
CHM 201: Introduction to Physical Chemistry II

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CHM 201:

Introduction to physical chemistry II

Course guide

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1.0 Introduction

CHM 122 is a second semester course in introductory physical chemistry. It is a continuation of CHM 115. In this course, there are several theoretical concepts and their practical applications. In fact, one expects that most of the fundamentals in the introduction to physical chemistry would have been covered. Some relevant concepts are however not covered in this course, especially in chemical thermodynamics, equilibrium, electrochemistry, photochemistry, and nuclear chemistry. These will be addressed later in other physical chemistry courses, as you proceed in your programme. Meanwhile, note that for you to effectively and successfully study CHM 122, you require such fundamental courses as Atoms and Molecules, Pure Mathematics, Mechanics (in Physics), and so on. This implies that when you are selecting electives, consideration should be given to some of those suggested, or more relevant courses that will facilitate your understanding of physical chemistry courses.

As pointed out in CHM 115, physical chemistry is one of the fundamental courses for a Bachelor's degree programme in Science (B Sc) and Science Education (B Sc.Ed) in any university in the world. This course is compulsory for students studying for degrees in Chemistry and Chemistry Education. It is a suitable elective for anyone who is undergoing a science or science-related professional programme. Just like CHM 115, it is a two-credit unit course and contains four modules, consisting of 20 units in all. The first module covers the terminology and first law of thermodynamics. The second and third laws of thermodynamics will be taught later in the programme. The second module focuses on thermochemistry. Here, enthalpy changes in different processes are dealt with. The third module examines the introductory aspects of the concepts of kinetics and equilibrium. In the fourth module, the concepts of ionic equilibria and some minor aspects of electrochemistry are discussed.

This course, though adapted from IGNOU course materials went through serious surgery to fit into the systems we are familiar with. You will be required to possess a scientific calculator, instrumental and problem-solving skills acquired through consistent practice, for you to successfully learn this course. Definitely, there are some implied practical works that you will be required to carry out in the laboratory, though they are not in some cases specified.

This Course Guide provides you with additional information on the course aims, objectives and learning procedures, to enable you to derive maximum benefit from the four modules prepared for the course.

2.0 Course aims

The aims of this course are to create that in-depth awareness that will enable students to have full understanding of the concept of energy, as the capacity for change in any chemical reaction; and to appreciate that strong relationship between energy and structure of matter, as the foundation of physical chemistry. Thus, the aims of this physical chemistry course are to:

1. discuss the mathematical viabilities and standard procedures required in effective study of physical chemistry;
2. explain the basic theories that elucidate various properties of matter;
3. discuss some aspects of physical phase equilibria;
4. build cases for the feasibilities of chemical reactions;
5. demonstrate the various energy relationships in chemical reactions;
6. give you an appreciation of systems at equilibrium and factors affecting such systems.

3.0 Course objectives

In order to achieve the course aims, there are some overall objectives set for the course. Moreover, each module and each unit has their respective objectives, which you and your course tutor must constantly refer to, so that no objective is skipped or unachieved. It is, therefore, important that you outline what you have been able to achieve after completing a unit and compare the list with the unit objectives. This will help you to ascertain whether you have accomplished what is required of you.

All the module and unit objectives are specifics of the course objectives. The course objectives are stated as follows:

At the end of the course, you should be able to:

- i) familiarise yourself with basic instruments for physical chemistry laboratory work;
- ii) write and apply correctly SI units;
- iii) measure in and convert to other units using SI units;
- iv) explain and compare the main features of gas, liquid and solids states;
- v) appreciate the reasons why real gases deviate from gas laws;
- vi) analyse the properties of completely, partially and immiscible liquids;
- vii) discuss the essence of types of solutions;
- viii) analyse phase changes in matter;
- ix) describe the conditions regulating the solubility of liquid solutions.

4.0 Working through this course

This course contains some packages that you will be given at the beginning of the semester, having satisfied the conditions for admission and registration. One of the packages is the course materials. The details of what constitute course materials will be discussed next. There are two areas you are expected to fulfil at the end of this course. These are your full participation in the continuous assessment and the final written examinations.

Though there is a practical course developed for this level, however it is advisable that some of the sections can be practicalised, with the assistance of the course tutor. Your tutor will be readily accessible to issue out the exercise you are to do and submit according to specified rules and regulations from the university authority.

For you to have been counted as successful in this course, you will be expected to pass at an average level, both in continuous assessment and the final written examination. Thus, certain materials have been packaged for you, to enable you to prepare adequately for both continuous assessment and the final written examinations. First and foremost is the study unit material, which consists of 20 units in all. However, the units have been packaged for you in modules, as shown below:



Study units

Module number	Module	Unit	Title
1	Introduction	1 2 3	Units and dimensions SI prefixes Separations techniques
2	Gaseous state of matter	4 5 6 7 8	Gases Ideal gas Kinetic theory of gases Real gases Liquefaction of gases
3	Solid and liquid states of matter	9 10 11 12 13	Solids states and solid types Nature of bonds in solids Structure of bonds in solids Liquids Other properties of liquids
4	Solutions and phase equilibria	14 15 16 17 18 19 20	Types of solutions Solutions of solids and gases in liquids Binary liquids solutions-1 Binary liquids solutions-2 Partially miscible liquids Some colligative properties Phase rule

By and large, you should be able to complete this two-credit unit course for about 30-35 weeks in a semester. Well spread out in each of the units are the introduction to the unit, specific objectives, reading materials on sub-topics, self-assessment questions (SAQ), exercises, a conclusion, summary, tutor-marked assignments (TMA) and references.

5.0 Course materials

Major course materials of the course are as follows:

1. **Course guide:** This looks like a blueprint that spells out what constitutes the course itself. It also extends to the basic information you require on how best to study this course.
2. **Study units:** These present an overview of what will be covered in the course and in how many units. The contents are spelt out under seven major headings: the introduction, objectives to guide, what to focus on, detailed content, conclusion, summary of the content, references (and other materials that will facilitate understanding) and tutor-marked assignments. In the body of content are exercises that should always attract your attention after every reading.
3. **Assignment files:** These files contain challenging and tutorial questions known as Tutor Marked Assignments (TMAs), which will enable you to assess yourself at the end of every assignment given by your tutor. Since we are operating a course unit system, your scores in these assignments will be added up, recorded and used for computing your cumulative grade score at the end of the course.



4. **Presentation schedule:** This will feature information on a recommended study time-table, suggested number of hours of study per unit/ module, and assignment-submission procedure for effective self-teaching and progress-monitoring.

6.0 Study units

Details of the study units have earlier been presented. It is spelt out in modules with corresponding units and titles. You will be expected to spend 3-4 hours studying a unit. The exercise items are provided to enable you to test your understanding of the areas covered and to help you monitor the progress made per sub-topic in the unit. There is also the TMA packages for you, but these will be given as assignments.

7.0 References and other resources

Apart from this study unit, some reference materials are provided as additional reading materials to support your study. It is not the responsibility of NOUN to provide them, but you may be lucky to spot them in the designated library.

8.0 Instructional media

As a distance learning university, several and relevant multimedia that can make learning more meaningful are available. Other instructional media will be disclosed and made accessible to you from time to time.

9.0 Assignment file

This has been discussed earlier. It is mandatory to always turn in your assignments to the tutor assigned.

10.0 Assessment

You will be expected to have completed at least ten assignments by the end of the course. Some of these will be in the form of a project, continuous assessment or written tests. Each of these ten assignments will carry ten marks, making a total of 100 marks. You will also be expected to write a final examination at the end of the course. Your overall (percentage) score at the end of the course will be the sum of your scores on continuous assessment and the written examination. The minimum pass score for the course will be 50% in continuous assessment and 50% in the written examination.



Module 1: Chemical thermodynamics

Unit 1: Energy relationships in chemical reactions

Contents

- 1.1 Introduction
- 1.2 Objectives
- 1.3 Thermodynamics terminology
- 1.4 The zeroth law of thermodynamics
- 1.5 Extensive and intensive variables
- 1.6 Conclusion
- 1.7 Summary
- 1.8 Tutor-marked assignment
- 1.9 References

1.1 Introduction

There is no chemical reaction in which energy is not involved. In the process of reacting substances, you either supply energy to the system or the reaction occurs on its own. But then, why and how do chemical reactions occur? What exactly is thermodynamics? Why do some chemical reactions occur without the supply of external energy? All these questions will be answered in this module. You will also be introduced to some of the terms used in thermodynamics.

1.2 Objectives

By the end of this unit, you should be able to:

- i) define the term thermodynamics;
- ii) explain the terms- system, surroundings and thermodynamic variables;
- iii) state the zeroth law of thermodynamics;
- iv) differentiate between extensive and intensive variables, providing two examples each.

1.3 Thermodynamics terminology

In this section, a number of commonly used terms in thermodynamics are defined and explained. These terms should be understood clearly before you proceed further.

Thermodynamics

In respect of chemical reactions, we are not only concerned about how and why reactions take place but also why some substances are even more reactive than others. There is no doubt that before a chemical reaction can occur, energy is required. The energy required may be related to the substances undergoing the reaction. However, where the quantities of energy possessed by the reacting species are not adequate to initiate the reaction or take the reaction to completion, energy may be supplied. In short, chemical reaction in a system requires some level of energy transformation. We have learnt before that heat is a form of energy.

Thermodynamics is a compound word. *Thermo* means 'of-heat' or 'concerned with heat' and *dynamics* means 'of physical power and forces producing motion'. Thermodynamics can thus be

defined as the science of heat motion. In fact, you should consider it as the science of heat flow or transfer or disappearance of work attending Chemical and physical processes.

Let us consider some examples of thermodynamics, as follows:

- 1 Natural process: Water flowing down from a hilltop. An example is Erin -ljesha water fall in Osun State.
- 2 Controlled chemical reactions: You can determine the dissociation constant (pK_a), e.g. for acetic acid.
- 3 Performance of engines: Any engine can be considered here, for instance, when you are determining the efficiency of a blender engine. We should draw our attention to one fact that thermodynamics cannot answer all questions due to its wide applicability. For instance, it cannot:
 - i) answer how fast a reaction occurs;
 - ii) give the character of the process of change.However, it can tell us whether a reaction will occur or not.

In brief, the term thermodynamics is defined as the study of energy transformation in a system. In fact, thermodynamics deals with systems. The system under consideration in this unit is a chemical one, hence, our consideration of the concept of chemical thermodynamics. What then is a system?

System

Any part of the universe that is under study is called a system. Systems can be in different states. A system can be as simple as a gas contained in a closed vessel, or as complicated as a rocket shooting towards the moon.

A system may be homogenous or heterogenous, depending on its contents and conditions. A system is homogenous if physical properties and chemical composition are identical throughout the system. Such a system is also called a single phase system. A heterogenous system consists of two or more phases separated by mechanical boundaries. Now, let us consider the surroundings of the reaction.

Surroundings

The rest of the universe around the system is considered as its surroundings. A system and its surroundings are always separated by boundaries across which matter and energy may be exchanged. The boundaries can be real (fixed or movable) or imaginary.

Based on the exchange of matter and energy between the system and the surroundings, a system can be classified into the following three types:

- i) isolated;
- ii) closed;
- iii) open.

An isolated system is one that exchanges neither energy nor matter with its surroundings. There is no perfectly isolated system, but, a system that is thermally well-insulated (i.e. does not allow heat flow) and is sealed to inflow or outflow of matter can be considered as an isolated system. A sealed thermos flask having some matter may be regarded as an isolated system.

A closed system allows for exchange of energy (heat or work) with the surroundings, but matter is not allowed to enter or leave it. A properly sealed system (to prevent the passage of matter across its boundary) can be considered as a closed system.

An open system allows exchange of both matter and energy with its surroundings. This is the most common system encountered in our daily life. All living things are examples of an open system, since they are capable of exchanging energy and matter freely with their surroundings. Also, reaction vessels with permeable membranes are open systems.

State variables

Any thermodynamic system must be macroscopic, i.e. must have sufficiently large size. This facilitates the measurement of its properties such as pressure, volume, temperature, composition and density. Such properties are, therefore, called macroscopic or bulk properties. These are also called state or thermodynamic variables. These do not depend on the past history of the system. A state variable which depends on other variables is called a dependent variable. Others, on which it is dependent are called independent variables. For example, if you write the ideal gas equation as:

$$\frac{V}{p} = nRT$$

Then, V is the dependent variable, whereas n , T and P are independent variables. We know that R is the gas constant. On the other hand, if you write this equation as,

$$P = \frac{nRT}{V}$$

then, P is the dependent variable, whereas n , T and V are independent variables. The choice of dependent and independent variables is a matter of convenience.

State of a system

The state of a system can be defined in thermodynamics once you establish a small set of measurable parameters. For example, when you have a gas confined in a container, the measurable parameters there will include pressure, volume, temperature and composition.

In essence, the state of a system is defined when the state variables have definite values. It is not necessary to specify all the state variables since these are interdependent. For example, if the system is an ideal gas, then its pressure, volume, temperature and amount of the gas (number of moles) are related by the gas equation. Thus, if we specify three of these, the fourth variable is automatically fixed. Similarly, many of its other properties, such as density, heat capacity, etc., are also fixed, although through more complicated relations.

We can change the state of a system by altering either the pressure or the volume.

Exercise 1.1

Identify the type of system in each of the following cases:

- i) a beaker covered with a lid.
- ii) a closed thermos flask.
- iii) a beaker without lid.

1.4 The zeroth law of thermodynamics

The zeroth law of thermodynamics is based on the concept of thermal equilibrium. It helps us in defining temperature. If two closed systems are brought together so that they are in thermal contact, changes take place in the properties of both systems. But, eventually a state is reached when there is no further change in either of the systems. This is the state of thermal equilibrium. Both systems are at the same temperature. In order to find if two systems are at the same temperature, the two can be brought into thermal contact, and then the changes in their properties observed. If no changes occur, they are at the same temperature.

The zeroth law of thermodynamics states that if a system A is in thermal equilibrium with system C , and system B is also in thermal equilibrium with C , then A and B are also in thermal equilibrium with each other. This is an experimental fact, which may be illustrated by assuming that systems A and B are two vessels containing different liquids, and C is an ordinary mercury thermometer. If A is in thermal equilibrium with C , then the mercury level in the thermometer will show a constant reading. This indicates the temperature of system A as well as that of C . Now, if A is also in thermal equilibrium with B , then the height of mercury level in the thermometer (in contact with B) is the same as before; B also has the same temperature as A . There is thermal equilibrium in both A and

B, or these are at the same temperature. Here we have only explained the concept of temperature, the temperature scale will be discussed later in this course.

1.5 Extensive and intensive variables

We have defined homogenous and heterogeneous systems in Section 1.3. Let us now discuss the difference between the two, with respect to the value of some variables. The parameters mentioned earlier are also called variables. There are two types of variables, namely extensive and intensive variables.

Extensive variables

An extensive property of a homogenous system is one which is dependent on the amount of a phase in the system or the mass of the system. For a heterogeneous system made up of several phases, the total value of an extensive property is equal to the sum of the contributions from its various phases. Mass, volume, and energy are examples of extensive properties. Thus, if a system at equilibrium consists of 0.100 kg of ice and 0.100 kg of liquid water at 273.15K, the total volume of the system is the sum of the two volumes, each of which is directly proportional to its mass.

$$\begin{aligned} \text{Volume of 0.100 kg of ice} &= \frac{\text{Mass of ice}}{\text{Density of ice}} \\ &= \frac{0.100 \text{ kg}}{917 \text{ kg m}^{-3}} \\ &= 1.09 \times 10^{-4} \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \text{Similarly, the volume of 0.100 kg of water} &= \frac{\text{Mass of water}}{\text{Density of water}} \\ &= \frac{0.100 \text{ kg}}{1.00 \times 10^3 \text{ kg m}^{-3}} \\ &= 1.00 \times 10^{-4} \text{ m}^3 \end{aligned}$$

$$\begin{aligned} \text{Total volume} &= (1.09 + 1.00) \times 10^{-4} \text{ m}^3 \\ &= 2.09 \times 10^{-4} \text{ m}^3 \end{aligned}$$

Intensive variables

An intensive property of a phase is independent of the amount of the phase. Thus, refractive index, density and pressure are intensive properties. However, if a system consists of several phases, then some of the intensive properties may be different. For example, density is an intensive property, but its value is different for ice and liquid water in equilibrium at 273.15K. For thermal equilibrium, the intensive property, i.e. temperature has to be the same throughout the system. Otherwise, heat will flow from one point of the system to another. Similarly, for mechanical equilibrium, the intensive property, i.e. pressure, has to be the same throughout the system. An extensive property when divided by mass or molar mass of the system becomes an intensive property.

Exercise 1.2

Identify the extensive or intensive variables from among those indicated below:

- i) energy required to cook your meals.
- ii) volume per unit mass of milk.
- iii) your body temperature.

1.6 Conclusion

We are now familiar with various terms used in thermodynamics. The zeroth law has been stated. The extensive and intensive variables, otherwise known as parameters are explained. In the next unit, we shall explain the terms: work, heat and heat capacity. We shall attempt to determine work done, using appropriate formulae derived in the course of explaining these concepts.

1.7 Summary

In this unit, you have learnt that:

- i) a system may be homogenous or heterogenous depending on its contents and conditions;
- ii) surroundings refers to all other things in the universe which may interact with the system;
- iii) intensive variable is independent of the quantity of matter present in a system.

1.8 Tutor-marked assignment

1. Which of the following are true or false:
 - a) Thermodynamics can explain how fast a reaction is.
 - b) Flooding of Nigerian roads is an example of thermodynamics.
 - c) In a closed system, heat neither leaves nor enters.
2. Define thermodynamics.

1.9 References

1. IGNOU (1991), *Chemical Thermodynamics: physical chemistry CHE-04*, New Delhi.
 2. Laidler, K J, and Meiser, J. H, (1982), *Physical Chemistry*, California: The Benjamin Cummings Publishing Company, Inc.
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Unit 2: Work, heat and heat capacity

Contents

- 2.1 Introduction
- 2.2 Objectives
- 2.3 Types of process
- 2.4 Work, heat and heat capacity
- 2.5 Conclusion
- 2.6 Summary
- 2.7 Tutor-marked assignment
- 2.8 References

2.1 Introduction

In Unit 1 of this course, we examined some terminology used in thermodynamics and the concept of thermodynamics itself in matter. In this unit, we will describe the various types of process. In addition, the definitions of work, heat and heat capacity will be stated and some calculations made.

2.2 Objectives

By the end of this unit, you should be able to:

- i) describe isothermal, adiabatic and cyclic processes;
- ii) differentiate between these types of processes;
- iii) explain the terms - work, heat and heat capacity;
- iv) perform some calculations on work, heat and heat capacity.

2.3 Types of process

When the state of a system changes, it is said to have undergone a process. Thus, a process means a change in at least one of the state variables of the system. The process may be accompanied by an exchange of matter and energy between the system and the surroundings. There are certain processes in which a particular state variable (such as temperature, pressure or volume) remains unchanged. Such processes are of the following types: isothermal, adiabatic, isobaric and isochoric processes.

In an isothermal process, the temperature of the system remains constant. When a system undergoes an isothermal process, it is in thermal contact with a large constant temperature reservoir (thermostat). The system maintains its temperature by exchange of heat with the thermostat.

In an adiabatic process, no heat is allowed to enter or leave the system. Systems which undergo a process occurs are thermally insulated from the surroundings. An adiabatic process may involve an increase or a decrease in the temperature of the system. We shall discuss these two processes in detail later in this course.

An isobaric process is one in which the pressure of the system remains unchanged. A process taking place in an open beaker is always at atmospheric pressure, and the process is, therefore, isobaric.

In an isochoric process, the volume of the system remains constant. Thus, a chemical reaction in a sealed flask of constant volume is an isochoric process.

A process is cyclic if the system (after any number of intermediate changes) returns to its

original state. The initial and final values of each thermodynamic variable are identical after the completion of a cyclic process. The summation of energy in a cyclic process will be zero. Hence, for any cyclic process, the integral of energy is zero. This simply means that if there is a cyclic process, the quantity of work we do must be equal to the total amount of energy put in, that is, the energy expended. From this discussion on cyclic process, we can conclude that any engine process or any device operating in cycles for the purpose of converting heat to work can never produce more than the heat added. With this conclusion, we can then rule out the construction of the so-called perpetual motion machine of the first kind.

Based on the value of the driving force applied, we can classify the processes into two types: reversible and irreversible. A reversible process is one in which at any time, the driving force exceeds the opposing force only very slightly. Hence, the direction of the process can be reversed by merely effecting a small change in a variable, such as temperature and pressure. The idea of a reversible process will become clear by considering the following example.

Consider a gas at pressure p in a cylinder fitted with an air-tight piston. If the external pressure on the gas is equal to the pressure of the gas, then there is neither expansion nor compression and the piston remains at its position. However, on increasing the external pressure (P_{ext}) infinitesimally, the gas can be compressed. On the other hand, by slightly decreasing the external pressure, the gas may be expanded.

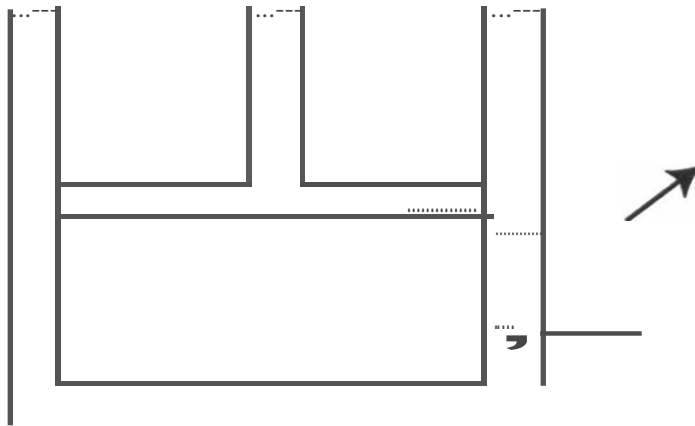


Fig. 2.1 Static system (since piston does not move)

Thus, if

$P_{ext} = p$, the system is static and the piston does not move;

$P_{ext} = p + dp$, the gas is compressed and the piston moves downwards, infinitesimally slowly;

$P_{ext} = p - dp$, the gas expands and the piston moves outwards, infinitesimally slowly.

Thus, for a reversible process, the direction is changed by changing the magnitude of the driving force by a small amount.

Any process that is not reversible is termed irreversible. All natural processes are irreversible.

The flow of heat from a high temperature body to a low temperature body is a natural process and hence, irreversible. So is the expansion of a gas against vacuum, known as free expansion. Irreversible processes are also called spontaneous processes. We will be studying reversible and irreversible processes in detail later in this course.

2.4 Work, heat and heat capacity

Work, heat and energy have the same unit, called the joule (J). Energy is a thermodynamic property of a system, whereas work and heat are not. Work and heat are meaningful only when a process takes place.

Heat

By now, we all recognise heat as a form of energy. Heat is not the property of a system but it is exchanged between a system and its surroundings during a process, when there is a temperature difference between the two.

Heat can be defined based on the ice-calorimeter. If we place ice in an ice-calorimeter and the stopper is pressed, there will be a rise in the level of H_2O in the capillary and one can read the calibrated capillary. If the reaction mixture is placed in the reaction chamber of the ice-calorimeter and corked, two things may happen. The reaction may absorb heat from the surrounding jar, or the reaction mixture may produce heat. Now, what happens if heat is absorbed? If your answer is that ice will be formed, then you are right. If the reaction mixture produces heat, more ice will melt.

Exercise 2.1

Complete the following:

Assuming that more ice melts,

- 1 g of ice will occupy space than 1 g of H_2O (less/more)
- the volume of the system will (increase/decrease).

Your answer to (a) above will reflect your understanding of the relationship between heat and volume change in a system. If the reaction absorbs heat from the surroundings, there will be a volume increase in the system as a result of ice-formation. There is a change in volume as a result of the quantity of heat that has been transferred between the calorimeter and the reaction chamber.

Heat is a measurable quantity.

Work

Let us now explain the term, *work*, and describe its different kinds. The amount of work which attends a thermodynamic state is very important. The simplest concept of work (W) is defined as the product of the force applied (F) and the distance (x) moved along the direction of the force.

$$W = \text{Force} \times \text{distance} (x)$$

$$W = F \cdot x \quad \dots\dots\dots 2.1$$

Forces have different physical origin, and work can be done in a variety of ways.

1. Gravitational work: When a body of mass m is moved through a height h against gravity, then force is equal to mg and the gravitational work done is mgh .
2. Electrical work: If an electric potential E is applied across a resistance R so that current I flows through it, then work done per second is EI and in t seconds it is equal to EIt .
3. Pressure-volume work: This is a type of mechanical work performed when a system changes its volume against an opposing pressure. This is also known as work of expansion or compression. We will study this in detail in later sections.

Work will be very constantly referred to as pressure-volume work in this unit. The energy gained or lost during heat exchange between the system and its surroundings can be stated in terms of heat capacity values.

Heat capacity

Heat capacity is the heat required to raise the temperature of a body by 1K. If, during the process, the volume of the system remains constant, then it is called *heat capacity at constant volume* (C_v). If the pressure remains unchanged, it is called *heat capacity at constant pressure* (C_p). For one mole of a pure substance, these are called molar heat capacity at constant pressure, C_p and molar heat capacity at constant volume (C_v). Heat capacity per unit mass is called specific heat. The heat

capacities change with temperature. This means that the heat required to change the temperature by 1K is different at different temperatures. However, over small ranges of temperature, these are usually taken as constant. The molar heat capacity and specific heat are intensive properties, whereas heat capacity is an extensive property.

By changing the temperature of a particular system by dT if the heat required is dq_v (at constant volume) or dq_p (at constant pressure), we have

$$C_v = n C_{v,m} = n C_v \frac{dq_v}{dT} \quad \text{..2.2}$$

$$C_p = n C_p = n C_p \frac{dq_p}{dT} \quad \text{..2.3}$$

where n is the amount, i.e. number of moles of the substance constituting the system.

From these equations, it is possible to determine the heat required for a process, by integration over the temperature range T_1 and T_2 . Hence,

$$C_v = \int_{T_1}^{T_2} C_v dT = \int_{T_1}^{T_2} n C_{v,m} dT \quad \text{.....2.4}$$

$$C_p = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} n C_{p,m} dT \quad \text{.....2.5}$$

In later sections, we will study the use of C_p and C_v in the calculation of energy changes. Let us give an example here for the calculation of q_p if n , C_p , T_1 and T_2 are given.

Example 2.1

The equation for the molar heat capacity of butane is $C_m = (19.41 + 0.233T) \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the heat necessary to raise the temperature of 3.00 mol of butane from 298 K to 573 K at constant pressure.

Solution

We have to calculate q_p as per Equation 2.5.

$$C_p = \int_{T_1}^{T_2} n C_p dT$$

where, $T_1 = 298 \text{ K}$

$T_2 = 573 \text{ K}$

$n = 3.00 \text{ mol}$

$C_p = (19.41 + 0.233T) \text{ J mol}^{-1} \text{ K}^{-1}$

$$\begin{aligned} C_p &= \int_{298}^{573} 3.00 (19.41 + 0.233T) dT \\ &= 3.00 \times 19.41 \int_{298}^{573} dT + 3.00 \times 0.233 \int_{298}^{573} T dT \\ &= [3.00 \times 19.41(573-298) + \frac{3.00 \times 0.233}{2} (573^2 - 298^2)] \text{ J} \\ &= 9.97 \times 10^4 \text{ J} \\ &= 99.7 \text{ kJ} \end{aligned}$$

Hence, heat required to raise the temperature of 3.00 mol of butane from 298 K to 573 K is 99.7 kJ.

We will now give two general formulae for integration. These two formulae will be useful throughout this course in working out numericals. In this unit, Formula 1 is used in Example 2.1 and Formula 2 in Example 2.2.

Formula 1

If m is not equal to -1 .

$$\int \frac{dx}{x^{m+1}} = \frac{x^{-m}}{-m} = -\frac{1}{m} x^{-m} = -\frac{1}{m} x^{-(m+1)}$$

where a is a constant.

Formula 2

If m is equal to -1 .

Formula 2 finds use throughout our course (although not in this example).

$$\int \frac{dx}{x} = a \ln \frac{x_2}{x_1}$$

Again, a is a constant. Note that 'ln' stands for logarithm to the base e . Since we use natural logarithm, i.e. logarithm to the base 10 in our calculations, it is better to modify formula 2 as follows:

$$\int \frac{dx}{x} = 2.303 a \log \left(\frac{x_2}{x_1} \right)$$

Note that $\ln x = 2.303 \log x$

Exercise 2.2

The molar heat capacity of ethane at constant pressure is $2.6 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the energy required to heat 3.00 mol of ethane from 305 K to 405 K at constant pressure.

Hints: i) Use Equation 2.5

ii) Integration is to be done as per formula 1 and 1 term in Example 2.1.

