrodes as we measure standard reduction potential. It is interesting to consider what happens if a zinc half-cell is combined with a copper half-cell through a voltmeter and the solutions are connected via a salt bridge as shown in Figure 3.11.

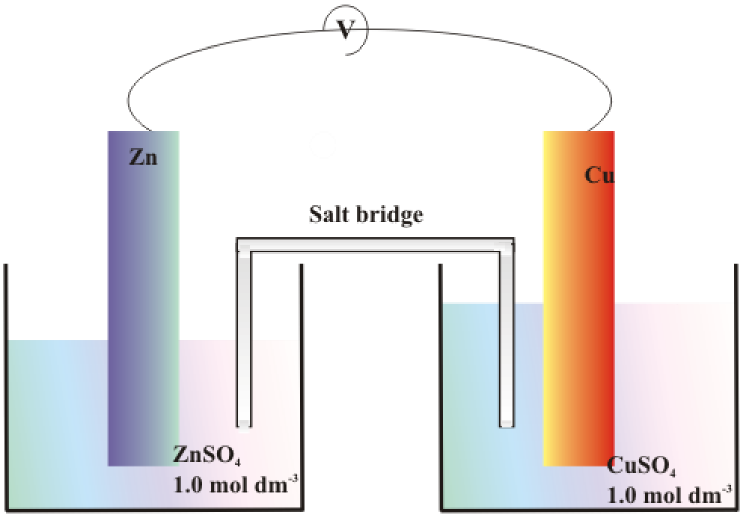


Figure 3.11 An electrochemical cell prepared by connecting two half-cells of Zn and Cu

This type of set up is defined as an **electrochemical cell** which **consists of two electrodes in contact with an electrolyte**. In an electrochemical cell, there can be a common electrolyte or may be in different electrolytes. In the latter case, electrodes in two different electrolytes are connected via a salt bridge. The potential generated due to presence of two different electrolytes in the electrode compartments is called “liquid junction potential”. However, this potential can be minimized if two electrolytes are joined using a salt bridge. A salt bridge is essentially a medium consisting of an electrolyte such as KCl or KNO_3 which is jellified with agar in an inverted “U” shaped tube. The two ends of liquid junction are dipped in respective electrode units. This liquid junction can also be made by a permeable membrane/ diaphragm/ porous partitioning which allows ions to pass through it.

The two equilibria which are set up in the above half cells are as follows.

$$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s) \qquad E^0 = -0.76\ V$$

$$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s) \qquad E^0 = +0.34\ V$$

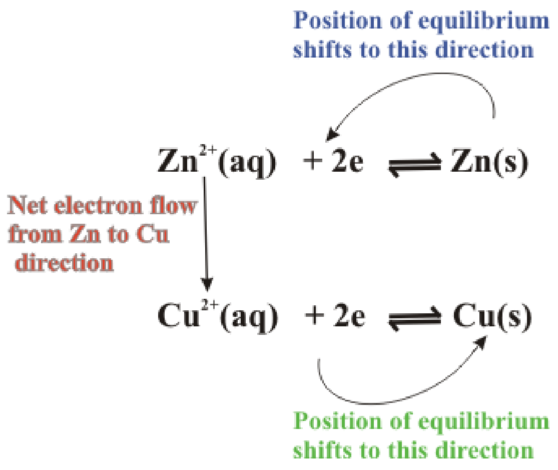
The negative sign of the $E°$ value for zinc shows that it releases electrons more readily than hydrogen does. The positive sign of the copper $E°$ for copper shows that it releases electrons less readily than hydrogen.

This allows us to compare the two electrode equilibria directly. The position of the zinc equilibrium lies further to the left than the copper equilibrium. Therefore, the voltmeter will show that the zinc as the negative electrode and copper is the (relatively) positive one. It will indicate a voltage showing the difference between them.

Usually the high resistivity voltmeter is used stop any current flow in the circuit. If the circuit is constructed without a voltmeter but two half-cells still connected, then electrons will flow from where there are lot of them (on zinc) to where there are fewer (on copper). The movement of the electrons is thus an electrical current. At this situation the equilibrium is disturbed, hence we may apply Le Chatelier's Principle to understand the changes in the system due to current flow. Here following two opposing effects are noticed.

On one side, electrons are flowing away from the zinc equilibrium, according to Le Chatelier's principle; the position of equilibrium will move to replace the lost electrons.

On the other side of copper, electrons are added onto the piece of copper in the copper equilibrium. According to Le Chatelier's Principle, the position of equilibrium will move to remove these extra electrons. As a result, the changes occur as shown in the following sketch and can be illustrated by Figure 3.12.



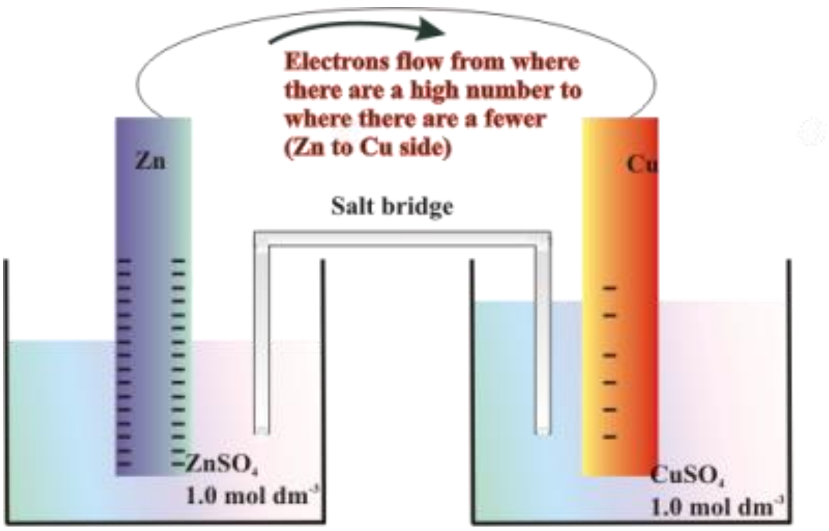


Figure 3.12 A Galvanic cell prepared by combining two half-cells of Zn and Cu without a voltmeter