At constant pressure, the change in volume of Van der Waals gas, is accompanied by temperature change. Therefore, we can have

$$W = P \Delta V = nR (T_2 - T_1) \dots\dots\dots 2.6$$

$$= nR \Delta T \text{ (does not apply to Vander Waals equation)} \dots\dots\dots 2.7$$

When you compress a gas, applying work on that gaseous system, the sign of work done will be negative. When a gas expands, the volume of the gas will be smaller than the final volume. The change in volume is positive. Therefore, work done is positive. When a system is doing work on the surroundings, the work done will be positive. When work is done by the surroundings on a system, the work done is negative.

Assuming you heat a known amount of water in a beaker, the amount of current passed is known, as well as the work done on it. If the water is heated to boil, as in Fig.2.2 (b), there is the same quantity of heat in the beaker when the water starts boiling. That is, the amount of heat does not increase the content of the beaker.

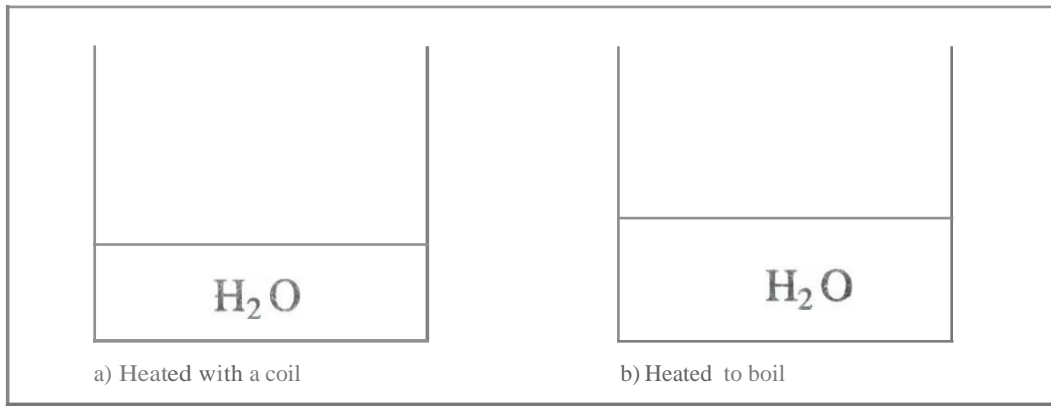


Fig. 2.2

Example 2.2

One mole of an ideal gas is heated at a constant pressure of 101.3 kNm^{-2} , from 273.2 K to 373 K .

- Calculate, in Joules, the work involved.
- If the gas expanded isothermally at 273 K from the pressure of 101.3 kNm^{-2} to some pressure, P , what must be the pressure of the isothermal work that is equal to the work in (a) above?

Solution

$$W = nR(T_2 - T_1)$$

$$= 8314 \frac{\text{Joules}}{\text{Kmol}} (373 - 273) \text{ K} (1 \text{ mole})$$

$$= 8314 \text{ J mol}^{-1}$$

$$\text{b) } W = \int_{V_1}^{V_2} nR \frac{dV}{V}$$

$$= nRT \ln \frac{V_2}{V_1} (1 \text{ mole})$$

$$8314 \text{ J/mole} = \frac{8314 \text{ Joules}}{\text{K-mol}} \times \frac{273 \text{ K} \ln(101.3 \times 10^3)}{P}$$

Since $n = 1 \text{ mole}$, then we have

$$= RT \ln \frac{V_2}{V_1}$$

It is known that: $P_1 V_1 = P_2 V_2$

We can now have $W = nR \ln \frac{P_1}{P_2}$

$$\text{i.e. } \frac{1}{V_1} = \frac{V_2}{V_1}$$

$$8314 \text{ J/mol} = \frac{8314 \text{ Joules}}{\text{Kmol}} \left(\frac{273 \text{ K} \ln(101.3 \times 10^3)}{P} \right)$$

$$P = \frac{8314 \text{ Joules}}{273 \text{ K} \ln(101.3 \times 10^3)} \times \frac{1 \text{ mol}}{8314 \text{ J}}$$

$$P = 273 \ln(101.3 \times 10^3) \times \frac{1 \text{ mol}}{8314 \text{ J}}$$

$$P = 273 (2.303 \ln 101.3 \times 10^3) \times \frac{1 \text{ mol}}{8314 \text{ J}}$$

$$= 6.37 \times 10^7 \text{ Nm}^{-2}$$

2.5 Conclusion

In this unit, we listed different processes and described each of them. In addition, the concepts of heat, work and heat capacity were explained. Some calculations were made on heat capacity and work. In the next unit, we shall be looking at the first Law of Thermodynamics.

2.6 Summary

In this unit, you have learnt that:

- i) work is the product of force and distance;
- ii) types of process are isobaric, isochoric, adiabatic, isothermal and cyclic;
- iii) these processes can be simply classified into two: reversible and irreversible;
- iv) the energy gained or lost during heat exchange between the system and the surroundings, can be stated in terms of heat capacity values;
- v) the molar heat capacity refers to the quantity of heat that is required to raise the temperature of 1 mole of a substance by 1K.

2.7 Tutor-marked assignment

1. Describe the following processes in one sentence:
 - a) Isochoric process
 - b) Adiabatic process
 - c) Isobaric process
2. A gas is expanded from $4.00 \times 10^{-3} \text{ m}^3$ to $8.00 \times 10^{-3} \text{ m}^3$ against a constant pressure of $1.00 \times 10^5 \text{ Pa}$ and it has been used to heat 0.010 kg of water. Calculate the final temperature of water. (Given: initial temperature of water = 296.2 K and C_p for water = $75.2 \text{ J mol}^{-1} \text{ K}^{-1}$).
3. Calculate the heat required to increase the temperature of 1.00 mol of methane from 298 K to 398 K at constant pressure. C_p for methane = $35.3 \text{ J mol}^{-1} \text{ K}^{-1}$.

2.8 References

1. IGNOU (1993), *Chemistry: Thermodynamics: part 4*, New Delhi.
2. Laidler, K. J, and Meiser, J. H, (1982), *Physical Chemistry*, California: The Benjamin/Cummings Publishing Company, Inc.

Unit 3: The first law of thermodynamics

Contents

- 3.1 Introduction
- 3.2 Objectives
- 3.3 The first law of thermodynamics
 - Internal energy
 - Mathematical forms of the first law of thermodynamics
- 3.4 Isothermal expansion
 - Isothermal irreversible process
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- 3.5 Conclusion
- 3.6 Summary
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3.1 Introduction

In Unit 1, we discussed some thermodynamics terminology. In this unit, we will still proceed to make some definitions. The first law of thermodynamics will be explained, with particular reference to isothermal processes.

3.2 Objectives

By the end of this unit, you should be able to:

- i) state the first law of thermodynamics
- ii) describe the internal energy of a system
- iii) calculate the work done on an ideal gas in an isothermal process.

3.3 The first law of thermodynamics

The first law of thermodynamics was first stated in 1840 by Mayer and Helmholtz in Germany, Joule in England, and Colding in Denmark. This law is also known as the *Law of Conservation of Energy*.

The first law of thermodynamics can be stated in any one of the following ways:

1. The energy of an isolated system remains constant.
2. Energy can neither be created nor destroyed, although it can be changed from one form to another.
3. It is not possible to construct a perpetual motion machine that can work endlessly without the expenditure of energy. (Such a machine is known as a *perpetual motion machine of the first kind*).

All the above statements are equivalent to the principle of conservation of energy. These statements point out that the energy of a system will remain constant unless it is disturbed. If, on the other hand, the system interacts with the surroundings, then its energy may change; but then, there will also be an equal and opposite change in the energy of the surroundings. Since work is a form of energy, it is not possible for a machine to do work indefinitely. As soon as its own energy is exhausted, it will require input to continue doing work. The first law of thermodynamics has no theoretical prohibition. Since the law has never been contradicted, its truth is taken for granted.

Einstein, in 1905, showed that matter and energy are equivalent according to the equation,

Internal energy
 This is not a state function. It depends on the path taken from the initial state to the final state. For example, if a system is heated and then cooled, the internal energy will be different from its initial value.

Internal energy

The internal energy of a system is the sum of the kinetic and potential energies of all the particles in the system. It is a state function, meaning it depends only on the state of the system, not on the path taken to reach that state.

The internal energy of a system is a state function. It depends only on the state of the system, not on the path taken to reach that state. For example, if a system is heated and then cooled, the internal energy will be different from its initial value.

internal energy
 of the system. A negative
 of its internal energy.

mathematical form

Mathematical form of the first law of thermodynamics.

The mathematical form of the first law of thermodynamics is given by the equation $dE = dq + dw$, where dE is the change in internal energy, dq is the heat added to the system, and dw is the work done on the system.

$$dE = dq + dw \quad \text{3.2}$$

This equation is for infinitesimal changes. If, however, a system is taken from its initial state to another state by a process in which the heat absorbed is q and work done on the system is w , then the net change in internal energy will be given by

$$\Delta E = E_f - E_i \quad \text{3.3}$$

where E_i and E_f are the initial and final internal energies of the system, and ΔE is the net change.

It is obvious that ΔE can have either negative or positive value, depending on q and w . But once the initial and final states of a system are fixed, ΔE is automatically fixed, no matter what path is adopted in carrying out the process. In other words, internal energy is a state function while heat and work are not. As an example, consider a system taken from the initial state where it has energy, E_i , to the final state having energy, E_f , along different paths I, II and III (Fig. 3.1). Then in all these cases, ΔE is same. If this were not so, then it would have been possible to construct a perpetual motion machine by reaching the final state via a high-energy change path (say, III) and coming back via a low-energy change path (IV), thereby releasing the energy difference for work. Equations 3.2 and 3.3 are mathematical expressions of the first law of thermodynamics.

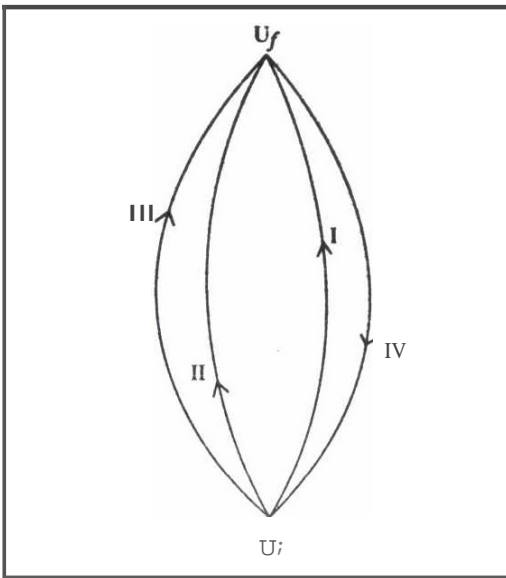


Fig. 3.1 Energy change through different onward paths, I, II and III and return path, IV

Exercise 3.1

Suggest a statement for the first law of thermodynamics, such that Conservation of Mass is not violated.

3.4 Isothermal expansion

In this section, we are going to calculate the work done on the gas in an isothermal process. For this, we must first arrive at a general expression for pressure-volume work done in an infinitesimal process. Suppose that a gas is enclosed in a cylinder fitted with an airtight piston of area A . Assume that pressure of the gas is P and the external pressure is P_{at} which is slightly less than the gas pressure. The gas will expand against an opposing force, which is given by,

$$F = P_{at} \cdot A \tag{3.4}$$

If during expansion, the piston moves through a distance dx , then this small amount of work dw' done by the system is given by,

$$dw' = F dx = P_{at} \cdot A dx \tag{3.5}$$

But $A dx$ is the change in volume of the gas, dV . Hence,

$$dw' = P_{at} \cdot dV \tag{3.6}$$

Thus, the work done by the system by the gas is dw' . Therefore, the work done on the gas is $-dw'$, which we shall denote by dw . Hence, work (dw) done on the system is

$$dw = -P_{at} dV \tag{3.7}$$

Equation 3.7 is a general expression useful in calculating pressure-volume work, whether isothermal or adiabatic process. It can be seen that dw is negative when the gas expands ($dV = +ve$ in expansion and $dV = -ve$ in compression).

We shall now calculate the work of expansion (as also of compression) under isothermal conditions. First, let us take up the work done under isothermal, irreversible conditions.

Isothermal irreversible process

Let us assume that the gas kept in a cylinder expands isothermally and irreversibly, against a constant pressure. This means that:

- i) the gas expands against a constant pressure (P_{at} , is constant);
- ii) there is a considerable difference between the gas pressure (inside the cylinder) and the external pressure;
- iii) the temperature does not change during the process.

Let the initial and final volumes be V_1 and V_2 respectively. The total work done, W , on the system is obtained by integrating Equation 3.7.

$$W = - \int_{V_1}^{V_2} P_{ext} dV = -P_{ext} \int_{V_1}^{V_2} dV \quad \dots\dots\dots 3.8$$

$$= -P_{ext} (V_2 - V_1) = -P_{ext} \Delta V$$

The symbol, ΔV , denotes the total change in volume during the process. Let us work out an example to illustrate the use of Equation 3.8.

Example 3.1

A gas expands from 10m^3 to 12m^3 , against a constant pressure of 1 bar, at 298K. What is the work done on the gas?

Solution

We have to calculate work done under constant pressure using Equation 3.8.

$$\text{Hence, } W = -P_{ext} (V_2 - V_1) = [-1 \times 10^5 \text{ Pa} \times (12\text{m}^3 - 10\text{m}^3)]$$

$$= -2 \times 10^5 \text{ Pa m}^3 \text{ because } 1 \text{ bar} = 1 \times 10^5$$

$$= -2 \times 10^5 \text{ J because } 1 \text{ Pa m}^3 = 1 \text{ J}$$

It can be seen that work done on the system is negative. This means that the system has actually done work equal to $2 \times 10^5 \text{ J}$ during expansion.

It is also possible to calculate the work done under irreversible isothermal conditions, when the external pressure changes continuously. But then, the equation to use is more complex than Equation 3.8. Let us now calculate the work done under isothermal, reversible process.

Isothermal reversible process

We have already mentioned that a reversible process can be carried out when external pressure (P_{ext}) is only infinitesimally different from the gas pressure (P) inside a cylinder. In such a case, $P_{ext} = P$ and hence, Equation 3.7 can be written as,

$$dw = -PdV \quad \dots\dots\dots 3.9$$

The total work done, W , as the gas expands isothermally and reversibly from a volume V_1 to a volume V_2 is then given by integrating Equation 3.9 within limits V_1 and V_2 .

$$W = - \int_{V_1}^{V_2} PdV \quad \dots\dots\dots 3.10$$

Let us assume that the gas behaves ideally. Hence,

$$P = \frac{nRT}{V}$$

Using Equation 3.10, we have

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$= -nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad \dots\dots\dots 3.11$$

$$= -nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{V_1}{V_2} \quad \dots\dots\dots 3.12$$

$$\text{Hence, } W = -2.303 nRT \log \frac{V_2}{V_1} = 2.303 nRT \log \frac{V_1}{V_2} \quad \dots\dots\dots 3.13$$

It can be seen that if V_2 is less than V_1 , then the gas has been compressed and W is positive. Also, the value of W then happens to be the minimum work required for compressing the gas from V_1 to V_2 . Similarly, if V_2 is greater than V_1 , then the gas undergoes expansion and W is negative. This means that work is done by the gas; $-W$ represents the maximum work available through expansion.

Equation 3.13 can also be given in terms of initial and final pressures (P_1 and P_2) of the gas. For an ideal gas temperature,

$$P_1 V_1 = P_2 V_2 \quad \dots\dots\dots 3.14$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \quad \dots\dots\dots 3.15$$

Using Equations 3.13 and 3.15

$$W = -2.303 nRT \log \frac{11}{12} \quad \dots\dots\dots 3.16$$

$$= 2.303 nRT \log \frac{12}{11} \quad \dots\dots\dots 3.17$$

Let us illustrate the use of Equations 3.16. and 3.17

Example 3.2

An ideal gas initially at 3.00×10^2 K and 3.00×10^5 Pa pressure occupies 0.831 volume of space. What is the minimum amount of work required to compress the gas isothermally and reversibly so that the final pressure is 6.00×10^6 Pa?

Solution

$$P_1 = 3.00 \times 10^5 \text{ Pa}; P_2 = 6.00 \times 10^6 \text{ Pa}$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}; T = 3.00 \times 10^2 \text{ K}$$

We have to calculate the value of n (the amount of the gas). In order to use Equation 3.17, the value of n can be found from the initial conditions using the ideal gas equation.

$$n = \frac{PV}{RT} = \frac{3.00 \times 10^5 \text{ Pa} \times 0.831 \text{ m}^3}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.00 \times 10^2 \text{ K}}$$

$$n = 1.00 \times 10^2 \text{ mol}$$

Substituting the values in Equation 3.17, we have

$$W = 2.303 \times 1.00 \times 10^2 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.00 \times 10^2 \text{ K} \log \frac{6.00 \times 10^6}{3.00 \times 10^5}$$

$$= 2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times (6.7782 - 5.4771) \text{ J} \quad \text{(step ii)}$$

$$= 2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times 1.3011 \text{ J} \quad \text{(step iii)}$$

$$W = 7.47 \times 10^5 \text{ J}$$

Exercise 3.2

Using the principles studied above, do this:

A gas expands against vacuum. What is the work done on it?

3.5 Conclusion

In this unit, you have been introduced to the first law of thermodynamics. The main aspects of this unit as follows:

- i) The term internal energy has been defined and discussed;
- ii) The formulae for the calculation of internal energy change in an isothermal process are derived.

3.6 Summary

In this unit, you have learnt that:

- i) the law of conservation of energy is the same as the first law of thermodynamics;
- ii) the work done on the gas in an isothermal process can be expressed as $dw = -P_{ext} dV$

3.7 Tutor-marked assignment

A sample of 0.200 mol of argon expands adiabatically and reversibly, such that the temperature drops from 298 K to 188 K. If the molar heat capacity of argon at constant volume is $12.48 \text{ J mol}^{-1} \text{ K}^{-1}$, calculate the change in internal energy and the work done on the gas.

3.8 Reference

IGNOU (1993), *Chemical Thermodynamics: Physical Chemistry CHE-04*, New Delhi.

Unit 4 Beat of readloo

Contents	
4.1	IN
4.2	Objecw"
4.3	Heat of rea
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4.1 Introduction

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Exampk 4.2

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Solution

According to the equ.ati.M

$2\text{HgO} + 207\text{KJ} \rightarrow 2\text{Hg} + \text{O}_2$
 207 KJ is needed to decompose 2 moles of HgO. For 2 moles of HgO, 207 KJ is used.

Therefore, for 1 mole of HgO, $\frac{207\text{KJ}}{2\text{moles}}$

Therefore, for $\frac{\text{Molar mass}}{216\text{g/mole}}$ mole of HgO, the energy required will be

$$\begin{aligned} & \therefore \frac{207\text{KJ}}{2\text{moles}} \times \frac{2.16\text{g}}{216\text{g/mole}} \\ & = \frac{207\text{KJ}}{2\text{moles}} \times \frac{\text{mole}}{100} \\ & = \frac{2.07\text{KJ}}{2} \\ & = 1.04\text{KJ} \end{aligned}$$

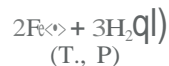
Example 4.3

Another example we can consider is reduction of iron (III) oxide (i.e. Ferric oxide).



This type of experiment, performed in the open laboratory, can exchange heat with the environment and this is enthalpic change. The above equation indicates that this reaction occurs under a condition in which the temperature and pressure are constant.

But when we perform this experiment, there will be a temperature change (i.e. rise from T_1 to $T_1 + \Delta T$).



One can say the first reaction is an adiabatic process and the second is not, because it allows the system to exchange heat with the surroundings and cool to temperature T_1 .

For an adiabatic process, $dq = 0$

$$dH = dq = 0$$

The second step, which is not an adiabatic process,

therefore

$$dH = dq + C_p dT$$

Thus, $dH = C_p dT$

This means that the heat of reaction is the heat exchange with the surroundings, when the reactants at temperature (T_1, P) are transformed to the products at (T_1, P) . For any chemical reaction, we can write ΔH as

$$\Delta H = (H_{\text{products}} - H_{\text{reactants}})$$

The heat of reaction = $\Delta H = H_{\text{products}} - H_{\text{reactants}}$

$$\text{i.e. } \Delta H = [2H_{\text{Fe}(\text{s})} + 3H_{\text{H}_2\text{O}(\text{l})}] - [H_{\text{Fe}_2\text{O}_3(\text{s})} + 3H_{\text{H}_2(\text{g})}]$$

ΔH is referred to as a molar quantity and we should not see it as an absolute quantity as well.

4.4 Heat change under constant volume

Reactions can be carried out under constant volume or under constant pressure conditions. Let us now arrive at an expression useful in calculating the heat change in a system under constant volume conditions.

Assuming that the work done on the system is only pressure-volume work, whereas electrical, magnetic or other types of work are not involved. In an,

$$dE = dq - PdV$$

$$1 \text{ or } dq = dE + PdV$$

If the process is carried out at constant volume, then,

$$dV = PdV = 0$$

$$\text{Hence, } dq = dE$$

For finite changes in internal energy, Equation 4.3 becomes

$$q_v = \Delta E$$

That is, heat absorbed by a system at constant volume is exactly equal to its internal energy change.

Let us try to correlate internal energy change with heat capacity at constant volume assuming that there is no phase change or chemical reaction. From Equations 4.2 and 4.3,

$$dE = C_v dT = n C_v dT$$

This holds good for n mol of an ideal gas.

Equation 4.4 can be written as,

$$dE = n C_v dT$$

i.e. heat capacity at constant volume is equal to change in internal energy per unit rise in temperature, at constant volume.

In order to obtain ΔE when an ideal gas is heated from temperature T_1 to T_2 at constant volume, the integrated form of Equation 4.4 is to be used.

$$E = \int_{T_1}^{T_2} C_v dT = \int_{T_1}^{T_2} n C_v dT$$

Hence, by knowing C_v over the temperatures T_1 and T_2 it is possible to obtain the value of ΔE .

We have defined C_v through Equation 4.4, what about C_p ? Is there some thermodynamic property to which C_p can be related in a similar way? For this purpose, we shall define the enthalpy, in Unit 5.

Exercise 4.1

1. Calculate the change in internal energy of an ideal gas undergoing isothermal compression, as discussed in Example 4.2.
2. What is the value of q for the same case?

4.5 Conclusion

In this unit, you have been introduced to the heat of reaction in an adiabatic process and under constant volume. In the next unit, we shall continue with topics in thermodynamics by examining the concept of enthalpy and enthalpy changes.

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Unit 5: Enthalpy changes

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- 5.1 Introduction
- 5.2 Objectives
- 5.3 Enthalpy and enthalpy changes
- 5.4 Relationship between C_p and C_v of an ideal gas
- 5.5 Adiabatic expansion
- 5.6 The Joule-Thomson effect
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- 5.9 Tutor-marked assignment
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5.1 Introduction

In the previous units of this course, we stressed the importance of energy in chemical reactions. It has been proved theoretically and practically that relationships exist between energy and chemical reactions. In Unit 3, you learnt that the first law of thermodynamics is the same as the law of conservation of mass. When the mass of a substance is destroyed, energy is produced. In this unit, the significance of enthalpy and enthalpy change of a system will be discussed. Towards the end of the unit, you will also study the importance of the Joule-Thomson effect.

5.2 Objectives

By the end of this unit, you should be able to:

- i) define the term *enthalpy*;
- ii) state the significance of enthalpy and enthalpy change of a system;
- iii) derive the relationships between C_p and C_v of an ideal gas;
- iv) explain the Joule-Thomson effect.

5.3 Enthalpy and enthalpy changes

Before we consider the concept of enthalpy, let us quickly examine some applications of the first law of thermodynamics again. In a constant volume process,

$$dV=0$$

And this means, therefore, that

$$W = PdV = 0 \quad \dots\dots\dots 5.1$$

Therefore,

$$q_v = dE \text{ (internal energy)} \quad \dots\dots\dots 5.2$$

Assuming it is a constant pressure process, work is given by

$$W = PdV \quad \dots\dots\dots 5.3$$

$$dE = q - W = q - PdV$$

$$q_p = dE + PdV \quad \dots\dots\dots 5.4$$

$$q_p = E + PV \quad \dots\dots\dots 5.5$$

$(E + PdV)$ is another state function. You may need to go over sections 4.3 and 4.4 of Unit 4. This state function $E + PdV$ depends on the initial and final states of the system but not on the path.

$$E + PdV \text{ is called } \mathbf{enthalpy} \quad \dots\dots\dots 5.6$$

Thus, the enthalpy of a system is defined by the relation

$$H = E + PV \quad \dots\dots\dots 5.7$$

Where E, P and V are the internal energy, pressure and volume of the system. Since E, P and V are state variables, H is also a state function. This means that the enthalpy of a system in a particular state is completely independent of the manner in which that state has been achieved. If H_1 and H_2 are the enthalpies of the initial and final states of a system, then the enthalpy change accompanying the process is given by,

$$\Delta H = H_2 - H_1 \quad \dots\dots\dots 5.8$$

$$= (E_2 + P_2 V_2) - (E_1 + P_1 V_1) \quad \dots\dots\dots 5.9$$

$$= \Delta E + (P_2 V_2 - P_1 V_1)$$

In the case of a constant pressure process $P_1 = P_2 = P$. Equation 5.9 can be written as,

$$\Delta H = \Delta E + P(\Delta V)$$

Rewriting Equation 4.2 of Unit 4 for a finite change, we get

$$q_p = \Delta E + P \Delta V \quad \dots\dots\dots 5.11$$

Using this equation in Equation 5.10, $q_p = \Delta H$ 5.12

The subscript p in q_p stands for the constant pressure condition.

In other words, the enthalpy change is equal to the heat absorbed by the system at constant pressure.

For a small change in enthalpy, we can write

$$dq_p = dH \quad \dots\dots\dots 5.13$$

Using Equation 4.4 in Unit 4 and assuming that there is no phase change or chemical reaction, we have,

$$dH = C_p dT = n C_p dT \quad \dots\dots\dots 5.14$$

In order to obtain ΔH value when an ideal gas is heated from temperature T_1 to T_2 at constant pressure, the integrated form of Equation 5.14 is to be used.

$$\Delta H = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} n C_p dT \quad \dots\dots\dots 5.15$$

Consider a change in state of a system of

$$\begin{aligned} \text{Initial state, } H_1 &= f_1 + P_1 V_1 \\ \text{Final state, } H_2 &= E_2 + P_2 V_2 \\ \therefore H_2 - H_1 &= dH = dE + d(PV) \end{aligned}$$

At constant pressure

$$dH = dE + PdV$$

For an ideal gas,

$$dH = dE + dnRT \text{ at constant temperature.}$$

The unit of R depends on the unit of energy being used. You should not forget that SI units also apply here. Table 5.1 below shows the units of energy and R for any conversion you may require in your calculation.

Unit of energy	Unit of R
Cal	1.987 Cal mol ⁻¹ K ⁻¹
Joules	8.314 J mol ⁻¹ K ⁻¹
Lit-atm	0.08205 Liter-atm/mol.K

Table 5.1

Example 5.1

A heat input of 40.59 kJ is required to vapourise 1 mole of water at 101.3 kN m⁻² pressure at 373.15 K.

a) What are the dH and dE for the process?

What are the dH and dE for the inverse process in which one mole of steam condenses to water at 373.15 K and at 101.3 kN m⁻²?

Solution

a) $dH = q_p$

$$\begin{aligned} PV &= P(V_2 - V_1) \\ &= PV = RT \\ &= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} (373.15 \text{ K}) \\ &= 3102.3 \text{ J mol}^{-1} \\ &= 3.102 \text{ kJ mol}^{-1} \end{aligned}$$

$$dH = dE + PdV$$

$$\begin{aligned} dE &= 40.59 - 3.102 \text{ kJ mol}^{-1} \\ &= 37.49 \text{ kJ mol}^{-1} \end{aligned}$$

b) $dH = -(q)$,

$$= -40.59 \text{ kJ mol}^{-1}$$

$$PdV = RT = -3.102 \text{ kJ mol}^{-1}$$

$$\text{therefore, } dE = dH - RT$$

$$= -40.59 \text{ kJ mol}^{-1} - (-3.102 \text{ kJ mol}^{-1})$$

$$= -40.59 + 3.102 \text{ kJ mol}^{-1}$$

$$= -37.49 \text{ kJ mol}^{-1}$$

Since many laboratory processes are carried out at constant pressure (atmospheric pressure), the enthalpy change of a system is of great significance. It must be noted that since the absolute value of the internal energy of a system is not known, it is also impossible to know the absolute enthalpy of the system. Fortunately, for most processes, we are only concerned with the changes in enthalpy which may be measured by taking any suitable reference states of elements. Those processes in which heat is supplied to the system are called endothermic processes and ΔH is given a positive sign. In exothermic processes (in which heat is evolved), ΔH is negative.

Enthalpy changes connected with certain typical processes are given special names. For example, enthalpy of vapourisation or evaporation is the enthalpy change accompanying the conversion of one mole of a liquid to its vapour. Similarly, enthalpy of fusion or sublimation is the enthalpy change accompanying fusion or sublimation of one mole of a substance. For a chemical reaction, the enthalpy of reaction is the difference in the enthalpies of the products and the reactants as per the stoichiometry given in the chemical equation. We shall study enthalpy changes in detail in the next unit.

5.4 Relationship between C_p and C_v of an ideal gas

The internal energy of an ideal gas depends only on its temperature and is independent of pressure and volume. This is quite understandable because in an ideal gas, there are no intermolecular interactions, and so, no attractive or repulsive forces have to be overcome during expansion. However, the enthalpy of the gas changes considerably when it expands or contracts.

For one mole of an ideal gas,

$$H = E + PV = E + RT \dots\dots\dots 5.16$$

On differentiating, we get

$$dH = dE + RdT \text{ (because } R \text{ is a constant)}$$

Using Equations 4.4 of Unit 4 and 5.14 (for one mole of an ideal gas)

$$C_p dT = C_v dT + RdT$$

$$C_p = C_v + R \dots\dots\dots 5.17$$

And hence, $C_p - C_v = R \dots\dots\dots 5.18$

Also, for n mole, $C_p - C_v = nR \dots\dots\dots 5.19$

This means that C_p is always greater than C_v for an ideal gas. This is because when the temperature of a gas is raised at a constant pressure, there will be expansion of the gas. This will require some extra amount of heat (as compared to heating an ideal gas under a constant volume condition). Hence, more heat will be required to raise the temperature of the gas through 1 K under constant pressure conditions than under constant volume.

5.5 Adiabatic expansion

In Unit 2, adiabatic process was referred to as one in which no heat is absorbed or evolved by the system. The heat capacity is, therefore, zero. In section 4.4 of Unit 4, we discussed the work done in an isothermal process. Let us now study how work is calculated in an adiabatic process.

In an adiabatic process, heat absorbed is zero, i.e. $dq = 0$.

Hence, from Equation 4.2 of Unit 4, $dE = 0 + dW = dW \dots\dots\dots 5.20$

But for one mole of an ideal gas, dE is given by Equation 4.4 in Unit 4 as

$$dE = C_v dT$$

During expansion, dW and hence, dE are negative. That is, as the system does expansion work, its internal energy decreases. This again, according to Equation 4.4 of Unit 4 means that dT is negative, i.e. temperature decreases. In other words, during adiabatic expansion, the temperature of the system decreases. This principle is used in Claude's method of liquefaction of gases.

Let us now study the temperature-volume relationship in a reversible adiabatic process. This

Will help us in determining the final temperature of a system undergoing adiabatic expansion or compression.

Temperature-volume relationship in a reversible adiabatic process

According to Equation 5.20, $dE = dW$.

Substituting for dW and dE from Equations 4.1 and 4.4 of Unit 4, we get for one mole of an ideal gas,

$$C_v dT = -PdV \quad \dots \dots \dots 5.21$$

For one mole of an ideal gas,

$$P = \frac{RT}{V}$$

Using this relationship in Equation 5.21, we get

$$C_v dT = \frac{-RTdV}{V} \quad \dots \dots \dots 5.22$$

Rearranging, we get

$$\frac{C_v}{T} dT = -R \frac{dV}{V} \quad \dots \dots \dots 5.23$$

Integrating Equation 5.23 between temperature limits T_1 and T_2 and volume limits V_1 and V_2 , we

$$\int_{T_1}^{T_2} \frac{C_v}{T} dT = -R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

$$= (C_p - C_v) \ln \frac{V_1}{V_2} \quad \dots \dots \dots \text{(using Equation 5.24)}$$

$$\ln \frac{T_2}{T_1} = \left(\frac{C_p}{C_v} - 1 \right) \ln \frac{V_1}{V_2}$$

$$= (y - 1) \ln \frac{V_1}{V_2} \quad \dots \dots \dots 5.25$$

Where y is the ratio of the molar heat capacity $\frac{C_p}{C_v}$

Taking antilogarithms of both sides, we have

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{y-1} \quad \dots \dots \dots 5.26$$

or $T_2 V_2^{y-1} = T_1 V_1^{y-1}$ or $T V^{y-1} = \text{Constant}$

This equation gives the volume-temperature relationship in a reversible adiabatic process. Also, we can get the pressure-temperature relationship knowing that, for an ideal gas,

$$\frac{T_1 V_1}{T_2 V_2} = \frac{P_2 T_1}{P_1 T_2}$$

$$\frac{V_1}{V_2} = \frac{P_2 T_1}{P_1 T_2} \quad \dots \dots \dots 5.27$$

Substituting this in Equation 5.26, we have

$$P_1 V_1^\gamma = P_2 V_2^\gamma \quad (5.28)$$

For any reversible adiabatic expansion, T_2 can be determined using Equation 5.26 or 5.28.

Also, it is possible to get the pressure-volume relationship in a reversible adiabatic process using the rearranged form of Equation 5.27, in Equation 5.26 as follows:

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1}$$

$$\frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

Cross-multiplying the terms,

$$P_2 V_2^\gamma = P_1 V_1^\gamma \quad \text{or}$$

$$P V^\gamma = \text{Constant} \quad (5.29)$$

Equation 5.29 describes the pressure-volume relationship for an ideal gas undergoing reversible adiabatic expansion (or compression).

ΔE and W in a reversible adiabatic process

The quantities dE and dW for an adiabatic process are related by Equation 5.20. Using this equation and Equation 5.21, we get for 1 mol of a gas,

$$dE = dW = C dT$$

In the case of an ideal gas

$$dE = dW = n C_v dT \quad (5.30)$$

The work done on the gas during an adiabatic expansion (W) and also the change in internal energy (ΔE) can be calculated by integrating Equation 5.20 within temperature limits T_1 and T_2 :

$$\Delta E = W = n C_v \int_{T_1}^{T_2} dT$$

$$= n C_v (T_2 - T_1) \quad (5.31)$$

Hence, ΔE and W can be calculated when n , C_v , T_1 , and T_2 are known.

Irreversible adiabatic expansion

If the work is done irreversibly and adiabatically, then the work done on the system is given by Equation 3.8 of Unit 3.

$$W = -P_{ext} \Delta V \dots\dots\dots 5.32$$

As in the case of irreversible isothermal process, we can arrive at the temperature-volume relationship for an adiabatic irreversible process as follows.

Using Equation 5.32 in Equation 5.31, derive an equation 5.33. Your instructor will lead you.

Hence, Equation 5.33 is useful in calculating the final temperature of an ideal gas undergoing adiabatic irreversible expansion while Equation 5.26 or 5.28 is of help in an adiabatic reversible process.

Exercise 5.1

Using Equation 5.33, show that against zero external pressure, the expansion is simultaneously adiabatic and isothermal.

5.6 The Joule-Thomson effect

Our discussion so far has centred around ideal gases. It was mentioned earlier that the internal energy of an ideal gas is independent of pressure or volume. This, however, is not true for real gas since intermolecular forces exist among their molecules. So, when a real gas is expanded, work has to be done in overcoming these forces. If no energy is supplied from an external source, then the internal energy of the gas is used up in doing this work. This results in a fall in the temperature of the gas. However, some gases show a rise in temperature. This phenomenon of change in temperature when a gas is made to expand adiabatically from a high pressure region to a low pressure region, is known as the Joule-Thomson effect. The phenomenon can be understood if we consider the apparatus shown in Fig. 5.1. It consists of an insulated tube fitted with a porous plug and two airtight pistons, one on either side of the plug. The gas is kept under pressures P_1 and P_2 in the two compartments. Note that P_1 is greater than P_2 . The left-hand-side piston is then slowly pushed inwards so that, without changing the value of P_1 , a volume V_1 of gas is introduced through the plug into the other compartment. This results in the outward movement of the other piston and also its volume increase. Let the final volume be V_2 . Accurate temperature measurements are made in both compartments.

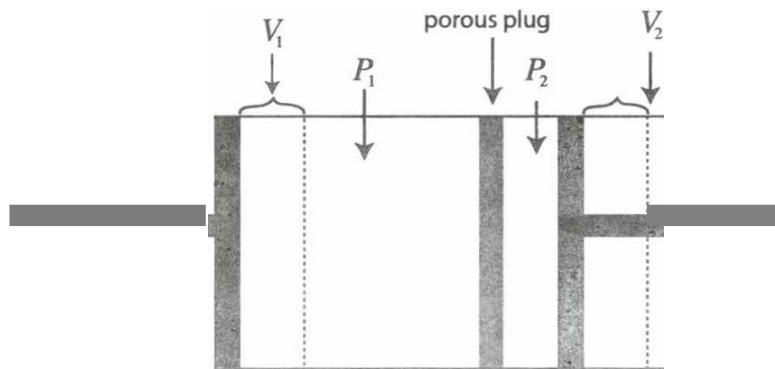


Fig. 5.1 The joule-Thomson experiment

The net work done on the system is given by

$$W = -(P_2 V_2 - P_1 V_1) = P_1 V_1 - P_2 V_2 \quad \dots\dots\dots 5.34$$

It should be remembered that $P_2 V_2$ is the work done by the system and $P_1 V_1$ is the work done on it. The conditions are adiabatic and so $q = 0$. For a finite process, Equations 5.20 and 5.34 can be combined and written as,

$$dE = W = (P_1 V_1 - P_2 V_2) \quad \dots\dots\dots 5.35$$

$$\text{or } dE + (P_2 V_2 - P_1 V_1) = 0 \quad \dots\dots\dots 5.36$$

Using Equation 5.9, $dE + (P_2 V_2 - P_1 V_1) = dH$

From Equations 5.9 and 5.36, we note that

$$dH = 0 \quad \dots\dots\dots 5.37$$

Hence, in the Joule-Thomson experiment, $dH = 0$ or enthalpy is constant.

Since in the Joule-Thomson experiment, we measure the temperature change with change in pressure at constant enthalpy, we define the Joule-Thomson coefficient, μ_J , as

$$\mu_J = \left(\frac{\partial T}{\partial P} \right)_H \quad \dots\dots\dots 5.38$$

If it is positive, expansion causes cooling and if it is negative, expansion causes heating. But if it is equal to zero, there is neither cooling nor heating due to Joule-Thomson expansion. The temperature at which μ_J is 0 is called the inversion temperature (T_i) of the gas. If a gas is expanded above its inversion temperature, it is heated. If it is expanded below its inversion temperature, it is cooled. In order to decrease the temperature of a gas and then to liquefy by the Joule-Thomson process, it is essential to bring its temperature below its inversion temperature. A detailed study of the Joule-Thomson effect is made in Module 3 of the course on thermodynamics and statistical mechanics.

The inversion temperature of hydrogen gas is well below the room temperature. Therefore, it is dangerous to open a compressed hydrogen gas cylinder under atmospheric conditions. As hydrogen gas is released from the cylinder, it expands, gets heated and also combines with oxygen present in the air. The latter reaction causes an explosion.

5.7 Conclusion

In this unit, we discussed the concept of enthalpy and enthalpy changes. The formulae for calculating work and internal energy in an adiabatic process were derived. The Joule-Thomson experiment was also described and its importance in the liquefaction of gases was indicated.

5.8 Summary

In this unit, you have learnt that:

- i) $E + PV$ is called enthalpy and is denoted by $H = E + PV$;
- ii) Joule-Thomson measured the temperature change in the Joule-Thomson experiment and found it to be zero;
- iii) the temperature at which the Joule-Thomson coefficient is zero for a gas is called inversion temperature;
- iv) the inversion temperatures of Helium and H_2 differ from those of other gases because they are above the upper inversion temperature;
- v) the principle of Joule-Thomson experiment can be used for the liquefaction of gases.

5.9 Tutor-marked assignment

According to the equipartition principle, the internal energy of n mol of Helium gas is $\frac{3}{2} nRT$. Find its C_P and C_V values. Assume that Helium behaves ideally.

5.10 Reference

IGNOU (1993), *Chemical Thermodynamics; Physical Chemistry CHE-04*; New Delhi

Module 2: Thermochemistry I

Unit 6: Standard enthalpy of formation

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- 6.1 Introduction
- 6.2 Objectives
- 6.3 Relationship between ΔU and ΔH
- 6.4 Standard enthalpy of formation
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6.1 Introduction

The branch of science dealing with heat changes during chemical reactions is known as Thermochemistry. In this unit, we shall deal with the heat change accompanying a chemical reaction when it is carried out under a constant volume or constant pressure. We shall define the standard enthalpy of formation.

6.2 Objectives

By the end of this unit, you should be able to:

- i) derive the relationship between ΔU and ΔH and make calculations based on this relationship;
- ii) define the standard enthalpy of formation.

6.3 Relationship between ΔU and ΔH

A chemical reaction can be carried out in two ways:

- i) in a closed vessel, so that there is no volume change, and
- ii) in a pressure-regulated vessel, so that there is no pressure change.

Accordingly, the heat change accompanying a reaction can also be measured in two ways: heat change at constant volume (q_v) and heat change at constant pressure (q_p).

From Equations 4.3 of Unit 4 and 5.12 of Unit 5, $q_v = \Delta U$ and $q_p = \Delta H$.

In thermochemistry, the enthalpy change accompanying a chemical reaction is called the reaction enthalpy and is denoted by the symbol $\Delta_r H$. Similarly, the internal energy change accompanying a chemical reaction is given the symbol $\Delta_r U$. The subscript r after the Δ sign indicates reaction. To denote formation, combustion and vaporisation processes, the subscripts used are f , c and v , respectively. As in the case of Equation 4.20 of Unit 4 and Equation 5.12 of Unit 5 respectively, we can write,

$$q_p = \Delta H \quad \text{..... 6.1}$$

and

$$dq_p = 0, \Delta H \quad \text{..... 6.2}$$

The significance of ΔU and ΔH can be explained by the following equations:

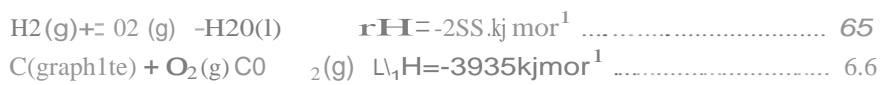
$$\Delta U = \dots, -E_{\text{e-a}} \quad \text{..... 6.3}$$

$$\Delta H = \Delta U + P\Delta V \quad \text{..... 6.4}$$

Since most reactions are carried out at a constant pressure, ΔH is more commonly used than ΔU .

Thermochemical equations

In a thermochemical equation, in addition to the chemical reaction, the physical states of the various chemical species and the energy change are also specified. For example,



are thermochemical equations. In such equations, s, l and g, refer to solid, liquid and gaseous states respectively. If a substance can exist in various allotropic forms, the particular form must be mentioned.

Relationship between ΔU and ΔH

If in a chemical reaction, the enthalpy of the system changes from H_1 to H_2 , and if P_1, V_1 and P_2, V_2 are the corresponding internal energies, pressures and volumes, then,

$$\Delta H = \Delta U + P\Delta V \quad \text{..... 6.7}$$

and

$$\Delta H = \Delta U + P\Delta V \quad \text{..... 6.8}$$

$$\Delta_r H = H_2 - H_1 = E_2 + P_2 V_2 - (E_1 + P_1 V_1) = E_2 - E_1 + (P_2 V_2 - P_1 V_1)$$

$$\text{Hence, } \Delta H = \Delta U + (P_2 V_2 - P_1 V_1) \quad \text{..... 6.9}$$

At constant pressure ($P_1 = P_2 = P$),

$$\Delta H = \Delta U + (P V_2 - P V_1) = \Delta U + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V \quad \text{..... 6.10}$$

Using Equations 6.1 and 6.2, Equation 6.10 becomes

$$dq_p = q_p + P\Delta V \quad \text{..... 6.11}$$

If we assume that all gaseous reactants and products are ideal and that there are n_1 and n_2 moles of gaseous reactants and products, respectively, then,

$$P_1 V_1 = n_1 RT \quad \text{and} \quad P_2 V_2 = n_2 RT$$

Hence, $P_2 V_2 - P_1 V_1 = (n_2 - n_1) RT$
 Since pressure is constant,

$$P(V_2 - V_1) = P\Delta V = (n_2 - n_1) RT \quad \text{..... 6.12}$$

Replacing $(-n_p)$ by Δn_g to represent the change in the number of moles of gaseous species in Equation 6.12,

$$PAV = t.n.RT \quad \dots\dots\dots 6.13$$

Using this in Equation 6.11,

$$qp = q_p + \Delta n_g RT \quad \dots\dots\dots 6.14$$

$$\text{or } \Delta H = \Delta H_f + \Delta n_g RT \quad \dots\dots\dots 6.15$$

The subscript Δn_g signifies that only the gaseous reactants and products are considered in the calculation of Δn_g . It may be noted that Δn_g can be:

- i) positive, if the number of moles of gaseous products is more than those of gaseous reactants;
- ii) negative, if the number of moles of gaseous reactants is more than those of gaseous products;
- iii) zero, if $\Delta n_g = 0$.

For example, consider the following reactions:



In Equation 6.16, $\Delta n_g = (0 - (1 + \frac{1}{2})) = -\frac{3}{2}$; there are no gaseous products, but one mole of hydrogen and half a mole of oxygen are present as gaseous reactants.

In Equation 6.17, $\Delta n_g = (1 - 1) = 0$, since there is one mole each of gaseous reactant and product.

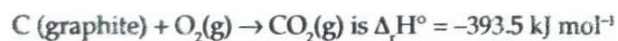
Exercise 6.1

Calculate Δn_g for the following reactions:



6.4 Standard enthalpy of formation

Now let us discuss the standard enthalpy of formation of chemical reactions. The standard enthalpy of formation of a compound is the enthalpy change accompanying the formation of one mole of the compound from its elements in their most stable state. All substances being in their standard states (1 bar pressure and any specified temperature). The standard enthalpy of formation is denoted by $\Delta_f H^\circ$. The superscript \circ indicates the standard state and the subscript f denotes formation reaction. Although, we do not know the absolute enthalpy of the compound, we know its relative enthalpy with respect to the elements from which it is formed. Therefore, we adopt an arbitrary convention that the standard enthalpy of formation of all elements is zero at any specific temperature at 1 bar. An element shows allotropy or exists in different phases, then the enthalpy is taken as zero for the most stable allotrope or phase. Phosphorus is an exception (yellow phosphorus is taken as standard). As a result of this, the enthalpy of any substance in its standard state is equal to $\Delta_f H^\circ$, the enthalpy change of the reaction in which one mole of the substance is formed from the elements in their standard state. For example, the enthalpy of the reaction:



Thus, we have $\Delta_f H^\circ = \Delta_f H^\circ (\text{CO}_2) - \Delta_f H^\circ (\text{graphite}) - \Delta_f H^\circ (\text{O}_2)$

$$= \Delta_f H^\circ (\text{CO}_2) - 0 - 0 = \Delta_f H^\circ (\text{CO}_2)$$

Therefore, the standard enthalpy of formation for CO_2 is equal to $\Delta_f H^\circ$ which is in turn equal to $-393.5 \text{ kJ mol}^{-1}$. If the temperature also has to be indicated, then it is shown in brackets. Thus, $\Delta_f H^\circ$ (298.15 K) means standard enthalpy of formation at 1 bar and 298.15 K. Most of the data are available at 298.15 K in thermodynamic tables. Standard enthalpy of formation of some substances are given in Table 6.1.

Table 6.1: Standard enthalpy of formation of some selected substances at 298.15 K

Substance	$\Delta_f H^\circ$ (298.15 K) kJ mol ⁻¹	Substance	$\Delta_f H^\circ$ (298.15 K) kJ mol ⁻¹
H ₂ (l)	-285.8	O ₂ (g)	-187.8
H ₂ (g)	-241.6	N ₂ (g)	+50.6
CO ₂	-393.5	N ₂ H ₄	+33.2
NH ₃ (g)	-46.1	NO ₂ (g)	+9.2
CH ₄ (g)	-74.81	N ₂ O(g)	-411.2
C ₂ H ₆ (g)	-84.68	NaCl(s)	-436.8
CH ₃ OH(l)	-238.7	KCl(s)	-1268.0
C ₆ H ₆ (l)	+49.0	Glucose(s)	

It is not always possible to get the heat of formation from direct reaction between elements that form compounds simply because:

- i) the reaction does not go into completion;
- ii) there are side reactions;
- iii) the compounds obtained are not pure enough.

We should remember that there is the problem of determining the heat of formation. Sometimes it involves finding a suitable chemical reaction from its compound.

Calculation of reaction enthalpies

It is possible to calculate standard reaction enthalpies using thermodynamic tables such as Table 6.1. The principle is that,

$$\Delta_r H^\circ = (\text{Sum of } \Delta_f H^\circ \text{ values of products}) - (\text{Sum of } \Delta_f H^\circ \text{ values of reactants}) \dots\dots\dots 6.18$$

This relationship can be explained using the general reaction of the following type:



Where p, q, r and s are the stoichiometric coefficients, and A, B, C and D are reactants and products. Let the standard enthalpies of formation of A, B, C and D be represented by $\Delta_f H^\circ$ (A), $\Delta_f H^\circ$ (B), $\Delta_f H^\circ$ (C), and $\Delta_f H^\circ$ (D), respectively. The standard reaction enthalpy for the reaction mentioned in Equation 6.19 is given by,

$$\Delta_r H^\circ = (r \Delta_f H^\circ (C) + s \Delta_f H^\circ (D)) - (p \Delta_f H^\circ (A) + q \Delta_f H^\circ (B)) \dots\dots\dots 6.20$$

Let us illustrate the calculation of $\Delta_r H^\circ$ using an example.

Example 6.1

For the reaction given below, calculate $\Delta_r H^\circ$ at 298.15 K.



Solution

Given that: $\Delta_f H^\circ$ values of propene, carbon dioxide and water at 298.15 K are 20.42, -393.5 and -285.8 kJ mol⁻¹, respectively.

$$\begin{aligned}\Delta_r H^\circ &= (3 \Delta_f H^\circ(\text{CO}_2) + 3 \Delta_f H^\circ(\text{H}_2\text{O})) - (\Delta_f H^\circ(\text{C}_3\text{H}_6) + 9 \Delta_f H^\circ(\text{O}_2)) \\ &= 3 \times (-393.5) + 3 \times (-285.8) - (1 \times 20.42) \quad (\text{since the standard enthalpy of formation of oxygen is zero}). \\ \Delta_r H^\circ &= -2058 \text{ kJ}\end{aligned}$$

Hence, we are in a position to calculate $\Delta_r H^\circ$ using $\Delta_f H^\circ$ values.

Enthalpy is a state property. Its value changes by the same amount irrespective of the path taken from reactants to the products. Hence, it is possible to calculate $\Delta_r H^\circ$ of a reaction from a sequence of reactions. This is generalised as Hess's law of constant heat summation. We shall study this law in the next unit.

Exercise 6.2

Express the standard reaction enthalpy of the reaction,



in terms of the standard enthalpies of formation of the components.

6.5 Conclusion

In this unit, some of the aspects of thermochemistry have been discussed. Specifically, the relationship between $\Delta_r E$ and $\Delta_r H$ has been derived and its use in the calculation of internal energy and enthalpy change has been indicated. We also defined the standard enthalpy of formation and the relationship between standard enthalpies of formation of substances and standard enthalpies of reactions with examples.

6.6 Summary

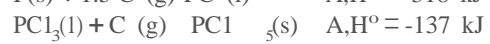
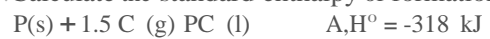
In this unit, you have learnt that:

- enthalpy change ($\Delta_r H$) is the heat absorbed in a process occurring at constant pressure;
- the enthalpy change which occurs when 1 mole of a compound in its standard state is formed from its elements in their standard states is called the standard enthalpy of formation.

6.7 Tutor-marked assignment

- For the reaction $\text{Fe}_2\text{O}_3(\text{s}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{Fe}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$, $\Delta_r H$ at 298 K is -35.1 kJ. What will be the enthalpy of reaction at 375 K, if the difference between the sum of the C_p 's of the products and of the reactants is 85.7 JK⁻¹, and it is independent of temperature?
- Using Table 6.1 for the standard enthalpies of formation for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, calculate the standard enthalpy of formation for naphthalene, if its standard enthalpy of combustion is -5153 kJ mol⁻¹.
- The standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ at 298 K is -285.8 kJ mol⁻¹. Calculate the standard internal energy change [$\Delta_r U$ (H_2O)] for the formation of water at 298 K.

4. Calculate the standard enthalpy of formation of $\text{PCl}_5(\text{s})$, using the following data:



6.8 Reference

IGNOU (1993), *Chemical Thermodynamics: Physical Chemistry CHE-04*, New Delhi.

Unit 7: Enthalpy changes in different processes and reactions

Contents

- 7.1 Introduction
- 7.2 Objectives
- 7.3 Hess's law of constant heat summation
- 7.4 Enthalpy changes in different processes and reactions
- 7.5 Experimental determination of enthalpy of combustion
- 7.6 Conclusion
- 7.7 Summary
- 7.8 Tutor-marked assignment
- 7.9 Reference

7.1 Introduction

We saw in Unit 6 that thermochemistry is a branch of science that deals with heat changes during chemical reactions. In this unit, we shall examine enthalpy changes in different chemical reactions. Finally, we will list some of the applications of Hess's law of constant heat summation.

7.2 Objectives

By the end of this unit, you should be able to:

- i) calculate the enthalpy of a reaction using enthalpies of formation of compounds;
- ii) describe the experimental method for determining the enthalpy of combustion;
- iii) state Hess's law of constant heat summation and explain its significance.

7.3 Hess's law of constant heat summation

It is good to note that the principle of additivity is called Hess's law. Hess's law states that: the standard enthalpy change for a reaction is the sum of the standard enthalpies of a sequence of reactions (at the same temperature and pressure). The overall reaction should be capable of being represented by the given sequence of reactions.

Hess's law is a direct consequence of the law of conservation of energy. It is not necessary that every reaction in the given sequence should be conducted in the laboratory. A particular reaction can also be imaginary. The only requirement is that the chemical reactions in the sequence must balance and add up to the equation for a particular reaction. Also, Hess's law enables arithmetic operations to be performed on chemical equations. This law is helpful in calculating enthalpies of reactions which cannot be experimentally determined. We only need to select a correct sequence of reactions. The use of Hess's law in calculating the enthalpies of some reactions is shown in Examples 7.1 and 7.2.

Example 7.1

Conversion of graphite to diamond



Solution

Subtracting, we get

$$\text{C (graphite)} - \text{C (diamond)} = 0 \text{ or } \text{C (graphite)} = \text{C (diamond)}, \text{ and } \Delta H = \Delta H_1 - \Delta H_2 \\ = -393.5 \text{ kJ} - (-395.4 \text{ kJ}) = 1.9 \text{ kJ}$$

Hence, we can find
 $\Delta H_f^\circ(\text{C (diamond)}) - \Delta H_f^\circ(\text{C (graphite)}) = 1.9 \text{ kJ mol}^{-1}$

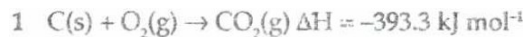
Example 7.2

Carbon(s) reacting with $\text{H}_2(\text{g})$ to give $\text{CH}_4(\text{g})$

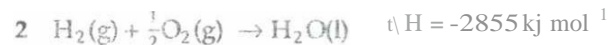
Solution

$\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$. (It is important to note that side products are formed, e.g. CO .)

Hence, we can perform an oxidation reaction on graphite, which can occur easily and also another oxidation reaction on hydrogen.



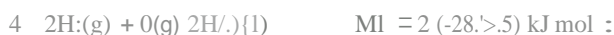
In excess oxygen the reaction goes to completion.



It is also possible for us to burn $\text{CH}_4(\text{g})$.



Since enthalpy is an extensive property of a system, we multiply Equation 2 by 2.



If we add Equations 1 and 4, and subtract Equation 3 from it, we obtain the final equation:
 $\text{C(s)} + 2\text{H}_2(\text{g}) \rightarrow \text{CH}_4(\text{g})$

Therefore, $\Delta H_f^\circ = -393.3 \text{ kJ mol}^{-1} + 2(-285.5 \text{ kJ mol}^{-1}) - (-889.5 \text{ kJ mol}^{-1})$

$$= -74.8 \text{ kJ mol}^{-1}$$

This is the heat of formation of $\text{CH}_4(\text{g})$. The standard enthalpy for compounds is also called heat of formation since the compound is formed from the elements.

Exercise 7.1

Calculate $\Delta_r H^\circ$ for the reaction $\text{C (graphite)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO(g)}$ at 298 K using the following thermochemical equations:



7.4 Enthalpy changes in different processes and reactions

Enthalpy change takes place in almost all physical and chemical processes. Due to their importance in science and engineering, special names have been assigned to enthalpy changes of some of such processes. Examples include enthalpy of combustion, enthalpy of solution and enthalpy of neutralisation.