In the above system, if electrons continue to flow from Zn side to Cu side, the positions of equilibrium keeps on shifting. Therefore, the two equilibria essentially turn into two one-direction (side) reactions. The zinc continues to ionize, and the copper(II) ions keep on collecting up electrons and the two reactions can be written as follows.

$$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$$

$$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$$

Therefore, on the whole we can see that there is a **net chemical reaction going on** in which zinc is going into solution as zinc ions, and is giving electrons to copper(II) ions to turn them into metallic copper. The overall reaction can be obtained by adding the above two reactions which are called half-cell reactions.

In the above, it is seen that the current is produced in the cell due to the occurrence of a spontaneous chemical reaction. Therefore, it is possible to categorize electrochemical cells into two types. If the cell is able to produce electricity through a spontaneous reaction, then it is called a **galvanic cell** or a **voltaic cell**. If the reaction is not spontaneous then an external source of current is required to operate the cell. Such a cell is called an **electrolytic cell.**

In a galvanic cell, oxidation and reduction reactions are responsible for the operation of the cell. When the cell is in operation, electrons released at one electrode due to oxidation travels to the other electrode resulting in reduction of the chemical species in that compartment. The electrode at which *oxidation* takes place is called the **anode** and the electrode at which *reduction* takes place is called the **cathode**. The overall cell reaction is obtained as combination of reduction and oxidation half reactions. Therefore, for the galvanic cell consisting of Zn and Cu electrodes which is named as Daniel cell, the overall reaction is given by the sum of the two half reactions.

Cathode (reduction half reaction): $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ (Right hand side electrode, RHE)

Anode (oxidation half reaction) : $\underline{Zn(s) \rightarrow Zn^{2+}(aq) + 2e}$ (Left hand side electrode, LHE)

Cell reaction : $\mathbf{Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)}$

It has to be noted that, if an external opposite potential is applied to the galvanic cell described above and increased slowly, we find that the reaction continues to take place till the opposing voltage reaches the value 1.1 V at which the reaction stops altogether and no current flows through the cell. Any further increase in the external potential again starts the reaction but in the opposite direction ($\mathbf{Cu(s) + Zn^{2+}(aq) \rightarrow Cu^{2+}(aq) + Zn(s)}$).

It now functions as an **electrolytic cell**, a device which uses electrical energy to carry non-spontaneous chemical reactions. Here, it is important to pay attention to the voltage of 1.1 V stated above and how it arises for the presently considered Daniel cell. This can be understood as follows.

The oxidation and reduction half reactions occur in two different parts of the Daniell cell. The reduction half reaction occurs at the copper electrode while the oxidation half reaction occurs at the zinc electrode. These two portions of the cell are also called **half-cells** or **redox couples** as mentioned earlier. The copper electrode may be called the reduction half-cell and the zinc electrode, the oxidation half-cell.

In a galvanic cell, the half-cell in which oxidation takes place (**anode)** has a **negative potential** with respect to the solution. The other half-cell in which reduction taking place (**cathode)** has a **positive potential** with respect to the solution. Thus, there exists a potential difference between the two electrodes and as soon as the switch is in the *on* position the electrons flow from negative electrode to positive electrode. The direction of current flow is opposite to that of the electron flow. The potential difference between the two electrodes of a galvanic cell is called the *cell potential* and is measured in volts. The ***cell potential*** is the difference between the electrode potentials (reduction potentials) of the cathode and anode. It is called the *cell* **electromotive force (emf)** of the cell *when no current is drawn through the cell*. It is now an accepted convention that we keep the anode on the left and the cathode on the right while representing a galvanic cell. If there is an electrochemical cell where two electrodes are in two different electrolyte solution, there is an additional potential difference arise across the boundary. This is termed as "***liquid junction potential***". The contribution of liquid junction potential can be minimized using a salt bridge to join two electrolyte solutions.

A Galvanic cell is generally represented by putting a vertical line between metal and electrolyte solution and putting a double vertical line between the two electrolytes connected by a salt bridge. Following points are important in writing the **cell notation.**

- *Electrode corresponding to the oxidation half reaction in a cell is always written on the left hand side and electrode where reduction half reaction take place is written on the right hand side.*
- *Phase boundaries are represented by a vertical bar "|"*
- *If there is a liquid junction potential present then a " ⁝ " is used between two electrodes*
- *If there is a salt bridge (i.e. no liquid junction potential), two electrodes are separated by a double vertical bars "||"*
- *Indication of the physical state is compulsory for all species and indication of conditions such as concentration, pressure, temperature must be in cooperated if known.*

According to the cell notation, the Daniel cell above can be written as,

$$Zn(s)|Zn^{2+}(aq,\ 1.0\ mol\ dm^{-3}))||Cu^{2+}(aq,\ 1.0\ mol\ dm^{-3})|Cu(s)$$

Other examples are:

$$Mg(s)|\ Mg^{2+}(aq,\ 1.0\ mol\ dm^{-3})\ ||\ H^{+}(aq,\ 1.0\ mol\ dm^{-3})\ |\ H_2(g)\ |Pt(s)$$

$$Pt(s)|H_2(g)\ |H^{+}(aq)\ ||\ Cl^{-}(aq)\ |Cl_2(g)\ |Pt(s)$$

When a common electrolyte HCl is used for both electrodes,

$$Pt(s)|H_2(g)\ |H^{+}(aq),\ Cl^{-}(aq)\ |AgCl(s)\ |Ag(s)$$

Under this convention the emf of the cell is positive and is given by the potential of the half-cell on the right hand side minus the potential of the half-cell on the left hand side i.e.,

$$E_{cell} = E_{right} - E_{left}$$

or

$$E_{cell} = E_{cathode} - E_{anode}$$

Thus, for the cell that we are considering,

$$E_{cell} = E_{Cu^{2+}(aq)/Cu(s)} - E_{Zn^{2+}(aq)/Zn(s)}$$

$$E_{cell} = 0.34\ V - (-0.76\ V)$$

$$E_{cell} = +1.10\ V$$

This can further be understood by the following example.

Consider the cell reaction:

$$Cu(s) + 2Ag^{+}(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

Half-cell reactions:

Cathode (*reduction*): $2Ag^{+}(aq) + 2e \rightarrow 2Ag(s)$

Anode (*oxidation*): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e$

It can be seen that the sum of half reactions leads to the overall reaction in the cell and that silver electrode acts as the cathode and copper electrode acts as the anode. The cell can be represented as:

$$Cu(s)|Cu^{2+(}aq)||Ag^{+}(aq)|Ag(s)$$

and we have ,

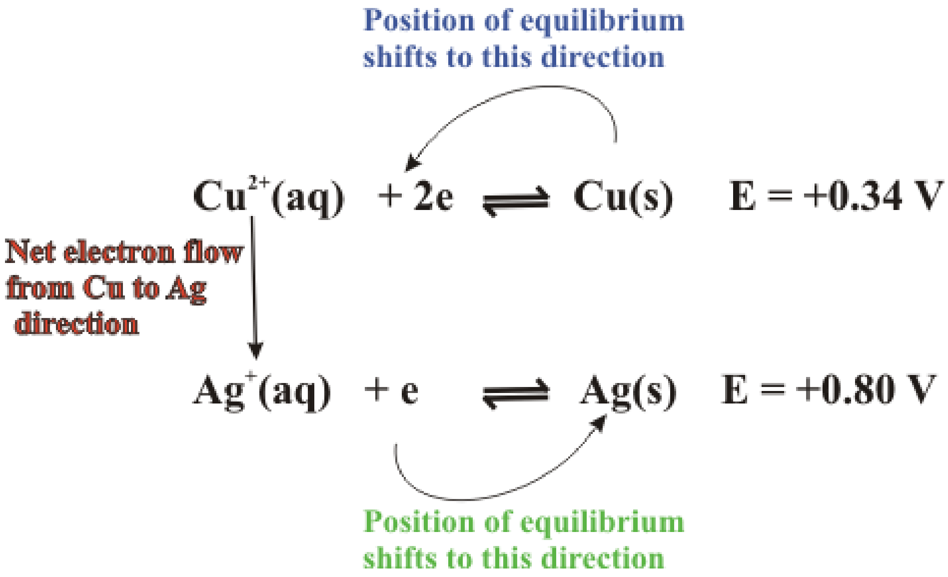
$$E_{cell} = E_{right} - E_{left} = E_{Ag^{+}/Ag} - E_{Cu^{2+}/Cu}$$

Therefore, by substituting corresponding reduction potentials of the half-cells the value of the emf of the cell can be estimated.

$$E_{cell} = +0.80\ V - (0.34\ V) = +0.46\ V$$

This reaction can also be treated like below.
Both of these *E*° values are positive. $E_{Ag+/Ag}$ = +0.80 V and $E_{Cu^{2+}/Cu}$ = +0.34 V indicating that neither copper nor silver produces ions and releases electrons as easily as hydrogen does.

However, of the two, copper releases electrons more readily as it has a less positive E^0 value. In a cell, copper would have the greater buildup of electrons, and is the negative electrode. If copper and silver are connected by a bit of a wire, electrons would flow from the copper to silver as described below.

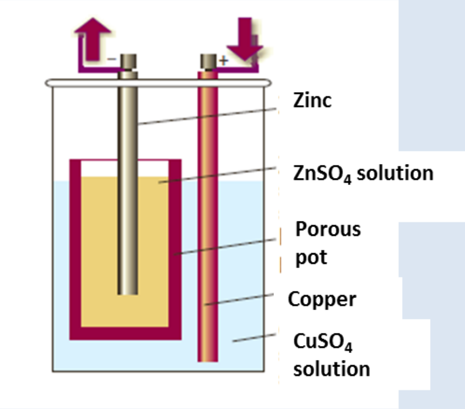


Therefore, it can be confirmed that the given cell reaction is feasible.

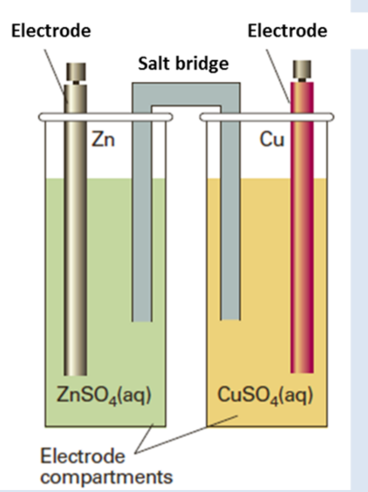
Example 3.2

Following diagrams indicate different versions of Daniel cells. Write the cell in standard notation.