Enthalpy of combustion

The change in enthalpy during the complete combustion of one mole of a substance in oxygen is called its enthalpy of combustion ($\Delta_c H^\circ$). The final oxidation products of a compound containing only C, H, O and N are $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and $\text{N}_2(\text{g})$. If a compound also contains Cl, Br, I, F, S and P, the final products include the aqueous solutions of HCl , HBr , HI , HF , H_2SO_4 and H_3PO_4 at infinite dilution. Thus, the enthalpy of combustion for methanol and urea are represented by the reactions:



The enthalpy of combustion is quite useful in determining the enthalpies of formation of those substances, which are difficult to measure experimentally. Here again, we make use of Hess's law.

Example 7.3

The enthalpy of combustion for methanol at 298.15 K is $-726.1 \text{ kJ mol}^{-1}$. What is its enthalpy of formation? (Given: $\Delta_f H^\circ(\text{CO}_2) = -393.5 \text{ kJ mol}^{-1}$ and $\Delta_f H^\circ(\text{H}_2\text{O}) = -285.8 \text{ kJ mol}^{-1}$.)

Solution

The combustion reaction of methanol can be written as



$$\Delta_c H^\circ = \Delta_c H^\circ(\text{CH}_3\text{OH}) = \Delta_f H^\circ(\text{CO}_2) + 2\Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_f H^\circ(\text{CH}_3\text{OH})$$

$$\text{(Since } \Delta_f H^\circ(\text{O}_2) = 0\text{)}$$

$$\text{Hence, } \Delta_f H^\circ(\text{CH}_3\text{OH}) = \Delta_f H^\circ(\text{CO}_2) + 2\Delta_f H^\circ(\text{H}_2\text{O}) - \Delta_c H^\circ(\text{CH}_3\text{OH})$$

$$= (-393.5) + 2 \times (-285.8) + 726.1 \text{ kJ mol}^{-1}$$

$$= -239.0 \text{ kJ mol}^{-1}$$

Enthalpy of solution

The formation of a solution (by the dissolution of a solute in a solvent) is also accompanied by heat changes, which are dependent on the nature of the solute and solvent, and the composition of the solution. Therefore, the enthalpy change accompanying the complete dissolution of one mole of a solute in a definite amount of a solvent so as to give a solution of specified concentration is defined as the integral enthalpy of solution (or integral heat of solution). As an example, consider the dissolution of 1 mol of NaCl in 200 mol of water as represented by the equation:



where $\Delta_{\text{soln}} H = 5.36 \text{ kJ mol}^{-1}$ represents the integral enthalpy of solution. In general, it can be positive or negative, depending on the nature of the solute and solvent. A special case of enthalpy of solution arises when a sufficiently large amount of solvent is used so that further dilution does not bring about any heat changes. This is defined as the enthalpy of solution at infinite dilution. For an aqueous solution, this reaction is represented by:



The symbol (aq) is used to represent an aqueous solution which is so dilute that additional dilution is not accompanied by any heat changes.

In contrast to integral enthalpy of solution, we define a quantity called differential enthalpy of solution. This is the enthalpy change when 1 mol of solute is dissolved in a sufficiently large volume of solution of concentration c , so that the final concentration remains almost unchanged. The differential enthalpy of a solution depends on the concentration of the solution. It can be calculated from the integral enthalpy of solution.

Another enthalpy term often used in solutions is the enthalpy of dilution ($\Delta_{dil}H$). This is defined as the enthalpy change when a solution containing one mole of solute at concentration c_1 is diluted by the addition of solvent so that the final concentration is c_2 . It is obvious that the enthalpy of dilution depends on both c_1 and c_2 .

Enthalpy of neutralisation

The enthalpy of neutralisation of an acid is the enthalpy change which accompanies the complete neutralisation of a dilute aqueous solution of an acid containing one mole of H^+ ions by a dilute aqueous solution of a base containing one mole of OH^- ions. For example,



It is observed experimentally that the enthalpy of neutralisation of strong acids or bases by strong bases or acids, respectively, is essentially the same, i.e. -57 kJ mol^{-1} . This is because strong acids and bases are completely dissociated in their aqueous solutions. The neutralisation of strong acids and bases is represented by

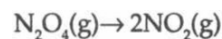


Hence, the enthalpy of neutralisation of strong acids and bases is the enthalpy of formation of one mole of water from one mole of H^+ ions and one mole of OH^- ions.

When a weak acid or base is neutralised, the enthalpy of neutralisation deviates from the value of $-57.3 \text{ kJ mol}^{-1}$. This is due to the low or incomplete dissociation of weak acids and bases. Some of the energy is used in dissociating the weak acids and bases.

Exercise 7.2

At 298 K, the standard enthalpies of formation of $NO_2(g)$ and $N_2O_4(g)$ are 33.2 kJ mol^{-1} and 9.2 kJ mol^{-1} . Calculate the standard enthalpy of the reaction:



7.5 Experimental determination of enthalpy of combustion

Calorimeters are used for determining the enthalpy changes in various processes. As a matter of fact, calorimetry is the most important experimental technique in thermodynamics and a lot has been done to make it very sensitive. At present, there are calorimeters that can measure heat and temperature changes accurately.

The enthalpy of combustion is determined using the Bomb calorimeter (Fig. 7.1).

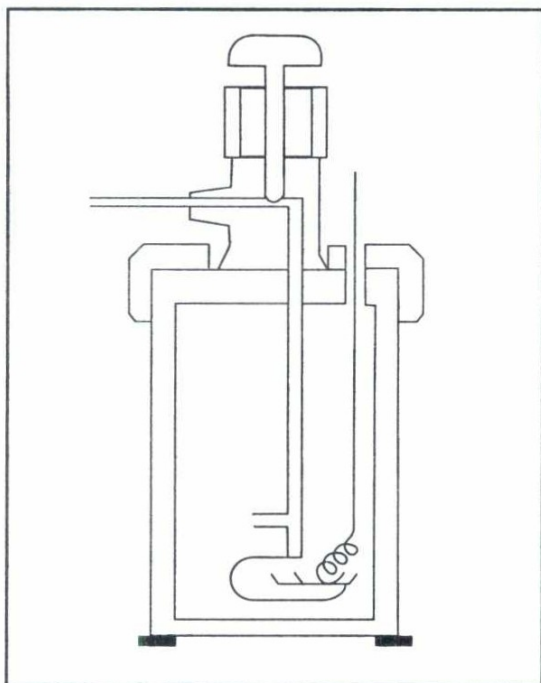


Fig. 7.1 The Bomb calorimeter

The method involves the combustion of a definite amount of substance in an inner vessel called the **Bomb**. The bomb is placed inside a definite quantity of water taken in an outer vessel which is thoroughly insulated. The temperature readings of the water in it are taken before and after the combustion, using a sensitive thermometer. From the heat capacity of the calorimeter, the amount of substance taken and the temperature readings, the enthalpy of combustion can be calculated. In general, using adiabatic calorimeters the enthalpies of reactions can be determined.

7.6 Conclusion

In this unit, some aspects of thermochemistry have been discussed. Specifically, we discussed enthalpy changes in different processes and reactions. Also, we stated the Hess's law of constant heat summation and some of its applications.

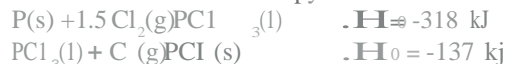
7.7 Summary

In this unit, you have learnt that:

- i) the enthalpy changes in various processes are determined by using calorimeters;
- ii) the Hess's Law is a direct consequence of the law of conservation of energy;
- iii) the Hess's law can be used to determine the enthalpies of reaction; and processes which cannot be determined

7.8 Tutor-marked assignment

Calculate the standard enthalpy of formation of $\text{PCl}_3(\text{s})$, using the following data



7.9 Reference

ICNOU (1993), *Chemical thermodynamics: Physical Chemistry CHE-04*, New Delhi.

Module 3: Kinetics and equilibrium

Unit 8-Reversible and irreversible reactions

Contents

- 8.1 Introduction
- 8.2 Objectives
- 8.3 Reversible and irreversible reactions
- 8.4 The Carnot cycle
- 8.5 Conclusion
- 8.6 Summary
- 8.7 Tutor-marked assignment
- 8.8 References

8.1 Introduction

We saw in Unit 2 that transfer of energy between a system and its surroundings takes place through heat and work. This is governed by the first law of thermodynamics discussed in Unit 3, which states that increase in the energy of a system must be accompanied by an equal decrease in the energy of the surroundings and vice versa. This law, however, does not tell us anything about the feasibility and direction of flow of energy. According to the first law of thermodynamics, all processes in which energy is conserved are possible.

In this unit, we shall examine the concept of reversible and irreversible reactions. The Carnot cycle shall also be described and some calculations shall be done on the efficiency of the Carnot engine.

8.2 Objectives

By the end of this unit, you should be able to:

- i) define reversible and irreversible reactions;
- ii) differentiate between reversible and irreversible reactions;
- iii) describe the Carnot cycle;
- iv) derive an expression useful in calculating the efficiency of the Carnot engine.

8.3 Reversible and irreversible reactions

In the introduction, we saw the limitation of the first law of thermodynamics in chemical reactions: it does not tell us anything about the feasibility and direction of flow of energy. For instance, if a cup of hot tea is left on a table, according to the first law, it may be cooled by transferring energy to the surroundings or be heated by absorbing energy from the surroundings. But we all know from our daily experience that the cup of tea will always cool till it acquires the temperature of the surroundings. Similarly, if a bottle of perfume is opened in a room, the perfume spreads throughout the room. The reverse process in which all the perfume vapours are collected in the bottle does not take place. These are examples of spontaneous processes which are irreversible and proceed only in one direction. Again, according to the first law, there exists a direct relationship between heat and work. But it does not tell us whether or not heat can be completely transformed into

work, and if so, what is the effect on the system and surroundings. These aspects are discussed in this section.

Chemical reactions are of two main types: reversible and irreversible. We can easily recognise reversible and irreversible reactions in the way their equations are written. As already mentioned in Units 4 and 5, all thermodynamic properties are state functions and independent of the path adopted by the system. Also, the internal energy change of a system is given by $E = q + w$. Here, E is independent of the path chosen, but q and w certainly depend on it. Thus, for the same E , different values of q and w are possible by bringing about the process in different ways. Also, the work done by a system is maximum if a reversible path is adopted and this maximum work can be determined from the initial and final states of the system.

Let us consider a reversible process and an irreversible process in which E is the same. Take a system of piston and cylinder in which the cylinder is not insulated. When the piston is pushed up or down, no work is done on the system, hence the piston is frictionless.

Assuming 10.1×10^5 Pa and 1 litre at the initial condition, with initial temperature T . If it is expanded isothermally at 1.0132×10^5 Pa, volume becomes 10 litres, but the final temperature will still be T , since it is an isothermal expansion. Assuming work is done under a vacuum, the initial pressure is 10.130×10^5 while the final temperature will be 0 . Then, we can say

$$q = PdV = 0 (10-1) \text{ litre} = 0$$

The amount of work obtained is zero. Since there is no pressure on the piston, the gas cannot be returned to the initial state. Hence, we can say that the process is irreversible.

But where we can put a weight equal to 1.013×10^5 Pa pressure in form of rings. When the gas expands at 1.013×10^5 Pa, it then stops. Then,

$$q = PdV = (1.013 \times 10^5 \text{ Pa}) (0.01 \text{ m}^3 - 0.001 \text{ m}^3) = 10.02 \times 10^3 \text{ Pa m}^3.$$

Assuming we put a weight equal to 10 atmosphere initially (in form of rings) and continue to remove them gradually in steps of 10, 7, 5, 2 and 1 litre, then,

$$q = (P_1 dV_1 + P_2 dV_2 + P_3 dV_3 + P_4 dV_4).$$

You can carefully replace the weights again to obtain the initial atmospheric pressure. This system is reversible. We can say

$$q_{\text{reversible}} = \sum_{i=1}^n (P_i dV_i) \dots \dots \dots 8.1$$

The larger the value of n , the closer to reversibility we are.

Example 8.1

For n moles of an ideal gas undergoing a reversible change from V_1 to V_2 what equations will establish the associated values of q and w ?

Solution

We can represent an isothermal change of volume of an ideal gas with

$$\int_{V_1}^{V_2} P_{\text{ext}} dV \dots \dots \dots 8.2$$

where P_{ext} is the external pressure on the gas. When the external pressure becomes almost equal to the internal pressure, we become closer to the reversibility system, such that

$$P_{\text{ext}} = P + dP \text{ (sliding forward and back easily)}$$

Then, we can have

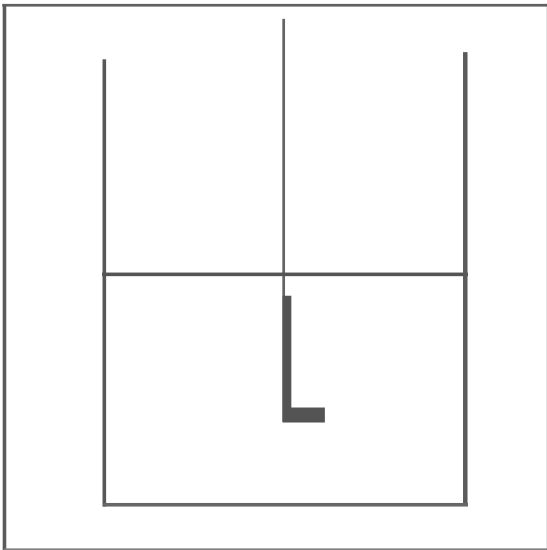


Fig. 8.1

$$q = \int_{v_1}^{v_2} (P + dP) dV \quad \dots\dots\dots 8.3$$

Expanding this, we get

$$q = \int_{v_1}^{v_2} (PdV + dPdV) \quad \dots\dots\dots 8.4$$

where the dP pressure quantity will be very small, i.e. tends to zero.

Thus,

$$q = \int_{v_1}^{v_2} PdV$$

For ideal gas, we know that

$$PV = nRT \quad \dots\dots\dots 8.5$$

$$P = \frac{nRT}{V}$$

Substituting, we can have

$$\begin{aligned} q &= nRT \int_{v_1}^{v_2} \frac{dV}{V} \\ &= nRT \int_{v_1}^{v_2} d \ln V \\ &= nRT \int_{v_1}^{v_2} \ln \frac{V_2}{V_1} \quad \dots\dots\dots 8.6 \end{aligned}$$

Work can be represented as

$$q_{rev} = nRT \log \frac{V_2}{V_1} = W_{rev} \quad \dots\dots\dots 8.7$$

Let us also consider a reversible process and an irreversible process in which ΔE is the same. No matter how we carry out the process (reversible or irreversible), ΔE depends only upon the initial and final states of the system.

- $\Delta E = q_{rev} + w_{rev}$, for reversible process 8.8
 and $\Delta E = q_{irrev} + w_{irrev}$ for irreversible process 8.9
 and so, $q_{rev} + w_{rev} = q_{irrev} + w_{irrev}$ 8.10

We know that the work done by a system under reversible conditions (w_{rev}) is larger than the work done by a system under irreversible conditions (w_{irrev}),

i.e. $-w_{rev} > -w_{irrev}$ 8.11
 Hence, $w_{rev} < w_{irrev}$ 8.12

This is true when we compare the work done on the system under reversible and irreversible conditions. Let us assume that the driving forces under the two conditions are fairly different, and that the processes are not adiabatic, so that q_{rev} or q_{irrev} is not equal to zero. Using Equations 8.10 and 8.12, we can write

$q_{rev} > q_{irrev}$ 8.13

This means that in a non-adiabatic process, heat absorbed by a system from the surroundings is more under reversible conditions than under irreversible conditions.

Now, let us consider ΔE , q and w values of a system in a cyclic process. A cyclic process is one in which the system after undergoing any number of processes returns to its initial state. This means that $\Delta E = 0$, hence the work done by the system during all these processes should be equal to the heat absorbed by the system, i.e.

$q_1 + q_2 + \dots = -(w_1 + w_2 + \dots) = -w$ 8.14

where q is the heat absorbed and w is the work done on the system in the entire cyclic process, consisting of several processes. In the individual processes, q_1, q_2, \dots , etc, are the heat absorbed by the system and w_1, w_2, \dots , etc, are the work done on the system.

Using Example 8.2, you can understand the validity of Equations 8.12 and 8.13.

Example 8.2

1.00 x 10² mol of an ideal gas at 3.00 x 10² K temperature and 6.00 x 10⁶ Pa pressure occupies 4.16 x 10⁻² m³ space initially. Calculate the work done on the gas and the heat absorbed by the gas if it undergoes expansion under the following conditions, such that the final volume and pressure are 0.832 m³ and 3.00 x 10⁵ Pa:

- a) isothermal reversible conditions
- b) isothermal irreversible conditions.

Solution

In an isothermal process, for an ideal gas, $\Delta E = 0$. Hence, $q = -w$,

i.e.

heat absorbed by the gas = -(work done on the gas).

This equation is applied to both the processes as now discussed.

- a) Let us first calculate q_{rev} and w_{rev} using the equation for the isothermal reversible expansion

$$\begin{aligned}
 w_{rev} &= -W_{rev} = -2.303nRT \log \frac{V_t}{V_i} \\
 &= 2.303nRT \log \frac{V_i}{V_t} \\
 &= 2.303 \times 1.00 \times 10^2 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.00 \times 10^2 \text{ K} \log \frac{4.16 \times 10^{-2} \text{ m}^3}{0.832 \text{ m}^3} \\
 &= 7.47 \times 10^5 \text{ J}
 \end{aligned}$$

Hence, the heat absorbed by the gas during isothermal reversible expansion (q_{rev}) = 7.47×10^5 J, and the work done on the gas (w_{rev}) = -7.47×10^5 J.

b) Let us calculate q and w for the isothermal irreversible process. In this process, the final pressure of the gas is equal to the external pressure (p_{ext}).

Hence,

$$q_{irr} = w_{irr} = P_{ext} (V_2 - V_1)$$

$$\begin{aligned} &= 3.00 \times 10^5 \text{ Pa} (0.832 \text{ m}^3 - 0.0416 \text{ m}^3) \\ &= 3.00 \times 10^5 \times 0.7904 \text{ J} \\ &= 2.37 \times 10^5 \text{ J} \end{aligned}$$

You can compare q and w values in these two cases to verify the validity of Equations 8.12 and 8.13.

$$w_{rev} = -7.47 \times 10^5 \text{ J}; w_{irr} = -2.37 \times 10^5 \text{ J}$$

Hence, $w_{rev} < w_{irr}$ as shown in Equation 8.12

$$= 7.47 \times 10^5 \text{ J}; \quad = 2.37 \times 10^5 \text{ J}$$

Hence, $q_{rev} > q_{irr}$, as shown in Equation 8.13

8.4 The Carnot cycle

Carnot analysed the functioning of an engine with the following features:

- 1 The engine works in cycles.
- 2 It absorbs heat from a reservoir, known as source.
- 3 It does some work out of the heat absorbed.
- 4 It returns the unused part of the heat to another reservoir, known as sink.
- 5 Finally, it returns to its original state.

Such an engine is known as the Carnot engine. The temperature of the source (T_H) is higher than that of the sink (T_C). The source and sink are assumed to be of infinite heat capacity, i.e. their temperatures are not affected by small amounts of heat exchange. Carnot showed that the entire amount of heat absorbed cannot be converted into work and this fraction is known as the efficiency of the Carnot engine. Let us now derive an equation useful in calculating efficiency.

For the sake of simplicity, let us assume that the engine consists of a cylinder and a piston having one mole of an ideal gas between the two and the cylinder has perfectly insulated walls and a perfectly conducting base while the piston is frictionless. It is only for the sake of convenience that we have assumed that the engine contains an ideal gas. Actually, there can be any suitable fluid. We make use of the following expressions for one mole of the gas.

$$w_{isothermal} = RT \ln \frac{v_{initial}}{v_{final}} \quad \dots \dots \dots 8.15$$

$$w_{adiabatic} = C_v (T_{initial} - T_{final}) \quad \dots \dots \dots 8.16$$

Where w is the work done on the system and C_v is the molar heat capacity of the gas.

The plot of pressure against volume is shown in Fig. 8.3

The Carnot cycle operation can be described by the following four steps: isothermal expansion, adiabatic expansion, isothermal compression and adiabatic compression.

Step 1: Isothermal expansion

Initially, the gas has pressure P_1 and volume V_1 . The cylinder is placed on a heat source maintain P_1 at temperature T_w . The gas is isothermally and reversibly expanded to volume V_2 at pressure P_2 . Let the work done on the gas be w and the heat absorbed from the source be q . In an isothermal process, $\Delta U = 0$.

Hence, using Equations 8.7 and 8.8, when $\Delta E = 0$, the work done on the gas is given by

$$w_{12} = RT_H \ln \frac{V_2}{V_1} \dots\dots\dots 8.17$$

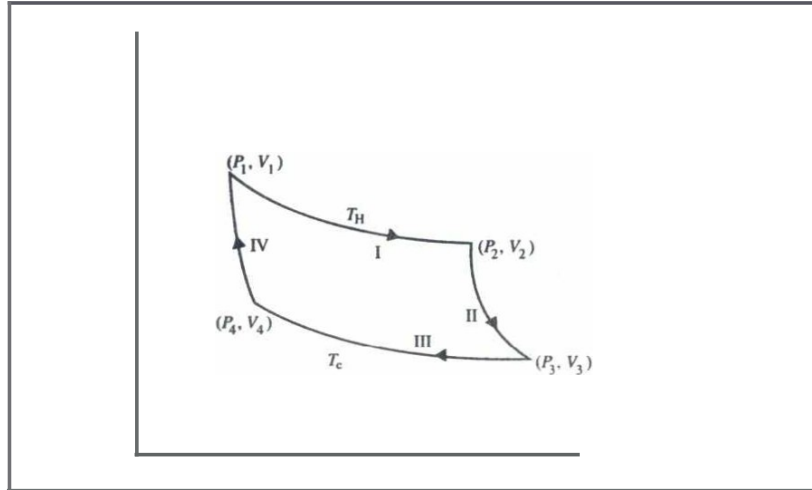


Fig. 8.2 The Carnot cycle

Step 2: Adiabatic expansion

The cylinder is now placed on a thermally-insulated stand and the gas is adiabatically and reversibly expanded until it attains pressure P_3 , volume V_3 and temperature T_c . During this period, no heat is absorbed by the system. The work done on the gas, w_2 , as the gas gets cooled from T_H to T_c is given by

$$w_2 = C_v (T_c - T_H) \dots\dots\dots 8.18$$

Step 3: Isothermal compression

The cylinder is now placed on a stand at temperature T_c and the gas is isothermally and reversibly compressed to volume V_4 at pressure P_4 . During the process, the work done on the gas is w_3 and the heat evolved to the sink is q_c (or q_c is the heat absorbed from the sink).

$$w_3 = -q_c = RT_c \ln \frac{V_4}{V_3}$$

$$\text{or } q_c = RT_c \ln \frac{V_4}{V_3} \dots\dots\dots 8.19$$

Step 4: Adiabatic compression

In the last step, the cylinder is again placed on an insulating stand and the gas is adiabatically and reversibly compressed until it reaches the initial state of volume V_1 , pressure P_1 and temperature T_H . Hence, the work done on the gas, w_4 is given by

$$w_4 = C_v (T_H - T_c) \dots\dots\dots 8.20$$

The net work done on the system, w is given by:

$$w = w_1 + w_2 + w_3 + w_4 \dots\dots\dots 8.21$$

$$\text{or } w = RT_H \ln \frac{V_1}{V_2} + C_v (T_c - T_H) + RT_c \ln \frac{V_3}{V_4} + C_v (T_H - T_c) \dots\dots\dots 8.22$$

$$\text{i.e. } w = RTH \ln \frac{v_1}{v_2} + R1C \ln \frac{v_3}{v_4} \dots\dots\dots 8.23$$

We can relate the initial and final values of volume and temperature of the two adiabatic processes described in steps 2 and 4, using the equation

$$\frac{1C}{1H} = \left(\frac{v_2}{v_3}\right)^{\gamma-1} \text{ for step 2}$$

Similarly, for step 4,

$$= \left(\frac{v_1}{v_2}\right)^{\gamma-1} = \left(\frac{v_3}{v_4}\right)^{\gamma-1}$$

Hence $\left(\frac{v_2}{v_3}\right)^{\gamma-1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$

$$\text{i.e. } \frac{v_2}{v_3} = \frac{v_1}{v_2} \dots\dots\dots 8.24$$

$$\left(\frac{v_2}{v_3}\right)^{\gamma-1} = \left(\frac{v_1}{v_2}\right)^{\gamma-1}$$

Using this Equation 8.23, $w = RTH \ln \frac{v_1}{v_2} + R1C \ln \frac{v_1}{v_2}$

we have, $w = RTH \ln \frac{v_1}{v_2} + R1C \ln \frac{v_2}{v_1}$

$$\text{or } w = RTH \ln \frac{v_1}{v_2} - R1C \ln \frac{v_1}{v_2} \dots\dots\dots 8.25$$

Hence, total work done on the system $= w = R(T_H - 1) \ln \frac{v_1}{v_2}$

or total work done by the system, $w^1 = -w = R(T_H - 1) \ln \frac{v_2}{v_1} \dots\dots\dots 8.26$

Since q_c is a negative and q_H is positive, $\frac{q_c}{q_H}$ is a negative quantity, so $1 + \frac{q_c}{q_H}$ is also less than 1.

Since work done by the system $= -(\text{work done on the system})$.

We know that the heat exchange between the gas and source or sink takes place only in isothermal processes (steps 1 and 3). In adiabatic processes (steps 2 and 4), there is no heat exchange. Again, q_H is the heat absorbed from the source in step 1 and q_c is the heat absorbed from the sink in step 3.

The total heat absorbed by the system is

$$q = q_H + q_c \dots\dots\dots 8.27$$

As expected, q turns out to be equal to $-w$ or w^1 , since for the overall cyclic process, $\Delta E = 0$.

$$\text{Hence, } q = q_H + q_c = w^1 = -w = R(T_H - 1) \ln \frac{v_2}{v_1} \dots\dots\dots 8.28$$

It may, however, be noted that out of the heat $q_H = RTH \ln \frac{V_2}{V_1}$ absorbed from the source, only some of it is converted to useful work and the rest is lost to the sink. Let us now calculate i.e. the ratio of the total work done by the system during one cycle to the heat absorbed in the first step. This quantity is called efficiency of a Carnot engine,

$$\text{Efficiency } (\eta) = \frac{\text{Total work done on the system}}{\text{Heat absorbed from the source}} \dots\dots\dots 8.29$$

$$\eta = \frac{q_H + q_C}{q_H} = \frac{R(T_H - T_C) \ln \frac{V_2}{V_1}}{R T_H \ln \frac{V_2}{V_1}} \dots\dots\dots 8.30$$

$$\eta = \frac{q_H + q_C}{q_H} = 1 - \frac{T_C}{T_H} \dots\dots\dots 8.31$$

Since T_C and T_H are always positive, and $\frac{T_C}{T_H}$ is less than 1, Equation 8.31 can be rearranged as follows:

$$\eta = 1 - \frac{T_C}{T_H} = 1 - \frac{T_C}{T_H} < 1 \dots\dots\dots 8.32$$

Since q_C is negative and q_H is positive, $\frac{q_C}{q_H}$ is a negative quantity, so $1 - \frac{T_C}{T_H}$ is also less than 1. This means that efficiency is always less than 1, i.e. all the heat absorbed at a higher temperature is not converted to work. It is also clear that efficiency will be more if the ratio $\frac{T_C}{T_H}$ is small. Therefore, for efficient working of the engine, it should absorb heat at as high a temperature as possible and reject it at as low a temperature as possible. It should also be noted that efficiency is independent of the nature of the fluid. This is called Carnot theorem. Hence, in all Carnot engines working between the same temperature of the source and the sink, the efficiency is the same.

8.5 Conclusion

In this unit, we described reversible, irreversible and cyclic processes; with how $q = -w$, is obtained for isothermal reversible expansion. We also described the Carnot cycle and derived its efficiency.

8.6 Summary

In this unit, you have learnt that:

- i) In a cyclic process, work is done by the system, $q = 0$;
- ii) In a reversible process, $q_{rev} = nRT \ln \frac{V_2}{V_1}$ and $w_{rev} = nRT \ln \frac{V_2}{V_1}$;
- iii) $q_{rev} = nRT \ln \frac{V_2}{V_1}$; in an isothermal expansion operation;
- iv) In a Carnot engine, the heat absorbed cannot be converted to work in a cyclic process, no matter how ideal the engine is.

8.7 Tutor-marked assignment

- 1 If the efficiency of a Carnot engine is 20% and the temperature of the sink is $3.00 \times 10^2 \text{ K}$. Calculate the temperature of the source.
- 2 A Carnot engine works between $5.00 \times 10^2 \text{ K}$ and $3.00 \times 10^2 \text{ K}$. Calculate the minimum amount of heat that must be absorbed by the engine from the source at $5.00 \times 10^2 \text{ K}$ in order to obtain 1.50 kJ of work.