(a)



(b)



Answer

(a) In this diagram, there is a liquid junction between the two different electrolytes. Therefore, cell notation is $Zn(s)|Zn^{2+}(aq)\vdots Cu^{2+}(aq)|Cu(s)$.

(b) In this diagram, the presence of liquid junction potential is minimized using a salt bridge. Therefore, cell notation is $Zn(s)|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu(s)$.

3.3.2 Factors affecting the electrode potential

The potential of an electrode depends on several factors as listed below.

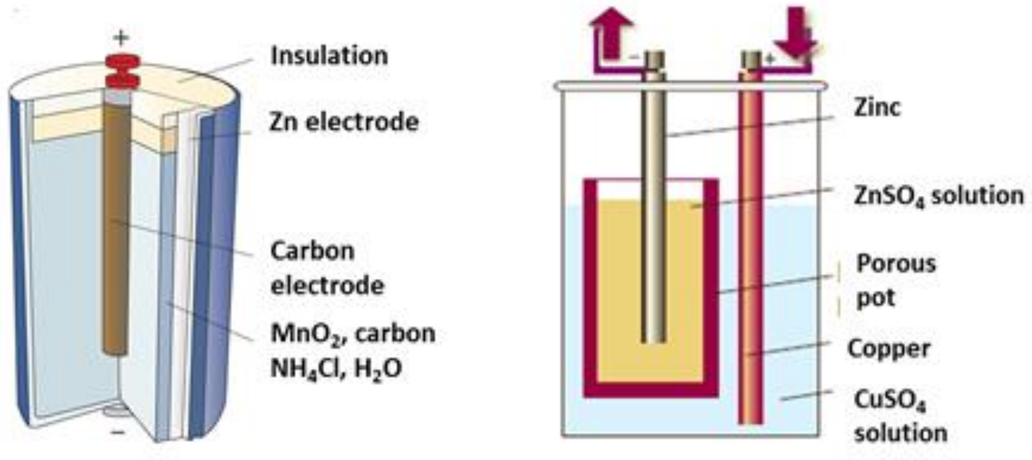
- temperature
- concentration of the electrolyte
- nature of the electrolyte
- pressure of the gas
- type of electrolyte

For an electrochemical reaction to take place, metal ions must collide with the electrode surface with proper orientation and energy. Therefore, temperature and concentration of the electrolyte are important when determining the electrode potential. The nature of the electrolyte is also important when considering charge transport during the operation of the cell. This is discussed under section 3.1.1. When gas electrodes are used, it is very important to mention the pressure of the gas as it can be used to define number of molecules in a unit volume.

The electrode potential of silver-silver chloride measured with respect to SHE is 0.220 V. However, if the concentration of KCl electrolyte used is 0.10 mol dm^{-3}, then the electrode potential is changed to 0.288 V and in the case of 1.00 mol dm^{-3} KCl it is further changed to 0.235 V.

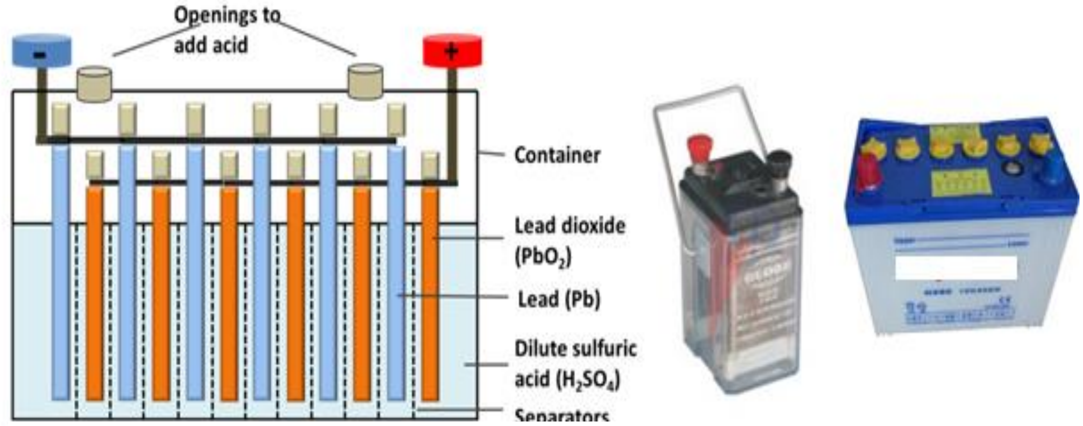
3.3.3 Different types of electrochemical cells

Electrochemical cells are used to convert chemical energy to electrical energy. Therefore, such electrochemical cells are employed in many aspects of daily life where electrical items are operated with 'batteries'. In these cells chemical reactions occur when two electrodes are connected externally using a conductor to generate the current. When the cell reaction cannot be reversed by providing electrical energy, such electrochemical cells are called "**primary cells**" (i.e. non rechargeable). Normal Leclanche cell in Figure 3.11(a) and Daniel cell in Figure 3.11 (b) are examples for primary cells.



(a) (b)

Figure 3.11 (a) Normal Leclanche cell (b) Daniel cell



(a) (b) (c)

Figure 3.12 (a) Schematic diagram of a lead accumulator (b) Lead accumulator (c) Commercial lead accumulator (car battery)

Another type of cell that is used in daily life is the lead accumulator. This is more commonly known as the “car battery”. These cells can be recharged by reversing the cell reaction (rechargeable), so these cells are referred as “**secondary cells**”. Figure 3.12 illustrates a lead accumulator.