8.8 References

- 1 Goldberg, David and Dillard, Cyllide (1974), *College Chemistry, 3rd revised edition*, New York, Macmillan Publishing Co, Inc.
- 2 IGNOU, (1993), *Chemical Thermodynamics; Physical Chemistry CHE-04*, New Delhi.
- 3 Sharma, K.K. and Sharma L.K. (1997), *A Textbook of Physical Chemistry, 3rd revised edition*, New Delhi, Vikas Publishing House PVT Ltd.

Unit 9: Entropy and free energy

Contents

- 9.1 Introduction
- 9.2 Objectives
- 9.3 Entropy
- 9.4 Free energy
- 9.5 Conclusion
- 9.6 Summary
- 9.7 References

9.1 Introduction

So far, we have examined some aspects of thermodynamics, and in the last unit, we described reversible and irreversible isothermal, adiabatic and cyclic processes. However, nothing was mentioned about the feasibility and direction of flow of energy. In this unit, we shall examine the concept of entropy and free energy.

9.2 Objectives

By the end of this unit, you should be able to:

- i) define entropy,
- ii) define free energy;
- iii) state with examples, processes that can increase or decrease the entropy of a system.

9.3 Entropy

In Units 5, 6 and 7, we studied the applications of the first law of thermodynamics. In this unit, we shall study the concept of entropy and internal energy changes of reactions. Some reactions, which occur spontaneously, do not tell whether or not a given reaction is feasible. If, therefore, the energy is converted to the form of energy.

You may have come across some reactions which occur spontaneously without the application of energy from outside. The systems are said to be spontaneous. Example:

- a) heat flow between two objects at different temperatures;
- b) the reaction between magnesium ribbon and hydrochloric acid;
- c) conversion of hydrogen peroxide to water and oxygen.

Exercise 9.1

Which of these reactions is spontaneous?

- a) Decomposition of hydrogen peroxide. (write an equation for the reaction; state, before answering the question.)
- b) The chemical reaction between Zn metal and copper ions in aqueous solution of Daniel's cell. (Write an equation for the reaction.)

Entropy refers to the randomness of a given system. It in fact explains how a system is ordered or disordered. A high-entropy system results when:

- a) there is a change from solid to liquid (melting process);
- b) a pure solid substance is heated to form a molten substance, e.g. molten sodium chloride and molten magnesium chloride;
- c) large hydrocarbons are broken to smaller hydrocarbons through cracking;

- d) ice is melted to liquid. This is a spontaneous process;
- e) a pure liquid water is evaporated.

A low-entropy system results when:

- a) a salt is crystallised out in a system;
- b) there is freezing of a liquid.

Exercise 9.2

Which of the following systems will have a high or low entropy?

- a) Increasing the number of moles of an ideal gas in a system.
- b) Dissolving sodium in water.
- c) Liquefying a gas.

9.4 Free energy

Recall that heat is a unique form of energy. At constant temperature, heat cannot be completely converted to any other form of energy. The heat content (enthalpy) of any system is considered in two parts: available energy and unavailable energy.

Available energy is the energy available for conversion to other forms of energy while unavailable energy is the one which is necessary to maintain the system at a specified temperature and is not available for conversion. These two parts of enthalpy can be represented as

$$H = G + TS,$$

where H is enthalpy, G is free energy, T is temperature and S is entropy. G is the available energy while the product of temperature and entropy is the unavailable energy.

Now, the difference between the enthalpy of the final state and the enthalpy of the initial state of the same system is ΔH .

Thus, for the two states of the system, we have:

$$\text{For state 1, } H_1 = G_1 + T_1 S_1$$

$$\text{For state 2, } H_2 = G_2 + T_2 S_2$$

Therefore, the difference in enthalpies of the two states of the system will be:

$$\Delta H = H_2 - H_1, \text{ that is,}$$

$$\Delta H = (G_2 - G_1) + (T_2 S_2 - T_1 S_1)$$

$$\Delta H = \Delta G - T \Delta S \quad (\text{Constant } T)$$

ΔH , G and ΔS are all thermodynamic functions and they are extensive properties. You will study this in detail under the second law of thermodynamics. Now, let's examine under what condition of ΔG will a reaction be spontaneous.

As previously stated, if a process is spontaneous, it requires no energy from outside the system. In other words, the energy within the system is sufficient to initiate the action by releasing free energy. When this occurs, it means the final state of the system has less available energy than its initial state.

$$\Delta H = \Delta G + T \Delta S,$$

$$\text{then, } \Delta G = \Delta H - T \Delta S.$$

Thus, from our last statement, ΔG will be negative, i.e. for any spontaneous reaction, ΔG will be negative. Whereas, if ΔH is positive, it means that the available energy of the initial state of the system is less than the one available in the final state, then ΔG is positive. This implies that the reaction cannot occur spontaneously, or rather, the reverse reaction will occur.

In a situation where ΔG is zero, neither the reverse process nor spontaneous reaction will occur. At this point, we say the system is in a state of equilibrium. You will study this later in this course.

9.5 Conclusion

In this unit, we have made an attempt to define thermodynamic functions of G and S. We hope the definitions of these thermodynamic functions will help you in your study of second and third laws of thermodynamics in due course.

9.6 Summary

In this unit, you have learnt that:

- i) free energy (G) is the available energy in a system that is convertible to other forms of energy and it is a thermodynamic function;
- ii) entropy expresses the randomness of a system;
- iii) enthalpy change of two states of a system can be expressed as $\Delta H = \Delta G + T\Delta S$ (constant temperature), for an isothermal process.

9.7 References

- 1 Goldberg, David and Dillard, Cyllide (1974), *College Chemistry, 3rd Revised edition*, New York, Macmillan Publishing Co, Inc.
- 2 IGNOU (1993), *Chemical Thermodynamics; Physical Chemistry CHE-04*, New Delhi.
- 3 Sharma, K.K. and Sharma L.K. (1997), *A Textbook of Physical Chemistry, 3rd Revised edition*, New Delhi, Vikas Publishing House Pvt Ltd.

Unit 10: Kinetics

Contents

- 10.1 Introduction
- 10.2 Objectives
- 10.3 Concepts of kinetics
- 10.4 Conclusion
- 10.5 Summary
- 10.6 Tutor-marked assignment
- 10.7 Reference

10.1 Introduction

There are many types of reactions that we come across in our study of chemistry. These include chemical reactions, electrical-induced reactions and nuclear reactions. *Over the course of this unit, we shall examine some basic concepts of kinetics. We shall also explain the dependence of rate of reaction on some factors.*

10.2 Objectives

By the end of this unit, you should be able to

- i) define rate of reaction;
- ii) list the factors affecting rate of reaction and their effects;
- iii) calculate rates of reactions.

10.3 Concept of kinetics

Chemical kinetics refers to the study of rates and mechanisms of chemical reactions.

Rates of reactions

Reactions proceed at different speeds and in different directions. There are some conditions that determine the rate at which reactions occur. There are also some mechanisms by which reactions proceed. The rate of a chemical reaction can be simply defined as the amount of reaction which occurs in a unit time. In fact, it is the amount (usually expressed in moles) of a reactant used up or produced in a stated time interval, usually in seconds.

We can also define the rate of reaction or the velocity of reaction at a specified time as the decrease in the concentration of a reactant or the increase in the concentration of a product per unit time. The rate of reaction at a specific time is also known as instantaneous rate of reaction.

It can be generally defined as the rate of change of concentration of a specified species at a particular instant. While specifying the reaction rate, we must mention the component with respect to which it is stated. Let us consider a simple reaction



The reaction stoichiometry shows that one molecule of B is formed for every molecule of A consumed. The reaction rate can be specified in the following ways:

- a) We can measure the concentration of the reactant A at various time intervals. From these values, we can specify the decrease in concentration of A with respect to time at any particular instant. This gives the rate of consumption of A, which is

Decrease in the concentration of A

Change in time

$$= \frac{\Delta[A]}{\Delta t}$$

$\Delta[A]$ means change in the concentration of A and $-\Delta[A]$ means decrease in the concentration of A.

While writing a rate expression with respect to a reactant, there is a preceding negative sign (since it is customary to express the rate of reaction as a positive quantity).

- b) We can measure the concentration of the product B at various time intervals. From these values, we can arrive at the rate of formation of B at any particular instant.

$$\begin{aligned} \text{Rate of formation of B} &= \frac{\text{Increase in the concentration of B}}{\text{Change in time}} \\ &= \frac{\Delta[B]}{\Delta t} \end{aligned}$$

The rate of consumption of reactants and the rate of formation of products are related through their stoichiometric coefficients. For example, consider the decomposition of NO_2



We can write the relationship between the rate of consumption of NO_2 and the rate of formation of NO and O_2 as follows:

$$\begin{aligned} -\frac{1}{2} \left(\text{Rate of consumption of } \text{NO}_2 \right) &= \frac{1}{2} \left(\text{Rate of formation of} \right. \\ &\left. \text{NO} \right) \\ &= \text{Rate of formation of } \text{O}_2 \end{aligned}$$

By convention, we can write this as:

$$\text{Reaction rate} = -\frac{1}{2} \frac{d[\text{NO}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}]}{dt} = \frac{d[\text{O}_2]}{dt}$$

You can understand this relationship if you bear in mind that if two molecules of NO_2 are consumed, two molecules of NO and one molecule of O_2 are formed. In other words, the reaction rate is equal to: half the rate of consumption of NO_2 , or half the rate of formation of NO or the rate of formation of O_2 . The symbol ' Δ ' is read as delta. It denotes change in a property.

Convention for expressing reaction rates

In order to obtain a single value for the reaction rate, it is necessary to divide the rate of consumption of a reactant or the rate of formation of a product by the stoichiometric coefficient of the respective species.

Consider the reaction:



In this reaction, A and B are reactants, C and D are products and a, b, c and d are the stoichiometric coefficients. The reaction rate is related to the rates of consumption of the reactants and the rates of formation of the products as follows:

$$\text{Reaction rate} = -\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = \frac{1}{c} \frac{d[\text{C}]}{dt} = \frac{1}{d} \frac{d[\text{D}]}{dt}$$

The rate of change of the concentration of a substance in the preceding equation is its stoichiometric coefficient.

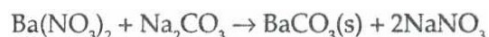
Factors affecting reaction rate

Factors which affect or influence rates of reactions include concentration of reactants, temperature, light, nature of reactants and catalyst.

Concentration of reactants

Chemical reactions occur when particles of the reacting substances come in contact. The rate of a reaction depends on the frequency with which the particles collide, and this in turn depends on their concentration. This is because when the number of reacting species per unit volume of the reaction system is increased, there will be an increase in contact, and then, rate. The more crowded the particles are, the more often we would expect them to bump into one another.

Consider the reaction between $\text{Ba}(\text{NO}_3)_2$ and Na_2CO_3 to form a precipitate of BaCO_3



As the concentration of $\text{Ba}(\text{NO}_3)_2$ increases, the rate of reaction also increases.

If the reactants involved in a chemical reaction have their concentrations increased in a

homogenous mixture, more frequent molecular collisions will occur and the reaction will proceed faster. Assuming we have gases in that homogenous system, increase in pressure implies increase in concentration since the concentration of a gas is directly proportional to its partial pressure. Thus, when the partial pressure of a gas is increased, the rate of reaction generally increases. Reactions in the liquid or solid state are not influenced by pressure to any appreciable degree. This is because liquids and solids are almost incompressible.

Temperature

Your experiences in daily life activities, especially in the kitchen laboratory, are enough proofs to show that when the temperature of a reaction is increased, the kinetic energy of the particles is increased and the reaction proceeds at an increased speed.

Light

Light is a source of energy and it can influence the rates of some chemical reactions. The molecules of some of the reactants involved. The reaction between Cl_2 and H_2 gases at ordinary pressure is negligible in darkness, slow in daylight but explosive in sunlight (at room temperature).

Other examples include the reaction between methane and chlorine and photosynthesis. You will learn more of photochemistry later.

Nature of reactants

There are several factors put together as nature of reactants. These include the particle size of the reactants, state of the reactants, i.e. whether solid, liquid or gas and the structure of reactants, e.g. discrete molecule or polymer's structure.

The particle size of the reactants influences the reaction rate. In any given reaction that involves a solid substance, the powdered form instead of lump or foil will be preferred. Concerning the state of reactants, for example in solutions, reactions between ions are more rapid compared to those between atoms. Furthermore, reactions involving transfer of electrons especially through wires are more rapid than reactions involving transfer of atoms.

Effect of catalysts

Perhaps, what we need here is to raise some questions regarding the influence of catalysts on rate of reaction. Let us start by you providing answers to these questions:

- What difference exists between positive and negative catalysts?
- Under what conditions does a catalyst have no effect on a chemical reaction?

Exercise 10.1

For what reactions are the following catalysts used:

- (a) MnO_2 (b) Reduced iron powder (c) Enzymes (d) NO and NO_2 ?

Calculation of reaction rate

Consider the reaction:



In Fig. 10.1, a, b and c are the plots of concentration (c) against time (t) for NO_2 , NO and O_2 using the values given in Table 10.1. The graphical method of calculation of the reaction rate for the consumption of NO_2 and the formation of NO and O_2 is illustrated. The reaction rate at any particular instant is obtained by calculating the slope of a line tangent to the curve at that point.

Table 10.1 Concentration of NO_2 , NO and O_2 at different time intervals at 673K

Time/s	$[\text{NO}_2]/\text{M}$	$[\text{NO}]/\text{M}$	$[\text{O}_2]/\text{M}$
0	0.0100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033

From the slope of the tangent drawn (corresponding to a particular time) to the concentration (c)

$$\begin{aligned} \text{At } t = 200\text{s, slope of curve} &= \frac{0.5}{3.2} \times \frac{0.001}{25} \text{ Ms}^{-1} \\ &= 6.25 \times 10^{-6} \text{ Ms}^{-1} \end{aligned}$$

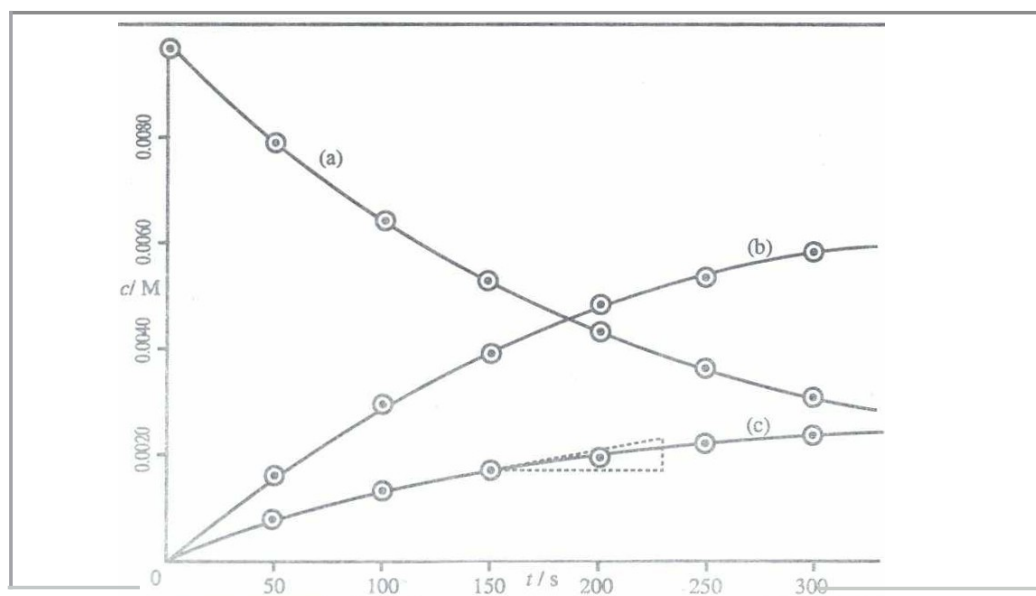


Fig. 10.1. Concentration against time plot for NO_2

against time (t) curve for a component, we can obtain the rate of reaction. Note the falling nature of the curve which is characteristic of concentration against time plot for a reactant.

10.4 Conclusion

In this unit, we examined some fundamental concepts of kinetics, such as rate of reaction, factors affecting rates of reactions and calculation of rates of reactions.

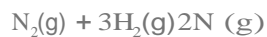
10.5 Summary

In this unit, you have learnt that:

- i) the rate of reaction refers to a decrease in the concentration of a reactant or an increase in the concentration of a product per unit time;
- ii) such factors, as temperature, pressure, concentration, light and catalysts affect reaction rates.

10.6 Tutor-marked assignment

In the formation of ammonia,



the rate of consumption of hydrogen at a particular instant is $4.78 \times 10^{-4} \text{ Ms}^{-1}$. What is the rate of formation of ammonia?

10.7 Reference

IGNOU (1993), *Dynamics and Macromolecules: Physical chemistry 5: CHE-04*, New Delhi.

Unit 11: Rates of reactions

Contents

- 11.1 Introduction
- 11.2 Objectives
- 11.3 Calculation of rates of reactions
 - Rate law and rate constant
 - Order of reaction and stoichiometry
 - Experimental methods of rate studies
- 11.4 Conclusion
- 11.5 Summary
- 11.6 Tutor- marked assignment
- 11.7 Reference

11.1 Introduction

We shall start the unit by calculating the rates of some reactions. We shall also define such terms as rate law, rate constant, order of reaction and stoichiometry of reaction. Finally, we shall examine some experimental methods of rate studies.

11.2 Objectives

By the end of this unit, you should be able to:

- i) define rate law, rate constant, stoichiometry of reaction and order of reaction;
- ii) discuss the effects of some conditions on rates of reactions;
- iii) differentiate between order of reaction and stoichiometry;
- iv) state the experimental methods of studying reaction rates.

11.3 Calculation of rates of reactions

We are mainly interested in the concentration against time plots for the reactants. In other words, we want to study the reactants under conditions where the rate of the forward reaction is significant but the rate of the reverse reaction is low. This is made possible if we study the reaction up to a point where the amounts of products are not high. For example, in the decomposition of NO_2 there could be a decrease in the concentration of NO_2 up to a particular time. Afterwards, enough nitric oxide (NO) and oxygen are formed and the reverse reaction could also take place, leading to the formation of NO_2 . In order to simplify the situation, it is better to study the reaction rates before significant amounts of products are formed. In general, rates of reactions are complex functions of the concentrations of reactants and products at a given temperature.

However, there are some reactions in which the rates are proportional to the simple powers of the concentrations of the reactants. We shall be mostly concerned with this class of reactions.

Decomposition of N_2O_5

The decomposition of N_2O_5 is represented by

$$2\text{N}_2\text{O}_5(\text{g}) \rightarrow 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$

The instantaneous rates of this reaction calculated from the plot of $[\text{NO}_2]$ against time are given in Table 11.1.

Table 11.1 Rates for the decomposition of N_2O_5 at 323K

(N_2O_5)	Rate (Ms^{-1})	Rate/a (N_2O_5)
0.300	2.73×10^{-1}	9.1×10^{-1}
0.150	1.37×10^{-1}	9.1×10^{-1}
0.075	9.10×10^{-2}	9.1×10^{-1}

From the first and second columns, you can see that the rate of decomposition of N_2O_5 decreases with decrease in the concentration of N_2O_5 . The third column gives the ratio of the rate of decomposition of N_2O_5 to the concentration of N_2O_5 . In all the three cases, it is constant. It shows that the rate is directly proportional to the concentration of N_2O_5 , i.e.

$$\text{Rate} \propto [N_2O_5]$$

Hence, $\text{Rate} = k[N_2O_5]$

Where k is a proportionality constant.

Decomposition of hydrogen iodide



The instantaneous rates of decomposition of hydrogen iodide were followed at a constant temperature and calculated using the plot of $[HI]$ against time. These values are given in Table 11.2.

Table 11.2 Rates for the decomposition of HI

$[HI]$	Rate (Ms^{-1})	Rate. t [I_2]	Rate. Ms (I_2)
3.00×10^{-1}	3.60×10^{-1}	1.8×10^{-1}	4.00×10^{-2}
2.00×10^{-1}	1.60×10^{-1}	8.0×10^{-2}	4.00×10^{-2}
1.50×10^{-1}	9.0×10^{-2}	6.0×10^{-2}	4.00×10^{-2}

From the first and second columns of Table 11.2, you can see that the rate of decomposition of HI decreases with decrease in the concentration of HI, just as in the case of the decomposition of N_2O_5 . Further, it is evident from the third column that $\text{rate}/[HI]$ is not a constant. The fourth column shows that $\text{rate}/[I_2]$ is a constant.

Hence, $\text{Rate} = k[I_2]$

Where k is a proportionality constant.

For many chemical reactions, the relationship between the reaction rate and concentration can be expressed in a simple way such as we have seen for the decomposition of N_2O_5 and HI. However, there are other reactions with more complex rate-concentration relationships.

Rate law and rate constant

The rate law is an equation expressing the relationship between the instantaneous reaction rate and the concentration of the reactants in a reaction. For a simple reaction with one reactant, the rate law may be expressed as

$$\text{Reaction rate} = k [\text{Reactant}]^n$$

where k is called the rate constant or rate coefficient or the specific rate of reaction. Thus by definition, the rate constant is independent of concentration, but it may depend on other factors. In this equation, n refers to the order of the reaction. The order, with respect to a component, is the power to which the concentration of that component is raised in the rate law.

The decomposition of N_2O_5 is a first order reaction and $n = 1$. The significance of this statement is that the reaction rate is proportional to the first power of concentration of N_2O_5 , i.e.

$$\text{rate} = k [\text{N}_2\text{O}_5]$$

where k is the first order rate constant. For the decomposition of HI , $n = 2$, i.e. the decomposition of HI is a second order reaction. Again, this means that the decomposition rate of HI is proportional to the second power or square of the concentration of HI , i.e. $\text{rate} = k [\text{HI}]^2$,

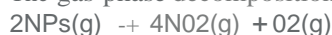
where k is the second order rate constant.

Order of reaction and stoichiometry

The rate law as well as the order of reaction must be determined experimentally. They cannot be predicted from the stoichiometry of the reaction. The stoichiometry of reaction gives the relationship between the amount of reactants and products. Examples 11.1 and 11.2 show the difference between stoichiometry and rate of reaction.

Example 11.1

The gas-phase decomposition of N_2O_5 yields N_2 and O_2 at a particular temperature.



The experimentally observed rate law for the reaction is $\text{rate} = k [\text{N}_2\text{O}_5]$.

Comment on the order and stoichiometry of the reaction.

Solution

It can be seen that the stoichiometric coefficient of N_2O_5 is 2 whereas the order of reaction is 1.

Example 11.2

The balanced equation for the decomposition of nitrous oxide is given as



The rate law is $\text{rate} = k [\text{N}_2\text{O}]^2$.

Comment on the order and stoichiometry of the reaction.

Solution

Again the stoichiometric coefficient of N_2O is 2, whereas, the order of reaction is 1.

In these two examples, the order of reaction and stoichiometry are not the same. But there are cases where the order and stoichiometric coefficient are the same. One example is seen in the reaction



$\text{Rate} = k [\text{HI}]^2$, i.e. the order of reaction is 2 and the stoichiometric coefficient of HI is also 2. You must bear the following points in mind while arriving at a rate law:

- In the case of simple reactions, the concentrations of the reactants appear in the rate law, but the concentrations of the products do not appear in the rate law. This is so because the rate measurements are done under conditions where the reverse reaction rate is negligibly low.

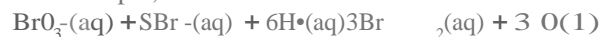
- b) The order of the reaction must be determined experimentally.
 c) The order of reaction need not be the same with the stoichiometric coefficient of the reactant.

So far, we have considered reactions involving only one reactant. In reactions involving many reactants, the rate of reaction may depend on the concentration of more than one reactant. In such cases, we can calculate the order of reaction with respect to the individual reactant. The overall order is the sum of the powers to which the individual concentrations are raised in the rate law.

In general, for a reaction $A + B + C \rightarrow \text{Products}$
 if the rate law is experimentally found to be $\text{rate} = k [A]^m [B]^n [C]^p$.

Then, the overall order of the reaction $= m + n + p$.

Example, in the reaction:



$$\text{Rate} = k [\text{BrO}_3^-] [\text{Br}^-]^2 [\text{H}^+]^3$$

The overall order of the reaction is 4, being first order in BrO_3^- , first order in Br^- and second order in H^+ .

The rate laws so far discussed are called differential rate laws. Such rate laws describe the dependence of reaction rate on concentration. From these differential rate laws, we can obtain the integrated rate laws through integration. The integrated rate laws help us in relating the concentration of a substance to time. In other words, using integrated rate laws, we can calculate the concentration of a substance at any specified time. We shall discuss the derivation of the integrated forms of rate laws later in this course.

Exercise U.1

In the decomposition of hydrogen iodide, what is the relationship between the rate of decomposition of HI and the rate of formation of H_2 ?

Experimental methods of rate studies

There are many physical and chemical methods useful for studying reaction rates. These include volume or pressure measurement, titrimetry, conductometry or potentiometry, spectrophotometry and polarimetry. Depending on the reaction under study, the concentration of a reactant or product is followed at various time intervals, using any of the methods. These values are then used for calculating the rate constant.

Volume or pressure measurement

When at least one of the components is a gas, the reaction rate can be followed by measuring the volume or pressure change. The partial pressures of the species are calculated using the reaction stoichiometry.

Titrimetry

Using acid-base or oxidation-reduction titrations, the reaction course can be followed if at least one of the components in the reaction is an acid or a base or an oxidising agent or a reducing agent.

Conductometry or potentiometry

If one or more ions are present or produced in the reaction, suitable methods can be designed, based on conductivity or potentiometric measurements.

Spectrophotometry

When a component of the reaction has a strong absorption band at a particular wavelength region, spectrophotometers can be used for measuring the reaction rate. Photoelectric colorimeters are cheaper instruments and are mainly useful for reaction rate studies in the visible region.

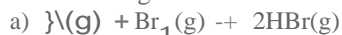
Spectrophotometers have arrangements for generation of nearly monochromatic radiations in visible and ultraviolet regions, and also for the measurement of radiations transmitted by the absorbing substances.

Polarimetry

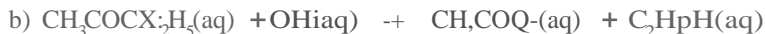
When at least one of the components of a reaction is optically active, the reaction rate can be studied from the measurement of optical rotation.

Exercise 11.2

State a suitable experimental method that can be used for monitoring the reaction rate in each of the following cases:



Hint Bromine absorbs strongly in the visible region, while hydrogen and hydrogen bromide do not.



11.4 Conclusion

In this unit, we examined the rate of reaction, rate law, order of reaction and stoichiometry. We also described some experimental methods for rate studies.

11.5 Summary

In this unit, you have learnt that

- the rate of reaction refers to the decrease in the concentration of a reactant or the increase in the concentration of a product per unit time;
- rate law is an equation expressing the relationship between the instantaneous reaction rate and the concentrations of the reactants in a reaction;
- some of the physical and chemical methods for studying reaction rates include volume or pressure measurement, titrimetry, conductometry, polarimetry and spectrophotometry.

11.6 Tutor - marked assignment

The rate constant for the decomposition of N_2O_5 at 340 K is $5.20 \times 10^{-3} \text{ s}^{-1}$.

This reaction follows first order kinetics. If the initial rate of decomposition of N_2O_5 is $2.60 \times 10^{-4} \text{ M s}^{-1}$, calculate

the initial concentration of N_2O_5 .

11.7 Reference

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Unit 12: Introduction to chemical equilibria

Contents

- 12.1 Introduction
- 12.2 Objectives
- 12.3 Reversible and irreversible reactions
- 12.4 Summary
- 12.5 Tutor-marked assignment

---6---R_c_f_e_c_e_s-----

12.1 Introduction

Three important aspects of a chemical reaction must be studied for a complete understanding of the subject. The first is whether a chemical reaction is feasible or not. The second is, if a reaction is feasible, at what stage does it stop? The third is how fast or slow does the reaction occur? You have learnt about the first and second aspects earlier in this course. This unit describes briefly the last aspect of a chemical reaction, i.e. up to what stage does a reaction proceed?

We have defined before, reversible and irreversible processes in general. However, for this purpose, irreversible reactions are those that go to completion, implying thereby, that the reaction proceeds until at least one of the reactants is completely used up. On the other hand, all those reactions which appear not to proceed beyond a certain stage after sometime even when the reactants are still available, are reversible reactions. They have only reached an equilibrium state. This unit also discusses the meaning of state of equilibrium.

12.2 Objectives

By the end of this unit, you should be able to:

- i) describe chemical equilibrium;
- ii) differentiate, between reversible and irreversible reactions using two illustrations;
- iii) express the equilibrium constant in concentration terms and apply it to homogeneous systems;
- iv) predict the shifts in equilibrium position with changes in concentration, temperature or pressure of the system.

12.3 Reversible and irreversible reactions

Generally, chemical reactions can be divided into two types: reversible and irreversible. Reversible reactions are those in which the products can combine again to form the reactants. However, in irreversible reactions, the same reactants cannot be formed from the products under normal experimental conditions. For the study of equilibrium, we are mainly concerned with reversible reactions. Reversibility of chemical reactions was first realised by Berthollet in 1799 when he was trying to explain the cause of substantial deposits of sodium carbonate around some salt lakes of Egypt. He proposed that these deposits were formed due to high concentration of sodium chloride in lake water, which reacted with the carbonates present on the shores. Normally in a laboratory experiment, we find that calcium carbonate is precipitated by the reaction of sodium carbonate and calcium chloride as represented by the equation:



What Berthollet proposed was indeed a reverse of this reaction, and the cause of reversibility was in some way connected to the high concentration of dissolved sodium chloride.

Thus, we realise that a chemical reaction such as this can proceed in both directions, i.e. from left to right or vice versa, depending on the experimental conditions. Such a reaction is usually written containing two half arrows, pointing in opposite directions (or a sign of equality between reactants and products) emphasising the fact that it is a reversible reaction:

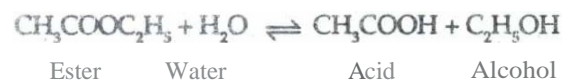


Further studies by Berthollet and Gilles in 1863 on the reaction between acetic acid and ethyl alcohol to produce ester and water, showed that the amount of ester formed varied with the initial concentrations of the reactants at a fixed temperature and pressure:



In 1864, Guldberg and Wagge showed experimentally that there exists an equilibrium between the reactants and products in a chemical reaction and that this equilibrium can be reached from either direction (starting from either reactants or products). Furthermore, the relationship between the concentrations of the reactants and products can be expressed by a simple mathematical expression. Let us consider two reactions to clarify these points.

Van t Hoff, in 1877, studied the hydrolysis of ethyl acetate:



He observed that the ratio of the product of concentrations of the products to the product of concentrations of the reactants is always constant at equilibrium and is independent of the initial concentration of ester. Expressed mathematically,

$$K = \frac{c_{\text{C}_2\text{H}_5\text{OH}} \times c_{\text{CH}_3\text{COOH}}}{c_{\text{CH}_3\text{COOC}_2\text{H}_5} \times c_{\text{H}_2\text{O}}}$$

where C represents the concentration of the species which are written as subscripts.

The constant K in the expression has a fixed value for a particular reaction at constant temperature and pressure and is a measure of the extent of reaction. A large value of K means the numerator is greater than the denominator. This indicates the presence of a high concentration of products as compared to the concentration of reactants at equilibrium.

Another example is the reaction involving hydrogen, iodine and hydrogen iodide, all in the gaseous state. If hydrogen and iodine are kept together in a closed vessel at 723 K, they will react chemically to give hydrogen iodide. However, if pure hydrogen iodide is put in a closed vessel and heated to the same temperature of 723 K, it decomposes to give hydrogen and iodine. In both cases, after a sufficiently long time, you will find all the three species, hydrogen, iodine and hydrogen iodide present in the container. At this stage, we say that an equilibrium has been reached between the reactants and the products as shown by the equation, $\text{I}_2 + \text{H}_2 = 2\text{HI}$. Furthermore, at equilibrium, there exists a definite relationship between the concentrations of hydrogen iodide, hydrogen and iodine.

This state of chemical equilibrium can be viewed from another angle. The reaction between two reactants A and B to give products C and D can be represented as:



Initially, there are only A and B present but as the reaction proceeds, some products C and D are formed. Once the products C and D are formed, they can also react to give A and B if the reaction is reversible. Since the concentrations of C and D are small in the beginning, it seems logical that the rate of the reverse reaction $\text{C} + \text{D} \rightarrow \text{A} + \text{B}$, should also be less than the rate of the forward reaction $\text{A} + \text{B} \rightarrow \text{C} + \text{D}$. However, as the reaction proceeds, more of C and D are produced.

Consequently, the rate of the reverse reaction will also increase. Ultimately, a point will be reached where the rate of the reverse reaction is exactly equal to that of the forward reaction. Since these are reactions in opposite directions, there is no change in composition with time and it seems the reactions have stopped. We then say that the reacting system is in the state of equilibrium. As a result, the reactions, in both directions, do take place but rates of forward and reverse reactions are equal. It is said that a state of dynamic equilibrium has been reached. At this stage, no further change in the concentrations of the products and reactants will take place.

In subsequent study of chemical equilibrium, derivation of the equilibrium constant and the expression in terms of partial pressures and mole fractions of the gaseous species will be addressed.

Equilibrium constants

We have established that a reaction is at equilibrium when the rates of the forward and reverse reactions become equal and there will be no further net change. In this section, we want to consider equilibrium constants. As we saw earlier, for a system



the equilibrium constant expression by Van't Hoff can be written as

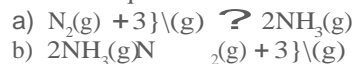
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

where the exponents of the concentration terms in the equilibrium constant expression are the coefficients of the constituents in the balanced chemical equation.

In your subsequent study of chemical equilibria, the equilibrium constant will be written in terms of activities instead of concentration and pressure. But since this is an introduction, we will be using concentrations.

Exercise 12.1

1 Write an equilibrium constant expression for the system



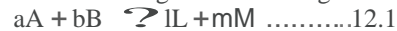
2 What can you say about the two constants?

Equilibrium constant expression in terms of concentration

We know that for an ideal gas,

$$P = \frac{n}{V} RT = cRT$$

Where c_i represents the molar concentration of a gaseous substance i . Other symbols have their usual meanings. Consider a general reaction



Assume we are at K_p at equilibrium $\dots\dots\dots$ 12.2

where P_L, P_M, P_A and P_B are the partial pressures of L, M, A and B at equilibrium.

$$K_p = \frac{P_L^l P_M^m}{P_A^a P_B^b} \quad \dots\dots\dots 12.3$$

where P_L, P_M, P_A and P_B are the equilibrium partial pressures and l, m, a and b are the respective values of L, M, A and B.

In terms of concentration, we can express equation 12.3 as

$$K_p = \left(\frac{RT \cdot c_i}{P^\ominus} \right)^{\Delta n} \dots\dots\dots (c_A^l c_B^m) / (c_A^a c_B^b)$$

$$= \frac{(c_{LRT})^1 (c_{MRT})^m \dots}{(c_{ART})^a (c_{BRT})^b \dots} \dots\dots\dots 12.4$$

i.e. $K_p = \prod_i (c_i)^{\nu_i}$ 12.5

Where ν_i represents the stoichiometric coefficient.
 K is defined by,

$\sum_i \nu_i \ln c_i$ 12.6

i.e. $K_c = \prod_i (c_i)^{\nu_i}$ J

The dimensions of K_c depend on the number of products and reactants. In this case, K_c is to be dimensionless, where c_o is the standard concentration, and is equal to 1 mol dm⁻³.

$$i.e. K_c = \frac{\prod_i (c_i)^{\nu_i}}{c_o^{\sum \nu_i}}$$

Example 12.1 is an application of Equation 12.6

Example 12.1

Calculate the equilibrium concentrations of all the species at 613 K for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, if the initial concentrations of the three gases is 0.15 M each, $K_c = 0.900$ at 613 K and the volume of the vessel is 1 dm³.

Solution

Suppose that x mol of PCl_5 has decomposed at equilibrium. Since volume is 1 dm³, the concentration expressed in molarity is equal to the number of moles of a particular substance.

	PCl_5	\rightleftharpoons	PCl_3	$+$	Cl_2
Equilibrium concentration/M	$0.15 - x$		$0.15 + x$		$0.15 + x$

Substituting the given values, we get,

$$0.900 = \frac{(0.15 + x) \cdot (0.15 + x)}{(0.15 - x)} \text{ M}$$

or $0.800 (0.15 - x) = (0.15 + x)^2$
or $x^2 + 1.1x - 0.0975 = 0$

Using the principle of solution of standard quadratic equation, we get,
 $x = 0.082 \text{ M}$ or -1.183 M

We take $x = 0.082 \text{ M}$, since the second root of the quadratic equation gives the concentrations of PCl_5 and Cl_2 as $(0.15 \text{ M} - 1.183 \text{ M}) = -1.033 \text{ M}$ which is impossible. Hence, the equilibrium concentrations are:

$[PCl_5] = (0.15 - 0.082) \text{ M} = 0.068 \text{ M}$
and $[PCl_3] = [Cl_2] = 0.15 + 0.082 = 0.232 \text{ M}$

We can verify the answer by substituting the values for concentrations in evaluating K_c

Exercise 12.2

How are K_p and K_c related to each other for a reaction between ideal gases?

Exercise 12.3

Calculate the equilibrium constant for the reaction

$\text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$ at 298 K if 1.00 mol of acetic acid and 1.00 mol of ethyl alcohol are mixed together. At the equilibrium point, the amount of water is 0.333 mol.

12.4 Summary

In this unit, you have learnt that:

- reversible reactions proceed in the forward and reverse directions;
- equilibrium is reached when the rates of the forward and reverse reactions become equal;
- equilibrium constants can be represented in terms of concentration and pressure.

12.5 Tutor-marked assignment

- In a reaction $\text{A} + 2\text{B} \rightleftharpoons 2\text{C} + \text{D}$, A and B are taken in a closed vessel at 300 K. The initial concentration of B is 1.5 times that of A. At equilibrium, the concentration of A and D are equal. Calculate the equilibrium constant at 300K.
- In a 10.0 dm^3 mixture of H_2 , I_2 , and HI at equilibrium at 698 K, there are 0.100 mol of H_2 , 0.100 mol of I_2 and 0.740 mol of HI. If 0.500 mol of HI is now added to this system, what will be the concentrations of H_2 , I_2 , and HI, once equilibrium has been re-established?

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Unit 13: Le Chatelier's principle and chemical equilibria

Contents

- 13.1 Introduction
- 13.2 Objectives
- 13.3 Determination of equilibrium constants
- 13.4 Le Chatelier's principle and chemical equilibria
- 13.5 Conclusion
- 13.6 Summary
- 13.7 References

13.1 Introduction

In this unit, we shall consider the determination of equilibrium constants. We shall also study the Le Chatelier's principle regarding chemical equilibria. Finally, we shall see the factors that affect the shift of equilibrium in a particular direction.

13.2 Objectives

By the end of this unit, you should be able to:

- i) state and explain the Le Chatelier's principle;
- ii) predict shift in equilibrium position with changes in concentration, temperature and pressure of the system.

13.3 Determination of equilibrium constants

In order to calculate equilibrium constant the initial concentrations and extent of the reaction must be known. In fact, to use any of the equations for determining equilibrium constant, we must be sure that equilibrium has indeed been reached. There are two criteria for confirming the presence of equilibrium condition. Firstly, the value of equilibrium constant should be the same when the equilibrium is approached from either side. Secondly, the value of equilibrium constant should be the same when the concentrations of the reacting substances are varied greatly.

Once it is established that equilibrium has been reached, the next step is to find out the equilibrium concentration of at least one of the reactants or products, in order to calculate the extent of the reaction. This can be achieved either by chemical analysis or by measurement of some physical property. The difficulty with chemical analysis is that the concentration will change during the course of the analysis. Hence, this method can only be used when the reaction can be stopped at equilibrium by some means, e.g. sudden cooling. Physical methods are more convenient since they do not require stopping the reaction. The physical properties commonly used for this purpose are density, refractive index, electrical conductivity and light absorption.

Relationships also exist between equilibrium constants and Gibbs' free energy. This will be studied later in your programme. Now, let us consider if it is possible to predict the shift in equilibrium position when a stress is introduced to the equilibrium system.

13.4 Le Chatelier's principle and chemical equilibria

Often, we are more interested in predicting qualitatively, the results of a change brought about by external forces on a system under equilibrium. For instance, if pressure, temperature or volume is changed for a system under equilibrium, what will be the effect, if any, on the equilibrium itself? However, this can be much more easily predicted with the help of Le Chatelier's principle. Le

Chatelier's principle states that: *If a stress is applied to any system under equilibrium, the system will tend to shift in such a way so as to neutralise the effect of that stress (if possible).*

The stress for a chemical reaction could be in form of a change in pressure, temperature or concentration at equilibrium. According to the principle then, equilibrium will shift in such a direction that the effect of these changes is neutralised. Let us consider the effect of each one of these factors on equilibrium.

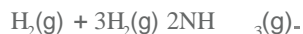
Effect of change of concentration

Let us consider the reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$ which has attained equilibrium. Now, if we add some to the equilibrium mixture, it will obviously upset the equilibrium. According to Le Chatelier's principle, the equilibrium will shift in such a way that will oppose the effect of this excess H_2 . It can do so by using up this excess to react with more I_2 to give more HI. We describe this process by saying that the final position of equilibrium has shifted to the right of the equation. In this final state of equilibrium then, more amount of HI is formed, compared to the earlier equilibrium state. Just the opposite of this will happen to the reaction if, instead of H_2 , some I₂ is added to the system under equilibrium. In short, by changing the concentration at equilibrium, the reaction will move forward or in the reverse direction, so that the equilibrium constant still has the same value.

Effect of change of pressure

Consider the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ again. Now, suppose that the pressure of the system is increased, perhaps by reducing the volume of the container, the system should react in such a way as to reduce the effect of the increase in pressure. However, there is no way by which this can be achieved. The forward reaction or the reverse reaction will not be favoured by pressure change since the total number of moles of the reactants is the same as the total number of moles of the products.

However, the situation changes if we consider the synthesis of ammonia:



If the pressure of the system is increased at equilibrium, the effect of this increase can be eliminated by the formation of more ammonia. It is becomes obvious if you realise that the total number of moles of the reactants is four while the number of moles of product is two. Four moles will exert greater pressure than two moles. So the system can reduce the external pressure by moving in the forward direction. On the other hand, if we reduce the external pressure on the system, more of ammonia will decompose to give nitrogen and hydrogen. Thus if we want to produce ammonia industrially, it is preferable to carry out the reaction at a high pressure.

Comparing these two reactions, we can conclude that changes in pressure at equilibrium will affect the amounts of products formed for only those reactions where the total number of moles of reactants are different from the total number of moles of products.

Effect of change of temperature

Consider once again, the synthesis of ammonia from nitrogen and hydrogen which is an exothermic reaction. If the temperature of the system is increased at equilibrium, Le Chatelier's principle tells us that the system should react in a way that will neutralise this effect. Let us see how this is possible. We know that the formation of ammonia is an exothermic reaction and therefore, the reverse reaction of decomposition of ammonia will be endothermic. Thus, the excess heat supplied by raising the temperature of the system can be absorbed by the system if the reaction goes more towards the left. This will increase the amounts of N_2 and decrease the amount of NH_3 at equilibrium. We can generalise this observation by saying that, raising the temperature of a system undergoing exothermic reaction will decrease the amount of products and increase the amount of the reactants. Just the opposite will be true for all endothermic reactions.

The effects of these factors gain special importance, when producing a substance on a large scale. In any industrial production of a substance, it is imperative to know the optimum conditions of temperature, pressure and concentration, in order to get the maximum yield at a mini-

mum cost. For instance, in the production of ammonia, we know from Le Chatelier's principle that high pressure and high concentration of N_2 and H_2 will favour the reaction. Similarly, Le Chatelier's principle also predicts that the reaction will be more favourable at a low temperature, since it is exothermic. However, we cannot carry out the reaction at a very low temperature because of another factor, which is, that the rate of the reaction becomes too slow at lower temperatures. Hence, the reaction is performed at a pressure of several megapascals and temperature of between 650 and 700 K.

Exercise 13.1

- Consider the reaction,
 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.
 How will the equilibrium be affected by:
 - the addition of Cl_2 ;
 - decrease in the volume of the container?
- If $\Delta H^\circ = 41 \text{ kJ mol}^{-1}$ for the reaction
 $H_2O(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$.
 What will be the effect of increase of temperature on the equilibrium?

13.5 Conclusion

In this unit, we learnt about Le Chatelier's principle and its use in predicting the shift in the position of equilibrium by changes in concentration, temperature and pressure of the system. We refer other details of chemical equilibria to another level for you to have better understanding.

13.6 Summary

In this unit, you have learnt that:

- we can determine the equilibrium constant by either chemical analysis or by measurement of some physical property;
- Le Chatelier's principle can be used to predict a shift in the position of the equilibrium of a system under stress.

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Unit 14: Ionic equilibria (I)

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14.1 Introduction

We have seen in Unit 8 that for any reversible reaction in a solution, the law of mass action can be applied and the equilibrium constant can be expressed in terms of concentrations of various reactants and products. In this unit, we are going to find out how the equilibrium expression can be applied to solve the problems relating to solutions of electrolytes. Solutions, as you know, consist of a solvent and at least one solute, as defined in Unit 8. Since majority of the reactions are carried out in water as the solvent, we shall consider the equilibria in aqueous solutions only. For simplicity, we shall study these equilibria in several steps. First, we shall apply the equilibrium expression to the solute system where the solute dissociates in water but is not affected otherwise by water. Next, we shall consider the equilibrium of water dissociation. Finally, those cases where the two equilibria have to be considered together will be studied. These studies find wide applications in the fields of analytical, industrial and biochemistry units.

14.2 Objectives

By the end of this unit, you should be able to:

- i) define acids and bases on the basis of different concepts;
- ii) write the equilibrium constant expressions for the dissociation of weak acids, weak bases and water;
- iii) define pH scale;
- iv) state the effect of the addition of a substance containing common ion on the dissociation of acids and bases.

14.3 Electrolytes and non-electrolytes: acids, bases and salts

In this unit, we shall confine our discussion to the solutions of electrolytes. It then becomes necessary that we must first know what are *electrolytes* and *non-electrolytes*. If we put two charged electrodes in pure water, a very small amount of electric current will flow. However, if we add a small quantity of common salt (NaCl) to water, current flows easily; the reason being that the salt dissociates in water into its constituent ions – sodium ions and chloride ions. Sodium ions, which are positively charged, will move towards negatively charged electrode and chloride ions will move towards the positively charged electrode. Thus current is carried by these ions in solution. All those substances which on dissolution in water conduct electricity are known as electrolytes; fa-

miliar examples are acids, bases or salts. On the other hand, all those substances which when dissolved in water do not conduct electricity are called non-electrolytes.

A substance may not necessarily ionise completely in solution. It may ionise to a small extent. We thus further classify, qualitatively, electrolytes into two groups. All those substances which dissociate almost completely are known as *strong electrolytes* and the substances which dissociate to a small extent are known as *weak electrolytes*. Most of the acids, like acetic acid, oxalic acid, sulphurous acid, etc., and a few salts, like lead acetate and mercuric chloride, are all weak electrolytes. On the other hand, most of the salts and a few acids, such as perchloric, nitric, hydrochloric, sulphuric, etc., fall in the category of strong electrolytes.

Most of our discussions will be confined to equilibria involving weak acids and weak bases. Presently acids and bases are being defined in many different ways. The application of equilibrium experiments remains the same in whatever way one defines these acids and bases; yet, it is advisable to have a clear understanding of these different concepts of acids and bases.

14.4 Concepts of acids and bases

Arrhenius concept of acids and bases

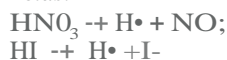
There is no doubt that you have learnt about acids, bases and salt in your secondary school days. Attempt to define acids and bases. We are all aware that by the reaction of acids and bases, we obtain salt and water. Though there are other ways of preparing salts. Do you say that acids can be referred to as ionic compound? Why do you believe that acids are ionic compounds? They are because in their aqueous forms their positive and negative charged particles break apart to form a hydrogen ion (H⁺).

Let us examine some definitions given by some chemists like Arrhenius, Lowry, Bronsted and Lewis.

Arrhenius definition of an acid

Arrhenius defined an acid as a compound which when dissolved in water gives hydrogen ion and a base, as a compound which dissociates in water to yield hydroxyl ion. When an acid reacts with a base, it gives salt and water and the process is known as a *neutralisation reaction*. Following examples would make the definition quite obvious:

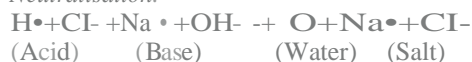
Acids:



Bases:



Neutralisation:

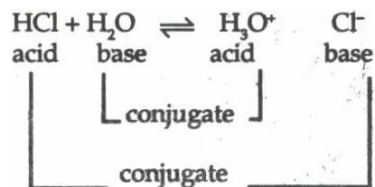


This is the most common and most frequently used concept. However, there are two main limitations to the concept. First, it does not take into account the role of the solvent in the process. Secondly, there are many substances which do not contain hydrogen ion or hydroxyl ions but behave like acids or bases in their reactions. For example, ammonia, NH₃ behaves like a typical base in reacting with an acid but does not contain hydroxyl ions. Similarly, BF₃ molecule does not contain hydrogen ions but does act as an acid toward; a base like ammonia in the reaction:



Lowry-Bronsted concept of acid and bases

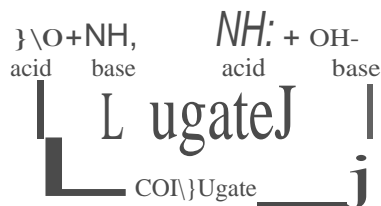
In 1923, two chemists, Lowry and Bronsted, proposed a wider definition of acids and bases. They defined an acid as any substance (molecule or ion) which can act as a proton donor and a base as a substance which can accept a proton. Since a proton cannot exist free in any solvent, it is always found associated with a conjugate base. Thus, any two substances related by the gain or loss of H^+ ion are known as conjugate acid-base pair. For example, HCl is an acid which has a conjugate base Cl^- ion. Every acid HA has a conjugate base A^- formed by the loss of a proton and every base A^- has a conjugate acid formed when the base accepts a proton. Let us look at the reaction of HCl with water:



Here, water molecule acts as a base (proton acceptor) towards the acid, HCl (proton donor), producing conjugate acid and base, respectively as H_3O^+ and Cl^- . It can be represented in another way as:



Acid and Base₁ form a conjugate pair just like Acid₂ and Base₂. Let us consider another case:

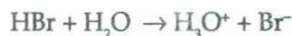
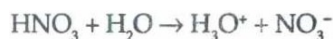


In this case, H_2O is acting as an acid and NH_3 as a base. Thus, we see that water acts as an acid in one case and a base in another. Further, a stronger base will snatch away the proton associated with a weaker base. Thus, water molecule acts as a stronger base than chloride ion to produce a stronger acid (H_3O^+) and a weaker base, OH^- ion. Table 14.1 gives a list of a few examples of Bronsted acids and bases.

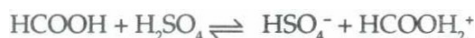
Table 14.1 Bronsted acids and their conjugate bases

Acid	Base
H_3O^+	H_2O
H_2O	OH^-
HCl	Cl^-
H_2SO_4	HSO_4^-
HSO_4^-	SO_4^{2-}
CH_3COOH	CH_3COO^-
NH_4^+	NH_3
NH_3	NH_2^-

Two main advantages of this concept are quite obvious. First, any substance which can accept a proton is defined as a base and therefore, it does not have to contain hydroxyl ion to be classified as a base. An obvious example is the above reaction where NH_3 having no OH^- acts as a base towards water. On the other hand, a compound containing a proton can behave like an acid only in the presence of an acceptor. For example, HCl gas cannot behave like an acid unless water is present to accept the proton. The second advantage is that the acid strength depends on the solvent. Hence, an acid which behaves like a strong acid in water may act as a weak acid in another solvent depending upon the proton accepting ability of the latter. For example, HClO_4 , HBr , HNO_3 etc. are all strong acids in water as shown in the following equations:



These reactions indicate that the equilibrium is shifted almost completely to the right side as their dissociation in water is complete; hence single arrows have been used. Under these conditions, therefore, we cannot differentiate as to which is stronger and which is weaker amongst them. The reason is obvious, water is a strong base for all these acids. Water reduces the strength of all these acids to the same level and these are all called strong acids in water. However, the situation will change if we dissolve all these acids in another solvent which is a weaker base than water, for instance, formic acid. The order of strength found with this case is: perchloric acid > nitric acid > hydrobromic acid. At first, the statement seemed ridiculous since we are calling formic acid a base, but a careful examination will clarify this confusion. There is no doubt that formic acid has a proton which can be given off to water; therefore it is classified as an acid. But, it can also accept a proton from a stronger acid and can thus **have** like a base towards such a stronger acid, as shown by the following reaction:



Thus, Bronsted definition of acids and bases is much wider than the Arrhenius concept.

Lewis acids and bases

There are a number of reactions which resemble acid-base neutralisation reactions but where protons are not involved. Obviously, Arrhenius or Bronsted concepts cannot be utilised for such reactions. Lewis defined acids and bases in a different fashion that has the widest application. According to Lewis, an acid is an electron pair acceptor and a base is an electron pair donor. In other words, any substance which can accept a pair of electrons is an acid and a substance which donates a pair of electrons is a base. A few examples of Lewis acid-base reactions are:



Bronsted bases, like OH^- or NH_3 in the above reactions, are also bases because they react with proton by donating electrons; but Lewis acid is not necessarily Bronsted acid since Bronsted acid must contain a proton which can be transferred to a base whereas Lewis acid does not have such a condition.

In our discussions, we shall be primarily concerned with aqueous solutions which involve proton transfer and therefore, for the sake of completeness and the wide application of Lewis concept, this has been included here

Exercise 14.1

Explain, with examples, the difference between Lewis and Bronsted acids

Attributes of acids and bases

When the characteristics of substances are known, undoubtedly, we will be cautious in handling and applying them for our benefits. Now, try to list out three characteristics of acids you know.

Generally, acids are sour though we do not expect you to taste the laboratory chemicals. But it is a known fact that natural foods containing acidic content are sour in taste. Can you mention some of the natural sources of these acids? Citrus fruits should be the major ones on your list. We also know that acid is contained in our stomach. In homes, vinegar, that we use to cleanse food items in the kitchen, is also acidic.

Now about bases, with the various description provided earlier on, what are the attributes of bases? They are bitter and feel slippery. You would recall that the use of some local soaps with excess base can burn the human skin. You often feel the heat in your palm, meaning excess of base is dangerous to our skin.

Exercise 14.2

Which of the following statements are correct about acids and bases?

- The strength of an acid is determined by the concentration of the hydroxyl ions.
- The smaller the OH⁻ ions the stronger the base.
- Ammonia is an example of a base.
- Neutralisation reaction between an acid and a base occurs only if an equal number of hydrogen and hydroxide ions are present.

14.5 Conclusion

In this unit we have examined the nature of electrolytes and non-electrolytes. We concluded that addition of a small quantity of electrolyte, e.g. common salt into pure water, makes electric current to flow easily. The current is carried by these ions in solution. Electrolytes, therefore, are defined as substances which on dissolution in water conduct electricity.

On the basis of Arrhenius definition of an acid, we saw two limitations of this concept,

- it does not consider the role of the solvent in the process;
- there are many substances which do not contain hydrogen ion or hydroxyl ions and yet they behave like acids or bases in their reaction.

The Lowry-Bronsted concept of acids and bases, gives a wider definition of acids and bases. The concept gave rise to conjugate acids and bases. The Lewis concept of acids and bases has the widest application and helps to explain better many chemical reactions.

14.6 Summary

At the end of this unit, you have learnt that:

- strong acids and bases are supposed to dissociate almost completely in water whereas weak acids and bases are not.
- we can determine the dissociation constants of acids and bases under equilibrium conditions in terms of concentration.
- water is a universal solvent and it is amphoteric in nature.
- the dissociation of water can be written as:



Unit 15: Ionic equilibria in weak acids and bases

Contents

- 15.1 Introduction
- 15.2 Objectives
- 15.3 Ionic equilibria in weak acids and bases
 - Weak acids
 - Weak bases
 - Polyprotic acids
- 15.4 Conclusion
- 15.5 Summary
- 15.6 References

15.1 Introduction

In the unit we shall concern ourselves with the ionisation equilibria of weak acids and bases. In particular, we shall consider a weak monobasic acid, acetic acid (CH_3COOH) and a weak base, ammonium hydroxide (NH_4OH). We shall also study ionisation of polyprotic acids, which are acids that contain more than one hydrogen atom per molecule. Such acids as phosphoric acid ionise through several steps.

15.2 Objectives

By the end of this unit, you should be able to:

- i) write the equilibrium constant expressions for the dissociation of weak acids, weak bases and water.

15.3 Ionic equilibria in weak acids and bases

Even in dilute solutions, weak electrolytes are dissociated to a very small extent and are never completely dissociated. Thus, for weak acids and bases, the ions produced on dissociation are in equilibrium with the undissociated molecules in solution and the law of mass action can be applied to such an equilibrium. The equilibrium constants for the dissociation of acids and bases are expressed by the symbols K_a and K_b respectively. These equilibrium constants, K_a and K_b are called *dissociation constants* of acids and bases.