Table 3.6 Summary on different types of electrochemical cells

Electrochemical cell	Normal Leclanche cell (primary cell)	Daniel cell (primary cell)	Lead accumulator (secondary cell)
Electrolyte	NH_4Cl / $ZnCl_2$	$ZnSO_4$ (aq)/ $CuSO_4$ (aq)	Dil. H_2SO_4
(+) pole	C/ MnO_2	Cu	PbO_2
(-) pole	Zn	Zn	Pb
Reaction at (+) pole (Cathode reaction)	$2NH_4^+(aq) + 2MnO_2(s) + 2e \rightarrow Mn_2O_3(s) + H_2O(l) + 2NH_3(g)$	$Cu^{2+}(aq) + 2e \rightarrow Cu(s)$	(During discharging) $PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e \rightarrow PbSO_4(s) + 2H_2O(l)$
Reaction at (-) pole (Anode reaction)	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$	$Zn(s) \rightarrow Zn^{2+}(aq) + 2e$	(During discharging) $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(aq) + 2e$
Cell reaction	$Zn(s) + 2NH_4^+(aq) + 2MnO_2(s) \rightarrow Zn^{2+}(aq) + Mn_2O_3(s) + H_2O(l) + 2NH_3(g)$	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	(During discharging) $PbO_2(s) + 4H^+(aq) + Pb(s) \rightarrow 2\,PbSO_4(s) + 2H_2O(l)$

3.4 Electrolysis

In Galvanic cells, a spontaneous chemical reaction can convert chemical energy to electrical energy. However, in daily life we come across situations where non-spontaneous redox reactions must be carried out to produce useful items. Examples are electroplating where precious metals like silver (Ag) can be coated on a less expensive metal to get a more appealing cover or can be used to coat a protective metal layer. In such a situation, the corresponding non-spontaneous chemical reaction can be driven forward giving electrical energy from outside. Conducting a non-spontaneous chemical reaction using electrical energy from outside is known as **electrolysis**. A direct current is passed through a molten substance or substance dissolved in a suitable solvent when conducting electrolysis. Chemical reactions at electrodes will result in the desired product.

When conducting electrolysis, the electrode connected to the positive terminal of the external source of electricity (battery) is the **positive electrode (anode)**. The electrode connected to the negative terminal is the **negative electrode (cathode).** When conducting electrolysis, positive ions in the solution are attracted towards the negative electrode (cathode) and undergo reduction. The opposite happens at the anode where negatively charged ions in the solution are oxidized.

3.4.1 Electrolysis of water

Water is a very stable chemical substance. Therefore, electrolysis of water to produce hydrogen gas and oxygen gas is not a spontaneous chemical reactions under atmospheric conditions (1 atm, 25 °C, ΔG^{θ} is 474.4 kJ mol^{-1}). In order electrolyse water, external electrical energy must be supplied to carry out the redox reaction.

Electrolysis of water can be performed using the setup given in the Figure 3.14.

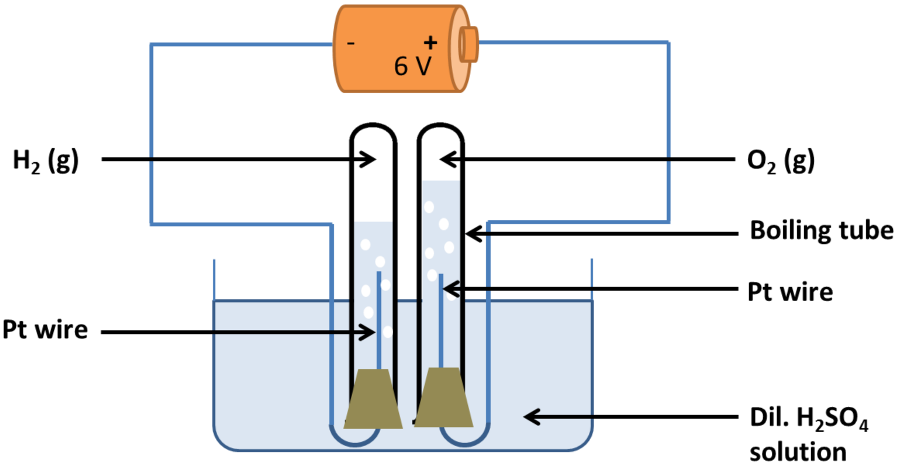


Figure 3.14 Experimental set up for electrolysis of water

The main ionic species in pure water are H^+(aq) ion and OH^-(aq) ions each having a concentration of 1×10^{-7} mol dm^{-3}. Therefore, dilute H_2SO_4 (0.10 mol dm^{-3}) is added to water to enrich $H^+(aq)$ ions in solution. This facilitates conducting electricity due to the presence of sufficient number of ionic species than in pure water.

The overall reaction is given by

Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode (reduction): $\underline{4H^+(aq) + 4e^- \rightarrow 2H_2(g)}$
Overall: $\mathbf{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$

It is clear from the overall reaction of electrolysis that H_2SO_4 concentration has no effect on the electrolysis.

Example 3.3
Using standard electrode potentials listed in Table 3.5, calculate the minimum voltage required for the electrolysis of water.

Answer
Standard electrode potentials for the electrolysis of water is given below.

Anode (oxidation): $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $(E^\ominus = 1.23\ V)$
Cathode (reduction): $\underline{4H^+(aq) + 4e^- \rightarrow 2H_2(g)}$ $(E^\ominus = 0.00\ V)$
Overall: $\mathbf{2H_2O(l) \rightarrow 2H_2(g) + O_2(g)}$

$E^\ominus$cell = $E^\ominus$cathode - $E^\ominus$anode = 0 V – (1.23 V) = **-1.23 V**
Since $E^\ominus$cell is negative, $\Delta G^\ominus$ is positive. Therefore, reaction is not spontaneous. In order to conduct this reactions external electrical supply must give a minimum voltage of 1.23 V.

3.4.2 Electrolysis of $CuSO_4(aq)$ using copper electrodes

Electrolysis of $CuSO_4$ (aq) solution using Cu electrodes is a method practiced commercially to purify copper. In general raw copper is extracted from the ore using carbon. However, copper produced in this way comprises many impurities. Therefore, pure Cu can be obtained when $CuSO_4$ (aq) solution is electrolysed with a positive electrode (anode) made of impure Cu and a negative electrode (cathode) of pure Cu. When the system is connected to an electrical source (e.g. 9V battery), impure Cu rod (anode) will dissolve providing Cu^{2+} ions to the solution while more Cu will deposit on the pure Cu rod (cathode) growing it's size.

Anode (oxidation): $Cu(s) \rightarrow Cu^{2+}(aq) + 2e^-$

Cathode (reduction): $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

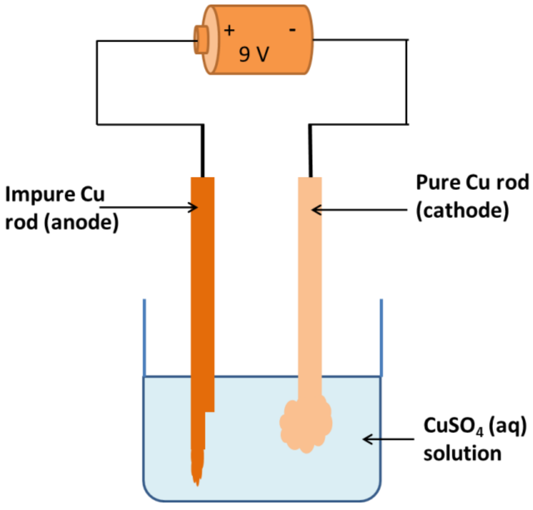


Figure 3.15 Experimental set up for electrolysis of $CuSO_4$(aq)

3.4.3 Electrolysis of $CuSO_4$(aq) using inert electrodes

A scenario different from above is observed when electrolysis of $CuSO_4$ solution is conducted using inert electrodes such as Pt or graphite. In this case, at the anode O_2 gas is released and deposition of Cu is observed at the cathode. The experimental set up used here is much similar to Figure 3.15. The only change is the use of inert electrodes.

Anode (oxidation):	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
Cathode (reduction):	$\underline{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$
Overall reaction*:*	$\mathbf{2Cu^{2+}(aq) + 2H_2O(l) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq)}$

In this experiment if ions that are present near the cathode (negative electrode) are considered, reduction of Cu^{2+} ions to Cu metal (+0.34 V) is easier compared to reduction f H^+ ions to H_2 gas (0.00 V) according to the values of standard reduction potentials listed in **Table 13.5.** Similarly, when anode (positive electrode) is concerned, SO_4^{2-} and OH^- ions are attracted. Among these ions, oxidation of water (+1.23V) is more feasible than the oxidation of SO_4^{2-}(aq) ion (+2.05 V). Therefore, at the anode, O_2 gas is released by oxidation of water.

3.4.4 Electrolysis of NaCl(aq) using inert electrodes

When considering electrolysis of NaCl(aq) solution, it is important to analyze oxidation and reduction reactions that can happen at the corresponding electrodes first. Then comparison of standard reduction potentials of competing reactions can be used to predict final products. Following are competing reduction reactions taking place near the cathode.

$2H^+(aq) + 2e \rightarrow H_2(g)$ $E^\circ = 0.00$ V (1)

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ $E^\circ = -0.83$ V (2)

$Na^+(aq) + e \rightarrow Na(s)$ $E^\circ = -2.71$ V (3)

When considering standard reduction potentials, the most probable reduction is reaction (1). However, this reaction requires standard conditions and also, $[H^+(aq)]$ in water is too low (10^{-7} mol dm^{-3}). Hence it is not possible under ordinary laboratory conditions. The reaction (3) which involves reduction of $Na^+(aq)$ ion cannot happen due to large negative potential. Therefore, when electrolysis of NaCl(aq) solution is considered, the most possible reduction reaction that can happen at the cathode is (2) which involves reduction of water to produce $H_2(g)$ and $OH^-(aq)$ ions.

In order to determine the most possible oxidation reactions that happen at the anode, first it is important to list all oxidation reactions.

$$2Cl^-(aq) \rightarrow Cl_2(g) + 2e \qquad (4)$$

$$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e \qquad (5)$$

Then we can write the standard reduction potentials for the reduction of above reactions before predicting the most possible reaction.

$$Cl_2(g) + 2e \rightarrow 2Cl^-(aq) \qquad E^\ominus = +1.36\text{ V} \qquad (4')$$

$$O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l) \qquad E^\ominus = +1.23\text{ V} \qquad (5')$$

According to above data, reduction reaction of (*4'*) is more feasible than (*5'*) i.e. oxidation of (5) is more feasible than (4). Therefore, according to standard reduction potentials, most favourable oxidation reaction is (5). However, when this experiment is conducted the gas evolved is Cl_2 and NOT O_2! That is because the actual potential that needs to be supplied for the reaction to take place is sometimes greater than the standard reduction potential. This extra potential is termed **over potential** (Detailed discussion of over potential is beyond the scope of G. C. E. (A/L) Chemistry syllabus). In other words, standard reduction potentials can be used to obtain minimum voltage values that can be supplied to drive the reaction of interest; however, actual voltage may be higher due to presence of over potentials. Therefore, Cl_2 (g) is observed, because over potential for reaction (5) (release of $O_2(g)$) could be much greater than for the reaction (4). Thus reaction (4) requires less potential to be supplied than for reaction (5).