Weak acids

If HA represents any weak acid, we can write the dissociation reactions as



And the corresponding dissociation constant expression as,

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \dots\dots\dots (15.2)$$

If the initial concentration of the acid is C_0 and α is the degree of dissociation, then the equilibrium concentrations would be:



Initial concentration	C_0
Equilibrium concentration	$(1 - \alpha) C_0$ αC_0 αC_0

Substituting these values in Equation 15.2, we get:

$$K = \frac{\alpha C_0 \times \alpha C_0}{(1 - \alpha) C_0}$$

Or

$$K = \frac{\alpha^2 C_0}{1 - \alpha} \dots \dots \dots (15.3)$$

Application of Equation 15.3 can be seen from the following examples.

Example 15.1

At 298 K, a 0.100 M solution of acetic acid is 1.34% ionised. Calculate the ionisation constant of acetic acid.

Solution

Since $\alpha = 0.0134$, $[\text{H}^+] = \alpha C_0 = 0.0134 \times 0.100 \text{ M}$
 $= 0.00134 \text{ M} = [\text{CH}_3\text{COO}^-]$;
 also $[\text{CH}_3\text{COOH}] = (1 - 0.0134) \times 0.100 \text{ M} = 0.09866 \text{ M}$
 $\therefore K = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(0.00134)^2}{0.09866}$
 or $K = 1.82 \times 10^{-5}$

Example 15.2

Calculate the concentration of H^+ ions in a solution of 1.0 M acetic acid at 298 K ($K = 1.8 \times 10^{-5}$).

Solution

As per Equation 15.1, we can write,



Equilibrium concentration	$C_0 (1 - \alpha)$	$C_0 \alpha$	$C_0 \alpha$
Initial concentration of acetic acid,	$C_0 = 1.0 \text{ M}$		
$\therefore [\text{H}^+] = C_0 \alpha \text{ M}$			
$= \alpha \text{ M}$			

The value of α can be found by substituting K and C_0 values in Equation 15.3;

$$1.8 \times 10^{-5} = \frac{\alpha^2}{1 - \alpha}$$

Solving for α , we get a value of 4.2×10^{-3} ; the other value, being negative, has no physical significance.

Hence, $[\text{H}^+]$ in 1M acetic acid = $\alpha \text{ M}$
 $= 4.2 \times 10^{-3} \text{ M}$

Equation 15.3 can be simplified further if the degree of dissociation is very small, i.e. if $\alpha \ll 1$, then $K = \alpha^2 C_0$.

Multiplying both sides by C_0 we get,

$$K \cdot C_0 = \alpha^2 C_0^2$$

$$\text{Or } C_0 \alpha = \frac{K}{C_0} \alpha C_0$$

$$\text{Or } [\text{H}^+] = \frac{K}{C_0} C_0$$

Remember that in deriving Equation 15.4, we have made two assumptions. First, that the degree of dissociation is much smaller than unity and secondly that water which has been used as a solvent has no effect on the equilibrium of the acid.

Weak bases

For a weak base, BOH, we can write the equation as,



$$\text{And } K_b = \frac{[\text{B}^{\ominus}][\text{OH}^{\ominus}]}{[\text{BOH}]} \dots\dots\dots (15.6)$$

If C_0 is the initial concentration of the base and α is the degree of dissociation, then,

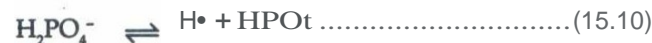
$$K_b = \frac{(\alpha C_0)(\alpha C_0)}{(1 - \alpha) C_0} = \frac{\alpha^2 C_0}{1 - \alpha} \dots\dots\dots (15.7)$$

$$\text{Also, } [\text{OH}^{\ominus}] = \alpha C_0 = \sqrt{K_b C_0} \text{ if } \alpha \ll 1 \dots\dots\dots (15.8)$$

Polyprotic acids

Those acids which contain more than one hydrogen atom per molecule and can release proton in more than one step are called polyprotic acids. Each ionisation step is associated with an equilibrium constant.

Consider the case of phosphoric acid which is a *triprotic acid*. It is also called a *tribasic acid*, implying that each mole of the acid can neutralise three moles of a base. The dissociation reactions are written as:



Each of these steps of dissociation is connected with an equilibrium constant which can be represented by,

$$K_{a1} = \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \dots\dots\dots (15.12)$$

$$K_{a2} = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \dots\dots\dots (15.13)$$

and

$$K_{a3} = \frac{[\text{H}^+][\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]} \dots\dots\dots (15.14)$$

The actual values for the three equilibrium constants have been found to be $K_{a1} = 7.5 \times 10^{-3}$, $K_{a2} = 6.2 \times 10^{-8}$ and $K_{a3} = 1.0 \times 10^{-12}$ which follows a decreasing order. This is to be expected since an undissociated molecule, H_3PO_4 , can lose its proton more easily than the negatively charged H_2PO_4^- ion, which in turn, can give off its proton more easily than a double-negatively charged HPO_4^{2-} ion. Hence, in a solution of phosphoric acid, the predominant species will be H_3PO_4 , H^+ and H_2PO_4^- with lesser amounts of HPO_4^{2-} and still less of PO_4^{3-} .

Another common example is H_2SO_4 which dissociates as,



$$K_1 = \frac{[H^+][HSO_4^-]}{[H_2SO_4]} = 1.0 \times 10^3$$



$$K_2 = \frac{[H^+][SO_4^{2-}]}{[HSO_4^-]} = 1.3 \times 10^{-2}$$

...A\$ a test of the understanding of the above concepts, answer the following exercise.

Exercise 15.1

1. Calculate the concentration of OH⁻ ions in a solution of 1.0 M NH₄Cl at 298 K (K_a = 1.8 × 10⁻⁵).

15.4 Conclusion

So far, we have been able to address the fundamental principles in ionic equilibria. Specifically, we have defined acids and bases on the basis of operations. Some equilibrium constants calculations were also performed.

15.5 Summary

At the end of this unit, you have learnt that

- i) strong acids and bases dissociate almost completely in water whereas weak acids and bases do not.
- ii) we can determine the dissociation constants of acids and bases under equilibrium conditions in terms of concentration.

15.6 References

1. IGNOU (1999) *Chemical Equilibrium and Electrolysis — Physical Chemistry 4 CHE - 04*. Sharma, K. L. Sharma, K. (1997) *A Textbook of Physical Chemistry, 3rd Edition*, New Delhi,
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Unit 16: Ionic product of water

Contents

- 16.1 Introduction
- 16.2 Objectives
- 16.3 Ionic product of water
- 16.4 pH scale
- 16.5 Common ion effect
- 16.6 Conclusion
- 16.7 Summary
- 16.8 References

16.1 Introduction

In this unit, we shall apply the equilibrium expression to the solute system where the solute dissociates in water but is not affected otherwise by water. We shall also consider the equilibrium of water dissociation itself. The ionic product of water will be studied. Next, we shall examine the pH scale and its application. Finally, the common-ion effect on a system at equilibrium shall be studied and its application in the study of *buffer* solutions shall be discussed.

16.2 Objectives

By the end of this unit, you should be able to:

- i) define ionic product of water;
- ii) write the equilibrium constant expressions for the dissociation of water;
- iii) define pH scale;
- iv) state the effect of the addition of a substance containing common ion on the dissociation of acids and bases.

16.3 Ionic product of water

Water is the most commonly used solvent and it is amphoteric in character. The dissociation of water can be represented as,



or



Although Equations 16.1 and 16.2 are representations of the same equilibrium, the latter is a better representation in the sense that a free proton having a high charge density and extremely small size is incapable of free existence in solution and, therefore, gets attached to a molecule of water. However, since our calculations on equilibrium constant will not be different in case of either representation, for simplicity sake, we represent the water equilibrium by Equation 16.1 and the equilibrium constant is written as,

$$K = [H^+] [OH^-] / [H_2O] \dots\dots\dots (16.3)$$

or
 $K = \frac{[H^+][OH^-]}{[H_2O]} \approx 1.0 \times 10^{-14}$ (16.6)

In pure water the concentration of H^+ and OH^- is approximately $1.0 \times 10^{-7} M$. Since the dissociation of H_2O is negligible in comparison with its concentration, we can assume that the concentration of H_2O is a constant quantity. Thus, K in Equation (16.6) can be replaced by a numerical constant, known as the ion product of water. Thus,

$$K_w = [H^+][OH^-] \quad (16.5)$$

Experimental determination gives a value of 1.0×10^{-14} for K_w at 298 K. Hence,

$$\frac{[H^+]}{[OH^-]} = \frac{K_w}{[OH^-]} \quad (16.6)$$

Since the amount of H^+ and OH^- produced by the dissociation of pure water is equal, concentration of each ion in solution is given by,

$$[H^+] = [OH^-] = 1.0 \times 10^{-7} \quad (16.7)$$

OR
 $[H^+] = \sqrt{K_w}$ (in pure water) (16.8)

In the next section, we shall discuss pH scale which is convenient in expressing the H^+ ion concentration of a solution. Like any equilibrium constant, K_w also depends on temperature.

16.4 pH scale

Before we examine the application of the reactions between acids and bases, we must know how to use the pH scale. What is a pH scale? A pH scale is a scale that is used in measuring the strength of an acid or base in a solution. Thus, we can say the pH scale is a measure of the strength of an acid (which is the hydrogen ion concentration in solution). We are also aware that this scale spans from 0–14 with the middle number of 7, often called pH 7, being the neutral point.

Consider the equilibrium of water as given in Equation 16.3,



Suppose that we add a small quantity of an acid to water, thereby increasing the concentration of H^+ ion at equilibrium. The equilibrium will immediately shift back to oppose the effect of this increase by the combination of the added H^+ ions with some OH^- ions to form undissociated water until Equation 16.1 is satisfied. Once the equilibrium is re-established, the concentration of the hydrogen ion will be more than the concentration of the hydroxyl ion in solution. Hence, at 298 K, whenever the concentration of hydrogen ion in water is greater than $1.0 \times 10^{-7} M$, the solution is said to be acidic and whenever it is less than $1.0 \times 10^{-7} M$, we refer to it as a basic solution. Instead of expressing these small concentrations as negative powers of 10, we can state them more conveniently and in a small number by expressing them in terms of their negative logarithm. Hence, instead of writing H^+ ion concentration as $1.0 \times 10^{-7} M$ we write it as $-\log(1.0 \times 10^{-7})$ or simply 7. The number is preceded by a symbol pH (small letter p, followed by capital letter H). Thus,

$$pH = -\log [H^+] \quad (16.9)$$

OR
 $[H^+] = 10^{-pH}$ (16.10)

where H^+ ion concentration is expressed in mol dm⁻³. The concept of negative logarithm can be used for defining the concentration of other ions also. For example, pOH represents the concentration of OH⁻ ion in solution and pM represents the concentration of the metal ion, M, in solution.

Example 16.1

Find the concentration of H^+ ions of a solution whose pH value is 4.5.

Solution

Using the equation,

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

$$\text{we get, } 4.5 = -\log [H^+]$$

$$\text{or } \log [H^+] = -4.5$$

$$\text{i.e., } [H^+] = 10^{-4.5} \text{ M}$$

$$= 10^{-(4+0.5)} \text{ M} \dots \dots \dots \text{Step (i)}$$

$$= 10^{-4} \times 10^{-0.5} \text{ M} \dots \dots \dots \text{Step (ii)}$$

$$= 3.2 \times 10^{-5} \text{ M} \dots \dots \dots \text{Step (iii)}$$

Pure water, where H^+ ion and OH⁻ concentrations are both equal to 1.0×10^{-7} (at 298 K), will thus have a pH value of 7. An acidic solution means that the pH should be less than 7 and a basic solution should have pH greater than 7.

Let us do a few simple calculations in order to appreciate quantitatively, what happens to the self-ionisation equilibrium of water when we add a small quantity of a strong acid to it. Consider a solution containing 0.010 mole of HCl in 1 dm³ of water. The concentration of hydrogen ion due to HCl will be 1.0×10^{-2} M. This addition of acid will disturb the water equilibrium and this equilibrium will shift to the left so that dissociation of water is suppressed. Thus, the concentration of H^+ ions produced by the self-ionisation of water (10^{-7} M) is negligible in comparison with the H^+ ion produced by the added acid (10^{-2} M). Hence, the contribution due to water dissociation can be neglected in such a case and the pH of the solution will be 2. The concentration of OH⁻ ion will then be given by

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-2}} = 1.0 \times 10^{-12} \text{ M}$$

or
pOH = 12

It can be stated differently that in 10^{-2} M acid solution, the concentration of OH⁻ ion (10^{-12} M) in the above example is less than the concentration of H^+ ion (10^{-2} M) and, the product of the two, which is always constant, is equal to 1.0×10^{-14} . It can be expressed as,

$$pH + pOH = 14 = -\log \dots \dots \dots (16.11)$$

Thus, in pure water or a dilute solution of an acid or a base, we can express the concentration of H^+ or OH⁻ by simply stating the pH of the solution. We have also studied that the contribution due to self-ionisation of water is negligible in cases of solutions of strong acids and bases as well as of moderately concentrated solutions of weak acids and weak bases. However, dealing with very dilute solutions of weak acids and bases, we cannot neglect the contributions due to self-ionisation equilibrium of water.

- To sum up, while calculating $[H^+]$ of an acid,
- i) $[H^+] = [H^+]$ from acid, if [acid] is far greater than 10^{-6} M.
 - ii) $[H^+] = [H^+]$ from acid + $[H^+]$ from water, if [acid] is between 10^{-6} and 10^{-8} M.
 - iii) $[H^+] = [H^+]$ from water, if [acid] is far less than 10^{-8} M.
- Now, practise with the following exercise which is based on the concept of pH.

Exercise 16.1

Calculate the pH of the following solutions:

- a) 1.0×10^{-3} MHO
- b) 1.0×10^{-10} MHO
- c) 1.0×10^{-10} MN H

16.5 Common-ion effect

Let us consider the dissociation of a weak acid such as acetic acid,



The equilibrium constant for the dissociation can be represented as,

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \text{..... (16.12)}$$

or

$$[\text{H}^+] = K_a \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \quad \text{..... (16.13)}$$

Let us consider what happens when we add some acetate ions in the form of solid acetate to the above solution. Sodium acetate is added in the solid form so as not to cause any change in the volume of the solution. Sodium acetate being a strong electrolyte will dissociate almost completely to give Na^+ ions and CH_3COO^- ions in solution. The acetate ions so added will disturb the equilibrium of acetic acid. The equilibrium will, therefore, shift to the left producing more of undissociated acetic acid in order to counteract the effect of added acetate ions according to the Le Chatelier's principle. The net result is that the dissociation of the acid has been suppressed by the addition of a common ion (acetate ion in the present case) at equilibrium. Thus any ion which is involved in a chemical equilibrium and comes from two different sources in solution is known as *common ion* and its effect finds great use in the study of *buffer solutions* and the solubility of sparingly soluble salts. These two concepts will form the subjects of latter units of this course.

On the basis of the above discussion, answer the following exercise.

Exercise 16.2

Addition of NH_4Cl to NH_4OH results in the decrease of OH^- ion concentration. Explain.

16.6 Conclusion

So far, we have explained several phenomena including pH scale, ionic product of water and 'common ion effect'. Some equilibrium constants calculations were also performed.

16.7 Summary

At the end of this unit, you have learnt that

- i) pH of acid is mathematically expressed as $-\log [\text{H}^+]$;
- ii) common-ion refers to any ion involved in a chemical equilibrium and comes from two different sources in solution.

16.8 References

- IGNOU (1997) *Chemical Equilibrium and Electrolysis-Physical Chemistry 4 CHE-04*.
- Sharma, K. L. and Sharma, K. (1997) *A Textbook of Physical Chemistry, 3rd Revised Edition*, New Delhi, Vikas Publishing House NT210.

Unit 17: Ionic Equilibria (II)

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17.1 Introduction

In Unit 16 we were concerned with ionic equilibria in acids and bases. We also covered the pH scale and common-ion effect. In this unit, we shall be dealing with the buffer solution, hydrolysis and indicators and their uses.

17.2 Objectives

By the end of this unit, you should be able to:

- i) explain the meaning of buffer solution and their applications;
- ii) state the meaning of hydrolysis and calculate hydrolysis constant.

17.3 Buffer solutions

In this section, we shall examine buffer solution. What exactly do we refer to a buffer solution? A solution that consists of a mixture of a weak acid and its salt (a conjugate base) or a weak base and its salt (a conjugate acid) is said to be a buffer solution.

A careful examination of equation 16.13 of Unit 16 reveals that the hydrogen ion concentration (or the pH of the solution) shall have a constant value equal to K_a (or pK_a), if the concentration of acetate ions and the undissociated acetic acid become equal to each other. In other words, find how this condition can be achieved and what are its uses. Consider a 1.0 M acetic acid solution for which $K_a = 1.8 \times 10^{-5}$. We can write,

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

or

$$1.8 \times 10^{-5} = \frac{[H^+]}{[CH_3COOH]}$$

Since, $[H^+] = [CH_3COO^-]$

Assuming that the amount of acetic acid dissociated is negligible in comparison to the initial concentration of acetic acid (1.0 M), we can write the amount of undissociated acetic acid as, 1.0 M.

Therefore $[H^+] = 1.8 \times 10^{-5} \times 1.0 \text{ M}$

Or

pH = 2.38; i.e., the pH of 1.0 M acetic acid is 2.38.

To this solution, if we add enough of solid sodium acetate to make it 1.0 M in acetate ion concentration, the dissociation of acetic acid will be further suppressed due to the common ion effect. Thus, the concentration of acetate ion arising from the dissociation of acetic acid is negligible in comparison with that supplied by sodium acetate. Hence, we can assume the concentration of acetate ion in solution to be 1.0 M. Similarly, if the dissociation of acetic acid is also negligible, the concentration of the undissociated acetic acid, [CJ\COOH}, can be taken as 1.0 M. Substituting these values in Equation 16.12 of Unit 16, we get,

$$1.8 \times 10^{-5} = \frac{[H^+](1.0)}{(1.0)}$$

or pH = 4.74; t.e., a solution which has 1.0 M acetic acid and 1.0 M sodium acetate has a pH of 4.74. Such a solution of a weak base and its salt is known as a *buffer solution* and it has an advantage of maintaining the pH of the solution almost constant even if small quantities of strong acids or bases are added to it. Let us see how a buffer solution does this.

Assume that to the solution of acetic acid and sodium acetate above, known as acetate buffer, we add hydrochloric acid such that its concentration in the solution becomes 0.01 M. As a result of this, 0.01 M H⁺ ions will react with 0.01 M acetate ions to form 0.01 M undissociated acetic acid. Thus, the concentration of the undissociated acetic will increase from 1.0 M to 1.01 M. The concentration of acetate ion will correspondingly decrease by 0.01 M and its concentration at equilibrium will be (1.0 M - 0.01 M) = 0.99 M. Substituting these values in Equation 16.13 of Unit 16, we get

$$[H^+] = \frac{1.8 \times 10^{-5} \times 1.01}{0.99} = 1.83 \times 10^{-5}$$

Therefore, pH = 4.74; hence, we find that by the addition of 0.01 M HCl, there is no change in the pH of the solution.

If the same amount of HCl is added to water, the pH of the solution changes from 7 to 2. Thus, for any weak acid, HA, in presence of its salt, say NaA, the following equation can be written:



We can therefore write,

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

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

The concentration of A⁻ is mainly due to the dissociation of the salt and negligible due to the dissociation of the acid. Similarly, the concentration of the undissociated acid is the same as the original concentration, since the amount dissociated is negligible.

Hence, we can write, [A⁻] = [salt] and [HA] = [acid]

$$\text{or } [H^+] = K_a \frac{[\text{acid}]}{[\text{salt}]} \dots\dots\dots (17.1)$$

In the case of a buffer of a weak base and its salt, we can write that,

$$[OH^-] = K_b \frac{[\text{base}]}{[\text{salt}]} \dots\dots\dots (17.2)$$

For an effective buffer, the ratio of the concentration of the acid (or base) to the concentration of Equations 17.3 and 17.4.

the salt should be between $\frac{1}{10}$ and 10 . Substituting, these values in Equation 17.1, we get

$$\text{Case (i)} : \frac{[\text{acid}]}{[\text{salt}]} = \frac{1}{10}$$

Using Equation 17.1, $[\text{H}^+] = K_a \cdot \frac{1}{10}$

$$\text{Taking logarithm, } \log [\text{H}^+] = \log K_a + \log 1/10 \\ = \log K_a - 1$$

$$\text{or } -\log [\text{H}^+] = -\log K_a + 1$$

$$\text{i.e., pH} = \text{p}K_a + 1$$

$$\text{Case (ii)} : \frac{[\text{acid}]}{[\text{salt}]} = 10$$

Again using Equation 17.1, $[\text{H}^+] = K_a \cdot 10$

Following the steps shown in case (i) we get,

$$\text{pH} = \text{p}K_a - 1 \dots\dots\dots (17.4)$$

Thus, pH is held within a range of unity on either side of pKa.

Buffers play an important role in nature. For example, blood contains $\text{CO}_2/\text{HCO}_3^-$ buffer that maintains the pH at 7.4; in the absence of a buffer, the sudden changes in the pH of blood or other cell fluids could cause severe damage to the system. Another example is that the oceans are maintained at about pH = 8.4 by a complex buffering action involving silicates and bicarbonates. In the absence of buffering action, sea-life could be severely affected.

In industrial processes like electroplating, paper manufacturing, alcohol brewing, leather tanning, etc., most of the chemical reactions are pH controlled. Applications of buffers in analytical chemistry are innumerable.

Exercise 17.1

A solution is prepared by adding 2.05×10^{-3} kg anhydrous sodium acetate to 0.10 dm^3 of 0.10 M HCl solution. What is the pH of the solution?

17.4 Hydrolysis

So far we have considered two equilibria — one, of the dissociation of weak acids and bases and the other one, of the self-ionisation of water — and made an assumption that the water equilibrium does not influence the acid-base equilibria since the dissociation of water is negligible. We now treat a situation where water equilibria play an important role. The process in which water acts not as a solvent but reacts with the solute is known as hydrolysis.

Suppose we dissolve sodium acetate in water, this being a strong electrolyte, would dissociate completely providing Na^+ ions and CH_3COO^- ions in solution.



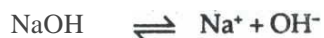
Acetate ions so produced react immediately with water giving undissociated acetic acid and hydroxyl ions according to the equation,



Since there are free OH⁻ ions in the solution, it becomes basic. The question arises as to "what happens to the Na⁺ ions in solution. The answer is that they do not react with water. Let us see why this is so. For the sake of argument, let us imagine that Na⁺ ions also react with water in the same fashion as acetate ion. Accordingly we can write,



However, NaOH so produced, will dissociate almost completely giving OH⁻ ions.



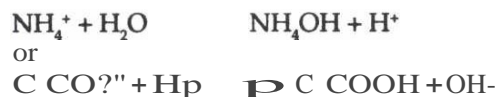
The OH⁻ and H⁺ ions would be equal in amount and these two will produce undissociated water. In other words, Na⁺ ions will not affect the water equilibrium.

Salts like sodium acetate can be thought of as a product of the reaction between a weak acid, CH₃COOH, and a strong base, NaOH. Thus, our conclusion would be that the salts of a weak acid and a strong base, when dissolved in water, will produce a basic solution.

Let us consider the case of a salt of a weak base and a strong acid like NH₄Cl. Similar to the previous example, in this case only NH₄⁺ hydrolyses as



which produces a weak base and excess of hydrogen ions in solution, thus rendering the solution acidic. Hence, we can say that the salt of a weak base and a strong acid will produce an acidic solution. In case of salts of a weak acid and a weak base, it is not possible to predict qualitatively whether the solution will be acidic or basic. Consider a salt like ammonium acetate, CH₃COONH₄, where both the cation and anion can hydrolyse according to the equations:



Hydrolysis of one ion gives hydrogen ions, whereas that of the other ion gives hydroxyl ions in solution. Therefore, the pH of the solution will depend on the extent of the hydrolysis of the two ions. If NH₄⁺ hydrolyses to a greater extent than CH₃COO⁻ ion, the solution will be acidic and, if the reverse is true, then the solution will be basic. If the extent of hydrolysis is exactly equal, then the solution should be neutral as if no hydrolysis is taking place.

The extent of hydrolysis is given by the equilibrium constant of the hydrolysis reaction, which is known as *hydrolysis constant*. Let us consider the equilibrium represented by Equation 17.5.



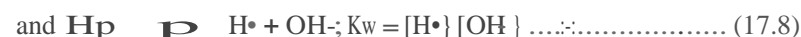
$$K = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}_2\text{O}]}$$

Since the concentration of water remains constant, we can write,

$$K_h = K(\text{H}_2\text{O}) = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]} \dots\dots\dots (17.6)$$

where K_h is known as the hydrolysis constant.

We can find another expression for K_h using the following equilibria.



From Equations 17.7, 17.8 we get,

$$\frac{K_w}{K_a} = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{H}^+][\text{CH}_3\text{COO}^-]} = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \dots\dots\dots (17.9)$$

Comparing Equations 17.6 and 17.9 we can write,

$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{O}^-\text{CH}_3\text{COO}^-]} = \frac{K_w}{K_a} \dots\dots\dots (17.10)$$

Similarly for the hydrolysis of an ion like NH_4^- , which produces a weak base, we can write,

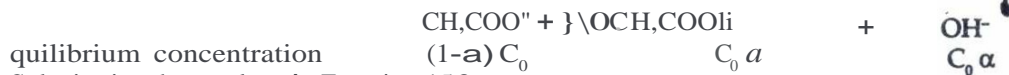
$$K_h = \frac{K_w}{K_b} \dots\dots\dots (17.11)$$

Also, it is possible to show that the K_h of a salt of a weak acid and weak base,

$$K_h = \frac{K_w}{K_a K_b} \dots\dots\dots (17.12)$$

Thus, we notice that the hydrolysis constant is directly related to K_a of the weak acid or weak base produced.

Let us now find out the relationship between the hydrolysis constant and the degree of hydrolysis for the reaction given by Equation 17.5. Suppose the concentration of sodium acetate is C_0 and its degree of hydrolysis is α . The equilibrium concentration of OH^- and CH_3COOH will each be $C_0 \alpha$ and that of CH_3COO^- will be $(1-\alpha) C_0$.



Substituting these values in Equation 15.3, we get,

$$K_h = \frac{(C_0 \alpha)(C_0 \alpha)}{(1-\alpha)C_0} = \frac{C_0 \alpha^2}{(1-\alpha)} \dots\dots\dots (17.13)$$

If the degree of hydrolysis is small in comparison to unity, we can write,

$$C_0 \alpha^2 \approx K_h C_0 \dots\dots\dots (17.14)$$

$$\text{or } C_0 \alpha^2 = (C_0 \alpha)^2$$

$$\text{or } C_0 \alpha = K_h C_0$$

$$\text{Or } [\text{OH}^-] = K_h C_0$$

$$\text{Or } [\text{OH}^-] = \frac{K_w}{K_a} C_0, \text{ since } K_h = \frac{K_w}{K_a} \dots\dots\dots (17.16)$$

Hence,

$$[\text{H}^+] = [\text{OH}^-] = \frac{K_w}{K_a} C_0 \dots\dots\dots (17.17)$$

Taking logarithms and multiplying by -1, we get

$$\text{Or } -\log[\text{H}^+] = -\log \left[\frac{K_w}{K_a} C_0 \right]$$

$$\left(\text{Since } \log \frac{1}{x} = -\log x \right) \therefore -\log[\text{H}^+] = -\log \frac{K_w}{K_a} - \log C_0$$

$$\therefore -\log[\text{H}^+] = \log \frac{K_a}{K_w} - \log C_0$$

$$\text{Or } \text{pH} = \text{p}K_a + \text{p}K_w - \text{p}C_0 \dots\dots\dots (17.18)$$

Example 17.1

In 0.10 M solution of sodium acetate, calculate

- i) K_a
- ii) The degree of hydrolysis (α)
- iii) $[OH^-]$
- iv) pH

At 298 K, $K_w = 1.0 \times 10^{-14}$ and K_a for acetic acid is 1.8×10^{-5}

Solution

i) Using equation, $K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$

$$1.8 \times 10^{-5} = \frac{[H^+][CH_3COO^-]}{0.10 - [H^+]}$$

ii) Using the equation, $\alpha = \frac{[CH_3COO^-]}{C_0}$

$$= \frac{5.6 \times 10^{-9}}{0.10} = 5.6 \times 10^{-8}$$

iii) Using the equation, $[OH^-] = \alpha C_0$

$$= 5.6 \times 10^{-9} \times 0.10$$

$$= 5.6 \times 10^{-10} \text{ M}$$

$$pK_a = -\log 1.8 \times 10^{-5} = 4.74$$

$$pK_w = 14$$

$$pH = 14 - pK_w + pK_a = 14 - 14 + 4.74 = 4.74$$

Using Equation 17.1

Hence, K_a and pH values of acetate can be calculated

Now that we have seen the importance to a group of compounds called indicators and are

K_a values are known of pH in the study of colour dependent in the experiment

Exercise 17.2

Show that for the hydrolysis of a salt of a strong acid and a weak base, the pH of the solution is given by

$$pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log C_0$$

17.5 Indicators

In this section, we will describe indicator. What exactly is an indicator? You use this often to identify the pH of the solution. An indicator is often referred to as a compound that changes colour as the pH of the solution changes. Mostly the major sources of indicators are organic dyes. There are several **examples** you must have seen before now, they include methyl red, phenolphthalein and methyl orange.