Finally, the reactions taking place at the cathode and anode when electrolyzing NaCl(aq) solution using inert electrodes can be written as follows.

Anode (oxidation): $2Cl^-(aq) \rightarrow Cl_2(g) + 2e$

Cathode (reduction): $\underline{2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)}$

Overall reaction: $\mathbf{2Cl^-(aq) + 2H_2O(l) \rightarrow Cl_2(g) + H_2(g) + 2OH^-(aq)}$

3.4.5 Electrolysis of NaCl(l) (molten NaCl) using inert electrodes

NaCl exits in solid form at room temperature, thus does not conduct electricity due to absence of mobile ionic species. However, if the temperature is raised to more than the melting point of NaCl(s) (i.e. > 801 °C), molten NaCl(l) consists of mobile Na^+ ions and

Cl^- ions. Therefore, electrolysis of molten NaCl will result in reduction of Na^+ ion to produce Na metal and Cl_2 gas as the oxidation product.

Anode (oxidation): $2Cl^-(l) \rightarrow Cl_2(g) + 2e$
Cathode (reduction): $\underline{Na^+(l) + e \rightarrow Na(l)}$
Overall reaction: $\mathbf{2Cl^-(l) + 2Na^+(l) \rightarrow Cl_2(g) + 2Na(l)}$

According to the standard reduction potentials listed in Table 3.5, the minimum voltage that should be supplied for the overall reaction to take place is 4.07 V. However, in practice, much higher voltage is required to drive the reaction due to the presence of a large over potential associated with the reaction. Industrially Na metal is extracted by this method by electrolyzing molten NaCl solution. The industrial set up is known as the **Downs cell**.

Example 3.4
Predict the gases evolved at the cathode and anode when Na_2SO_4 (aq) solution is electrolyzed using inert electrodes.

Answer
Step 1: Identify possible oxidation reactions that can happen near the anode (Hint: Anions are likely to be oxidized at the anode) and write standard reduction potentials using **Table 13.5**.
$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e$ (Standard reduction potential = +2.05 V) …..(1)
$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ (Standard reduction potential = +1.23 V) …..(2)

When over potential is not considered, the lower the standard reduction potential easier is to oxidize when the direction of oxidation is concerned.
At the anode O_2 gas will be evolved.

Step 2: Identify possible reduction reactions that can happen near the cathode (Hint: cations are likely to be reduced at the cathode) and write standard reduction potentials using **Table 3.5**.
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ (Standard reduction potential = -0.83 V) ……(3)
$Na^+(aq) + e \rightarrow Na(s)$ (Standard reduction potential = -2.71 V) ……(4)

The higher the negative value of standard reduction potential of a species, it is more likely to be in the oxidized form. Reduction of Na^+ has a higher negative value compared to reduction of water as listed above. Therefore, Na^+ tends to stay in the Na^+ state while H_2O will be reduced at the **cathode to produce H_2 gas.**

Both half reactions involve oxidation and reduction of water instead of OH^- ions and H^+ ions. That it is because Na_2SO_4 is a neutral salt which keeps the solution at a pH of approximately 7. Therefore, H_2O oxidize and reduce itself due to the absence of high concentrations of OH^- and H^+ ions.

Step 3: Write the overall reaction combining cathode and anode reactions.

Anode (oxidation): $2\ H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$

Cathode (reduction): $\underline{4\ H_2O(l) + 4e \rightarrow 2H_2(g) + 4OH^-(aq)}$

Overall reaction: $\mathbf{2\ H_2O(l) \rightarrow O_2(g) + 2H_2\ (g)}$

3.4.6 Quantitative aspects of electrolysis

Michael Faraday was the first scientist who described the quantitative aspects of electrolysis. Faraday's laws stem from what has been discussed earlier.

Faraday's laws of electrolysis

The following well known Faraday's two laws of electrolysis is mainly used for quantitative analysis in electrolysis.

(i) First Law: *The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).*

(ii) Second Law: *The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights (Atomic Mass of Metal / Number of electrons required to reduce the cation).*

The quantity of electricity Q, passed is given by

$$\mathbf{Q = It}$$

Q is in coloumbs when I is in ampere and t is in second. That is **1 C = 1 A × 1 s**

The amount of electricity (or charge) required for oxidation or reduction depends on the stoichiometry of the electrode reaction. For example, in the reaction:

$$Ag^+(aq) + e \rightarrow Ag(s)$$

one mole of electrons is required for the reduction of one mole of silver ions. We know that charge on one electron is equal to 1.6021×10^{-19}C.

Therefore, the charge on one mole of electrons is equal to:

$N_A \times 1.6021 \times 10^{-19}\ C = 6.02 \times 10^{23}\ mol^{-1} \times 1.6021 \times 10^{-19}\ C = 96487\ C\ mol^{-1}$

This quantity of electricity is called **Faraday (constant)** and is represented by the symbol **F**.

For approximate calculations we use 1F ≃ 96500 C mol^{-1}.

For the electrode reactions:

$$Mg^{2+}(aq) + 2e \rightarrow Mg(s)$$

$$Al^{3+}(aq) + 3e \rightarrow Al(s)$$

it is obvious that one mole of Mg^{2+} and Al^{3+} require 2 moles of electrons (2F) and 3 moles of electrons (3F) respectively.

Application of Faraday constant to electrochemical calculations

When electrolysis experiments are conducted, it is important to know quantitatively the yield of the products at the cathode and the anode. The yield is associated with the current passed through the cell for a known period of time. For example, consider following reduction reactions.

$$Na^{+}(aq) + e \rightarrow Na(s)$$

$$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^{-}(aq)$$

In order to produce 1 mole of Na(s) metal, 1 mole of electrons must be used to reduce Na^{+}. Similarly, to produce 1 mole of H_2 gas, 2 moles of electrons are required.

The charge in coulombs for a one mole of electrons is given by the **Faraday constant** which is **96485 C mol^{-1}**. Therefore, if the charge in coulombs passed through the cell is known, then the amount product of consumption of reactants can be calculated. In general, the current passed though the electrolytic cell for given period of time is known. Then the following relationship can be used to calculate the charge associated during that period of time when the current passed through is given in amperes (A) and time in seconds (s).

Current(A) × time(s) → coulombs(C) → moles of electrons → moles of product or reactant

Example 3.5

Calculate the volumes of gases evolved at the cathode and anode when dil. H_2SO_4(aq) solution is electrolyzed using inert electrodes for a period of 5 h passing a current of 1.5 A under 25 °C and 1 atm pressure.

Answer

Step 1: Identify possible oxidation reactions that can happen near the anode (Hint: anions are likely to be oxidized at the anode) and write standard reduction potentials using **Table 13.5**.

$2SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e$ (Standard reduction potential = +2.05 V) …..(1)

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ (Standard reduction potential = +1.23 V) …..(2)

As illustrated in **Example 3.4**, the reaction at the cathode is (2). Therefore, **at the anode O_2 gas is evolved**.

Step 2: Identify possible reduction reactions that can happen near the cathode (Hint: Cations are likely to be reduced at the cathode) and write standard reduction potentials using **Table 3.5**.

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ (Standard reduction potential = -0.83 V) …..(3)

$H^+ (aq) + e \rightarrow H_2 (g)$ (Standard reduction potential = 0.00 V) …..(4)

Since it is a dilute H_2SO_4 solution, there is sufficient H^+ concentration present for reaction (4) to take place preferably at the cathode. Therefore, **the gas evolved at the cathode is H_2 gas**.

Step 3: Write the overall reaction combining cathode and anode reactions.

Anode (oxidation): $2\ H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$

Cathode (reduction): $\underline{4H^+ (aq) + 4e \rightarrow 2H_2 (g)}$

Overall reaction: $\mathbf{2\ H_2O(l) \rightarrow O_2(g) + 2H_2 (g)}$

Step 4: Calculate the amount of charge passed through during electrolysis period.

Charge = current (A) × time (s) =1.5A × (5 ×60 ×60) s = **27000 C**

Amount of moles of electrons = 27000 C × (1/96485 C mol^{-1})

= **0.28 moles of electrons**

Step 5: Calculate volume of O_2 gas evolved at the anode

According to the oxidation half reaction,

4 moles of electrons → 1 mole of $O_2(g)$

Amount of moles of O_2 (g) produced

$$= 0.28 \text{ moles of electrons} \times \frac{1 \text{ mole of } O_2(g)}{4 \text{ moles of electrons}}$$

$$\mathbf{= 0.07 \text{ moles of } O_2 (g)}$$

Apply ideal gas equation to calculate volumes of O_2 (g) produce, $V = nRT/P$

Volume of $O_2(g) = (0.07 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) / 1\times10^5 \text{ Pa}$

$= 173.4 \times 10^{-5} \text{ m}^3 = \mathbf{1.734 \text{ dm}^3}$

Step 5: Calculate the volume of H_2 gas evolved at the cathode.

According to the reduction half reaction,

2 moles of electrons → 1 moles of $H_2(g)$

Amount of moles of H_2 (g) produced

$$= 0.28 \text{ moles of electrons} \times \frac{1 \text{ mole of } H_2 (g)}{2 \text{ moles of electrons}}$$

$$\mathbf{= 0.14 \text{moles of } H_2 (g)}$$

Apply ideal gas equation to calculate volumes of H_2 (g) produce, $V = nRT/P$

Volume of $H_2(g) = (0.14 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}) / 1\times10^5 \text{ Pa}$

$= 346.8 \times 10^{-5} \text{ m}^3 = \mathbf{3.47 \text{ dm}^3}$

3.4.7 Comparison of galvanic cells and electrolytic cells

The main difference between the two types of cells is the spontaneous nature of the cell reaction. In Galvanic cells, the cell reaction is spontaneous and chemical energy is converted to electrical energy. Therefore, electricity is produced in galvanic cells. The anode in a Galvanic cell is negatively charged due to electrons left behind during oxidation. The cathode is positively charged due to taking up of electrons for the reduction half reaction.

The opposite is taking place during electrolysis or in electrolytic cells. The overall cell reaction is not spontaneous. Therefore, it is necessary to pump electrons from an external source to proceeds the reaction. Therefore, a battery is used in electrolysis to supply electricity for the chemical reaction to take place. Here, the anode is connected to the positive terminal of the battery. The oxidation reaction taking place at the anode will generate electrons that are attracted towards the positive terminal of the battery. Therefore, the anode is positively charged. The opposite is true for the cathode and it is connected to the negative terminal of the battery. So the cathode in electrolytic cell is negatively charged.

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