There are a number of organic substances (dyes) for which the colour depends on the concentration of hydrogen ion in solution. To put it simply, the pH of the solution governs the colour of the dye. For example, phenolphthalein is an organic compound and it shows a pink colour in basic medium but becomes colourless in acidic medium. Such substances are either weak acids or weak bases and when dissolved in water, their dissociated form acquires a colour

different from that of the undissociated form. If the concentration of the undissociated form is more in solution we see one colour; on the other hand, if the concentration of the dissociated form is more, we see another colour. The colour of the dissociated or undissociated form depends

on the pH of the solution. Further the dissociation of the indicator HIn is such that it does not affect the pH of the solution. The equilibrium of an indicator, which is a weak acid can be represented by,



Where HIn is the undissociated form of the indicator and In^- is the dissociated form. These two forms have different colours I and II, respectively. The pH of the solution determines the ratio of $[HIn]$ to $[In^-]$ in the solution. We can write the equilibrium constant expression for the reaction corresponding to (17.19) as,

$$K = \frac{[H^+][In^-]}{[HIn]}$$

or $\frac{[HIn]}{[In^-]} = \frac{[H^+]}{K} \quad (17.20)$

The human eye can detect the change in colour if the ratio of the two forms of indicator ranges between 0.1 to 10. Thus, in order to use the indicator effectively in this region, we should have a solution for which $[H^+]$ concentration is very near to K value of the indicator. It is for this reason that we use different indicators for different systems. The list of some common indicators and the pH ranges in which these are useful are given in Table 17.1.

Table 17.1 pH range of indicators

Indicator	Acid	Alkaline	pH range
Litmus	Red	Blue	5.0 - 8.0
Phenolphthalein	Colourless	Pink	8.3 - 10.0
Methyl orange	Red	Yellow	2.1 - 4.4
Methyl red	Red	Yellow	4.2 - 6.3
Bromothymol blue	Yellow	Blue	6.0 - 7.6

The maximum use of indicators is found in the titration of acids and bases in analytical chemistry.

17.6 Conclusion

In this unit, we have defined what buffer solutions are and explained their roles in maintaining the pH of a solution.

Similarly, we have described the concept of hydrolysis and the selection of indicators.

17.7 Summary

At the end of this unit, you have learnt that:

- i) Some salts of strong acid and weak base, weak acid and strong base or weak acid and weak base undergo hydrolysis.
- ii) A solution containing a weak acid (or a weak base) and its salt is defined as a buffer solution.
- iii) The effect of common ion in the form of a salt affects the dissociation equilibrium of weak acids (or weak base) so that the pH of the solution remains constant.

- v) The pH of the hydrolysed solution depends on the dissociation constants K_a and K_b .
- v) Indicators are weak acids or bases that exhibit different colours in dissociated and undissociated forms.
- vi) Since different indicators change their colours in different pH regions, the use of a particular indicator for a titration is decided by the range of pH change near the equivalence point.

17.8 Tutor-marked assignment

Calculate the concentration of Cl_3CCOOH , Cl_3CCOO^- and H^+ in a 0.25 M solution of trichloroacetic acid

(K_a for Cl_3CCOOH , 0.22)

Hint- Note that K_a is not much low.

- 2) Calculate the molarity of HCN solution that is 0.010% ionised at equilibrium.

(K_a for HCN = 6.0×10^{-10})

Hint- Note that K_a is very much low.

17.1 References

IGNOU (1997) *Chemical Equilibria and Electrolysis — Physical Chemistry 4 CHF-04*.

Sharma, K. L. and K. Sharma (1997), *A Textbook of Physical Chemistry, 3rd Revised Edition*, New Delhi, Vikas Publishing House NT210.

Unit 18: Solubility and solubility product.

Contents

- 18.1 Introduction
- 18.2 Objectives
- 18.3 Solubility
- 18.4 Solubility product
- 18.5 Common ion effect and the solubility of a sparingly soluble salt
- 18.6 Conductance
- 18.7 Summary
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18.1, Introduction

In this unit we shall be discussing solubility and solubility products for different salts, common ion effect and the solubility of sparingly soluble salts.

18.2 Objectives

By the end of this unit, you should be able to:

- i) find the relationship between solubility and solubility product for different salts, and
- ii) state its application in precipitation reactions.

18.3 Solubility

In Unit 10, we studied solubility and saturated solutions. We used some familiar words then namely soluble, slightly soluble and insoluble. These we used to describe the decreasing tendencies of solutes to dissolve in a particular solvent at a given temperature. You would recall that we mentioned gas solution, liquid solution and solid solution. Earlier too, we concluded that one of the most useful applications of chemical equilibria studies is on sparingly or slightly soluble salts like AgCl , CaF_2 , As_2S_3 and BaCrO_4 etc. We shall first derive a relationship between solubility of a salt and a quantity called solubility product. Then we shall study the applications of this relationship to different systems. Let us consider a salt with a general formula A_xB_y where x and y are the number of moles of ions A and B present in one mole of the salt respectively.

- e.g. i) for AgCl , $x = 1$, $y = 1$
ii) for As_2S_3 , $x = 2$, $y = 3$
iii) for CaF_2 , $x = 1$, $y = 2$

In a saturated solution, there will be equilibrium between the sparingly soluble solid A_xB_y and its ions A and B in solution. For the sake of simplicity, we are omitting letters such as s, aq, J, C, in a usual equilibrium.



For the present moment, we shall neglect counting of charges on the cation A and x -charges on the anion B.

18.4 Solubility product

The equilibrium constant for the reaction given in Equation (18.1) can be written as.

$$K_c = \frac{[\text{A}]^x [\text{B}]^y}{[\text{A}_x\text{B}_y]}$$

...[A^xB^y] represents the concentration of the solid A.B.; this quantity is constant. Hence, we can introduce a new constant K_{sp} in place of $K[A^x B^y]$, which is known as *solubility product constant* or simply *solubility product*. Thus Equation (18.2) can be written as.

$$K_{sp} = [A]^x [B]^y \quad \dots (18.3)$$

Expressed in words, Equation (18.3) says that the solubility product of a saturated solution of a salt is equal to the product of the concentration of ions raised to suitable powers. Let S mol dm^{-3} be the solubility of the salt. Then the corresponding concentrations of cation and anion are xS mol dm^{-3} and yS mol dm^{-3} , respectively. Substituting these values of concentration in Equation 18.3 we get,

$$K_{sp} = (xS)^x (yS)^y \quad \dots (18.4)$$

Let us apply equation (18.4) to the sparingly soluble salts such as $AgCl$, CaF_2 and $Al(OH)_3$.

In case of $AgCl$, $x = 1$, $y = 1$

Hence, Eq. (18.4) gives $\dots (18.5)$

$$K_{sp} = 4S^2$$

Let us examine an alternative method also.

The equilibria between solid $AgCl$ and its ions can be represented as



For this reaction,

$$K = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Or $K[AgCl] = [Ag^+][Cl^-]$

$$\text{Or } K_{sp} = [Ag^+][Cl^-] \quad \dots (18.7)$$

If the solubility of $AgCl$ is S mol dm^{-3} , then the concentration of Ag^+ and Cl^- ions in solution will each be equal to S mol dm^{-3} . Substitution in Equation (18.7) gives

$$K_{sp} = 4S^2 = 4$$

Example 18.1

At 298 K, the solubility of silver chloride is 1.37×10^{-5} M. Calculate its solubility product.

Solution

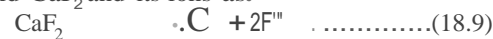
Using Equation (18.5), $K_{sp} = 4S^2 = (1.37 \times 10^{-5})^2 = 1.88 \times 10^{-10}$

In case of CaF_2 : $x = 1$, $y = 2$; substituting these values in Equation (18.4) we get,

$$K_{sp} = 4S^3$$

$$K_{sp} = 4S^3 \quad \dots (18.8)$$

Just like the previous case, the alternative method would be to write the equilibrium between solid CaF_2 and its ions as:



$$\text{And for this reaction } K_{sp} = \frac{[Ca^{2+}][F^-]^2}{[CaF_2]}$$

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

$$\text{or } K_{sp} = (S)(2S)^2 \quad \dots (18.10)$$

$$\therefore K_{sp} = 4S^3$$

$$K_{sp} = 49$$

As yet another example, let us consider the equilibrium



Where, $K_{sp} = [Ag^+][CO_3^{2-}]$

US is the solubility of Ag_2CO_3 , then $[Ag^+] = 2S$ and $[CO_3^{2-}] = S$.

Substituting the proper values, once again we get,

$$K_{sp} = 4S^3$$

We can get the same result by substituting, $x = 2$ and $y = 2$ in equation (18.4)

Finally, let us consider the equilibrium:



Where $x = 2$ and $y = 3$, if S is the solubility of $Fe(OH)_3$, then

$$K_{sp} = 4 \times 27 \times S^4$$

$$K_{sp} = 108 S^4$$

$$K_{sp} = 108 S^4$$

Exercise 18.1

At 298 K, the solubility product of $Bi(OH)_3$ is 4.0×10^{-31} , calculate its solubility.

18.5 Common-ion effect and the solubility of a sparingly soluble salt

We have already seen that the solubility of $AgCl$ in pure water is 1.37×10^{-5} M and its K_{sp} is 1.88×10^{-10} . Let us now proceed to find out what will happen to the solubility of $AgCl$ if it is dissolved in a solution containing Ag^+ ions. A qualitative answer to this question can be easily found on the basis of Le Chatelier principle. When the concentration of Ag^+ ion is increased, the equilibrium described by Eq 18.6 will shift towards the left forming more of solid $AgCl$ in order to oppose the effect of the increase in concentration of Ag^+ ion. Thus, there will be a decrease in the solubility of $AgCl$ in presence of a common ion such as Ag^+ as compared to that in pure water. Let us arrive at expressions useful in calculating the solubility of salts in the presence of common ions.

Solubility of silver chloride in the presence of silver nitrate

Assume that silver chloride is dissolved in a solution containing C mol dm^{-3} of $AgNO_3$. In the solution then, there will be Ag^+ , Cl^- and NO_3^- ions present. The Cl^- ions in solution are provided by the dissolution of $AgCl$ in water only. However, there are two sources for the presence of Ag^+ ions in solution, one is from the dissolution of $AgCl$ and the other from NO_3^- . A solution of C molar concentration of $AgNO_3$ will provide C mol dm^{-3} of Ag^+ ions in one solution. Assuming this contribution to be much larger in comparison with Ag^+ ion concentration due to dissolved $AgCl$, we can write,

$$[Ag^+] = C$$

Substituting this value in Eq. (18.7), we get

$$K_{sp} = C[Cl^-]$$

$$[Cl^-] = \frac{1.88 \times 10^{-10}}{C} \quad \dots\dots\dots(18.11)$$

The chloride ion concentration must be equal to the number of moles of $AgCl$ dissolved in $1 dm^3$ of solution (or equal to its solubility). Hence,

$$S = \frac{1.88 \times 10^{-10}}{C} \quad \dots\dots\dots(18.12)$$

wmpktB.2

Find the solubility of AgCl in 1 M AgNO₃ solution and compare it with its solubility in water.

Solution

The solubility of AgCl(s) in presence of 1 M AgNO₃ is 1.88 × 10⁻¹⁰ M. You can see that, as compared to the solubility of AgCl in water (1.37 × 10⁻⁶ M), its solubility in presence of 1 M AgNO₃ is 10⁵ times less.

Example 18.3

Find the solubility of CaF₂ in

- i) water ii) 0.10 M NaF iii) 0.10 M Ca(NO₃)₂ (K_{sp} = 4.0 × 10⁻⁹)

Solution

- i) Let us assume that the solubility of CaF₂ in water is S. Since 1 mole CaF₂ can give 1 mole of Ca²⁺ ion and 2 moles of F⁻ ion in solution, we can write the concentrations of Ca²⁺ and F⁻ ions as follows:

$$[Ca^{2+}] = S \text{ and } [F^-] = 2S$$

Hence,

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

$$4.0 \times 10^{-9} = S(2S)^2 = 4S^3$$

$$\therefore S = (1.0 \times 10^{-11})^{1/3} = (10 \times 10^{-22})^{1/3} = 2.2 \times 10^{-4} \text{ M (approximated to two places)}$$

Hence the solubility of CaF₂ in pure water is 2.2 × 10⁻⁴ M.

- ii) In 0.10 M NaF

In the presence of NaF, the solubility of CaF₂ is given by

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

Total [F⁻] = [F⁻] from CaF₂ + [F⁻] from NaF.

Since [F⁻] from NaF is much larger than [F⁻] supplied by CaF₂, the total fluoride ion concentration is equal to the NaF concentration which is 0.10 M. Substituting the proper values we get,

$$[Ca^{2+}] = \frac{4.0 \times 10^{-9}}{(0.10)^2} = 4.0 \times 10^{-9} \text{ M}$$

Hence, solubility of CaF₂ in 0.10 M NaF is 4.0 × 10⁻⁹ M.

- iii) In 0.10 M Ca(NO₃)₂

First we have to find [F⁻]

$$[F^-] = \frac{K_{sp}}{[Ca^{2+}]} \text{ or } [F^-] = \frac{K_{sp}}{[Ca^{2+}]}$$

Substituting the given values, we get,

$$[F^-] = \frac{4.0 \times 10^{-9}}{0.10} = 4.0 \times 10^{-8} \text{ M}$$

Since each mole of CaF₂ produces 2 moles of F⁻ ion in solution, the solubility of CaF₂ will be equal to one half the concentration of the fluoride ion in solution or 2.0 × 10⁻⁸ M.

When dealing with problems of this nature, two important points must be remembered. First, if the solubility of a salt like CaF₂ is given as S, then the concentration of Ca²⁺ ions would be S, but the concentration of fluoride ions would be 2S. This is so because each mole of CaF₂ which goes in solution, gives 1 mole of Ca²⁺ and 2 moles of fluoride ions. The second point, which is a source of common confusion and where error can arise, is in writing the concentration of one ion in terms of

the concentration of the other. For example, the concentration of fluoride ion in a saturated solution of CaF_2 can be expressed as,

$$[\text{F}^-] = 2[\text{Ca}^{2+}]$$

but not, $[\text{Ca}^{2+}] = 2[\text{F}^-]$

No doubt when 1 mole of CaF_2 goes into solution, it will yield 1 mole of Ca^{2+} -ions and 2 moles of fluoride ions, but to the equivalence, we must write,

$$2 \times (\text{number of moles of } \text{Ca}^{2+}) = [\text{F}^-]$$

Now that we have seen how the presence of a common ion affects the equilibrium of a sparingly soluble salt, we can now arrive at the following conclusions regarding the solubility of a sparingly soluble salt.

- i) In a saturated solution $K_{sp} = \text{ionic product}$.
- ii) When the product of the concentration of ions raised to suitable powers (i.e. the ionic product) is less than the solubility product value, the concentration of the ions can be increased by dissolving more of the salt. Hence, for an unsaturated solution $K_{sp} > \text{ionic product}$
- iii) When the concentration of either ion in solution is increased by the addition of a soluble salt containing a common ion, the ionic product increases. Hence, the equilibrium of the sparingly soluble salt is shifted such that it is precipitated. In other words, precipitation will occur when ionic product $> K_{sp}$

Let us see the applications of these generalisations with the help of a few examples.

Example 18.4

Show that it is impossible to prepare a solution of chromium hydroxide, $\text{Cr}(\text{OH})_3$ having 0.1 M concentration of Cr^{3+} ions at $\text{pH} = 7$; K_{sp} for $\text{Cr}(\text{OH})_3 = 6.3 \times 10^{-31}$

Solution

When the ionic product of $\text{Cr}(\text{OH})_3$ is equal to its solubility product, the solution will be saturated. This will indicate the state of maximum concentration of Cr^{3+} ions in solution.

Thus in a saturated solution,

$$\text{Solubility product} = \text{ionic product} = [\text{Cr}^{3+}][\text{OH}^-]^3$$

Substituting the given values we get,

$$6.3 \times 10^{-31} = [\text{Cr}^{3+}](1.0 \times 10^{-7})^3$$

$$\text{Therefore, } [\text{Cr}^{3+}] = \frac{6.3 \times 10^{-31}}{1.0 \times 10^{-21}} \text{ M}$$

(since at neutral pH, $[\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$)

Hence, at $\text{pH} = 7$, the maximum concentration of Cr^{3+} ions in solution would be $6.3 \times 10^{-31} \text{ M}$ and it is impossible to prepare a solution having 0.1 M concentration of Cr^{3+} ions at this pH.

An important fact that emerges from this example is that the precipitation or solubility of a hydroxide compound is directly related to the OH^- ion concentration or pH of the solution. This is not only true for the solubility of metallic hydroxides, as in the above example, but also for many other cases where OH^- ion is produced due to hydrolysis. For instance, consider the equilibrium of CaF_2 once again, the K_{sp} for CaF_2 is 4.0×10^{-11} and the solubility is $2.2 \times 10^{-4} \text{ M}$. The fluoride ions present in the solution through the dissolution of CaF_2 could further react with water, though to a small extent, according to the equation.



If some H^+ ions in the form of an acid are added to the above solution, they will react with the free OH^- ions and the equilibrium will shift to the right. This will reduce the concentration of F^- ions in solution; and more of CaF_2 will dissolve.

Many a times, two or more ions are separated from a mixture by means of a technique called selective precipitation. As an example, let us assume that from a solution containing Ag^+ , Ni^{2+} and Cu^{2+} ions, Ag^+ ions are to be separated from the other two. This can be achieved by the addition of

a substance which will produce a silver salt whose K_{sp} is very low. Thus, the addition of a calculated amount of chloride ion will cause the ionic product of the sparingly soluble $AgCl$ exceed its K_{sp} value; hence $AgCl$ is precipitated. Under this condition, $NiCl_2$ and $CuCl_2$ remain in solution since their K values are larger than their ionic product values. The precipitated $AgCl$ can be separated by filtration.

In qualitative analysis of salts, a number of metal ions are precipitated as sulphides using hydrogen sulphide. However, some of these ions are precipitated in acidic medium and some others in basic medium. The overall dissociation reaction of H_2S can be represented as



The equilibrium constant for this reaction is 1.3×10^{-21} and the concentration of H_2S in a saturated solution is 0.1 M. Substituting these values in the equilibrium constant expression, we get,

$$1.3 \times 10^{-21} = \frac{[H^+]^2 [S^{2-}]}{[H_2S]}$$

$$\text{or } [S^{2-}] = \frac{1.3 \times 10^{-21} \times 0.1}{[H^+]^2}$$

Thus the sulphide ion concentration can be controlled by the adjustment of the pH of the solution. The trivalent sulphides, which have low K_{sp} values, can be precipitated with rather small concentrations of sulphide ions in solution. This is achieved if the solution is acidic. The metallic sulphides, which have higher K_{sp} values, need higher concentration of sulphide ions for their precipitation and a higher pH ($pH > 7$) of the solution is to be maintained.

As an example, let us consider a solution of $pH = 3$, which contains 0.010 M each of Mn^{2+} and Cu^{2+} ions at $pH = 3$. Let us pass H_2S through this solution such that $[H_2S] = 0.1$ M. At this pH, the concentration of sulphide ion would be,

$$[S^{2-}] = \frac{1.3 \times 10^{-22}}{(1.0 \times 10^{-3})^2} = 1.3 \times 10^{-16} \text{ (since } [H^+] = 1.0 \times 10^{-3} \text{ at } pH = 3)$$

And therefore

$$[Cu^{2+}][S^{2-}] = (1.0 \times 10^{-3})^2 (1.3 \times 10^{-16}) = 1.3 \times 10^{-16}$$

The K_{sp} for $CuS = 6.3 \times 10^{-36}$. Hence, we find that the ionic product (IP) $> K_{sp}$, CuS will precipitate from the solution. However, K_{sp} for MnS is 3×10^{-10} which is much greater than its IP (1.3×10^{-16} M), therefore MnS remains in solution, then by increasing the concentration of sulphide ion to a limit such that MnS also precipitates. It is this combined use of the selective precipitation technique and proper control of pH which are the guiding principles in the qualitative analysis of salt.

Exercise 18.2

The solubility product of magnesium hydroxide, $Mg(OH)_2$ is 1.8×10^{-11} . What is the pH of a saturated solution of $Mg(OH)_2$?

18.6 Conclusion

In this unit, we have examined the concepts of solubility, solubility products, common-ion effect. We studied the solubility of sparingly soluble salts as well as the precipitation of salts.

18.7 Summary

At the end of this unit, you have learnt that:

- In case of a sparingly soluble salt, the product of the concentration of ions in a saturated solution raised to their appropriate powers is known as the solubility product.

- ii) The wider differences in the solubility product values of different salts are made use of in analytical chemistry for their separation.

18.8 References

1. IGNOU (1997) *Chemical Equilibria and Electrolysis-Physical Chemistry 4 CHE-04*
2. Sharma, K. L. and K.Sharma, (1997), *A Textbook of Physical Chemistry, 3rd Revised Edition*, New Delhi, Vikas Publishing House, NT210.

Unit 19: Faraday's laws of electrolysis

Contents

- 19.1 Introduction
- 19.2 Objectives
- 19.3 Interactions in solutions
- 19.4 Faraday's laws of electrolysis
- 19.5 Conclusion**
- 19.6 Summary
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19.1 Introduction

We have already seen in Units 15 and 16 that an electrolyte on dissolution in water dissociates to give positive and negative ions which may carry single or multiple charges. For example, when sodium chloride is dissolved in water, the sodium ions, Na^+ , and chloride ions, Cl^- are formed and get dispersed throughout the solution homogeneously. Do you know that these ions are responsible for the passage of current through sodium chloride solution. In order to find the amount of current carried by these ions and the charges brought about by the passage of current through a solution, we should learn more about the nature and properties of the solvent. For instance, depending on the nature of the solvent, there are many kinds of interactions possible in an electrolytic solution. Two of these are *ion-dipole* and *ion-ion* interactions. We shall study a few possible interactions which influence the passage of current through aqueous solution, since water is a common used solvent.

19.2 Objectives

By the end of this unit, you should be able to:

- i) describe the nature of ions in solution;
- ii) list the possible interactions among the ions;
- iii) state Faraday's laws of electrolysis.

19.3 Interactions in solutions

Now, there is no doubt that water is the most commonly used solvent. This has made us to confine ourselves to reactions in water. You would recall the structure of water as explained in previous inorganic and physical chemistry courses you had taken in this programme.

Based on a number of physico-chemical studies, the water molecule may be represented as shown in Fig. 19.1

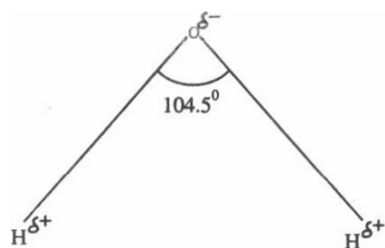


Fig.19.1 Structure of a water molecule

It is a bent molecule with H-O-H bond angle being approximately 104.5° . It shows polar character due to a large difference in the electronegativities of oxygen and hydrogen atoms. It thus has a permanent dipole moment. We should, therefore, expect water molecules to interact with each other. This kind of interaction between permanent dipoles is called *dipole-dipole interaction*. Due to this interaction, there is a net force of attraction between the molecules. In addition, there will be hydrogen bonds present between oxygen atom of one molecule and hydrogen atom of other molecules. When a salt is dissolved in water, it will produce ions in solution. As a result, there will be additional interactions between ions and water as well as between the ions themselves. We shall now consider such interactions in detail.

Ion-solvent interaction

An ion in solution will create an electrical field around it and solvent molecules with dipole moment will strongly interact with the field due to the ion. The water molecules will thus orient themselves in such a way that the dipoles lie along the field direction in order to minimise the energy of the system. The negative end of the water dipole will point towards the cation and the reverse will be true for the anion. Thus, each ion will be surrounded by a number of water molecules. Of course, generally, this number will depend on the size and charge of the ion and the nature of the solvent molecules. These ions are therefore called *solvated ions*, in case of water, they are known as *hydrated ions*. The ion-solvent interaction is strong enough to hold a certain fixed number of solvent molecules (called *coordination number*) around it. But we need to note that the interaction is not so strong to always produce different chemical species in solution.

What happens when the interaction is strong? Whenever the interaction is strong enough to give different product, we define it as *solvolysis* and in case of water, it is called *hydrolysis*. Solvent molecules, so held by the central ions are known to form the first solvation shell. The first hydration shell for most of the cations usually contains either four or six molecules of water. For example, Co^{2+} or Ni^{2+} is present as $(\text{Co}(\text{H}_2\text{O})_6)^{2+}$ or $(\text{Ni}(\text{H}_2\text{O})_6)^{2+}$ in aqueous solution. The solvent structure far away from the ion differs a little from the bulk structure of the solvent. In between these two extremes, there is a region of solvent structure where solvent molecules are under the influence of two forces, one from the ions present in the solution and the other due to intermolecular forces of the solvent. The solvent molecules in this region are consequently oriented randomly. To sum up, we can say that an electrolyte on dissolution in a solvent produces solvated ions. There is an inner or a primary solvent shell in which the solvent molecules are bound through the strong ion-dipole interaction. There is an outer or secondary solvent layer where molecules are not aligned in any particular fashion either by the field of the ion or by the forces that act in bulk solvent. The solvation number of an ion is defined as the mean number of solvent molecules in the primary solvation shell.

Ion-ion interaction

Any two ions present in a solution will interact with each other. You must be familiar with a scientific fact that says like charges will repel each other whereas unlike charges will attract each other. The electrostatic forces between any two ions is governed by the Coulomb's law. Thus, a sodium ion in a solution of sodium chloride will be repelled by other sodium ions in its vicinity but it will be attracted by chloride ions. However in solution, a well-ordered structure as found in the solids, where each ion is surrounded by a definite number of oppositely charged species at a fixed distance, is not possible. In solutions, the thermal motion will not leave the ions at fixed positions. The net result is that at any given moment, on an average, there will be an atmosphere of excess negative ions around each positive ion and reverse will be true for the negative ion as shown in Fig. 19.2.

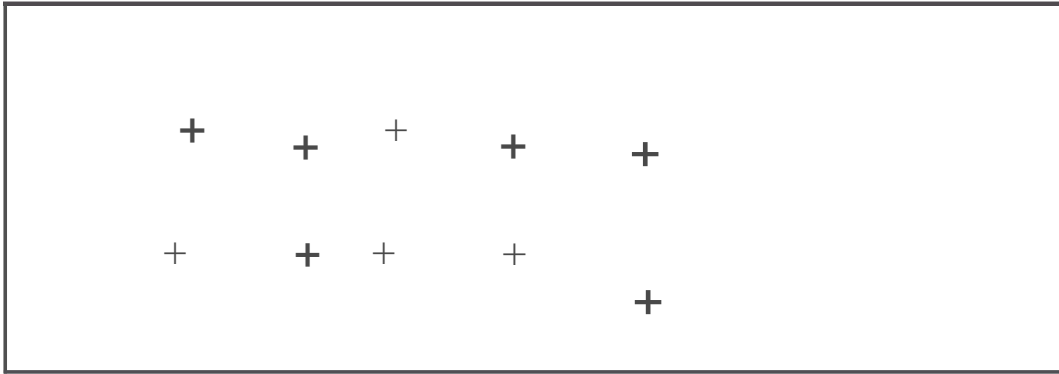


Fig.19.2 Atmosphere of oppositely charged ions around each cation and anion

The measure of an electrostatic interaction is given by a term called, *ionic strength, I*. The ionic strength depends on the concentration of the ions present and the charge carried by the ions. It is given by the expression,

$$I = \frac{1}{2} \sum_i m_i Z_i^2 \quad \dots\dots\dots 19.1$$

where m_i is the molal concentration of ion 'i' in solution and Z_i is the charge associated with the same ion. In the case of a dilute solution (of density, d), its molarity (c_i) is related to its molality (m_i) as in Equation 19.2.

$$c_i = m_i d \quad \dots\dots\dots 19.2$$

Substituting the value of Equation 19.2 into Equation 19.1 we get.

$$I \approx \frac{1}{2} d \sum_i c_i Z_i^2 \quad \dots\dots\dots 19.3$$

Equation 19.3 indicates that the electrostatic interaction between any two ions in solution is directly proportional to the concentration of the solution. This has been experimentally verified in terms of a quantity called *ion-atmosphere radius*. It is defined as the effective radius at which the atmosphere of opposite charges is situated around an ion. The radii of ion-atmosphere around sodium ion in $1.0 \times 10^{-2} M$, $1.0 \times 10^{-4} M$ and $1.0 \times 10^{-6} M$ sodium chloride solutions have been calculated to be in the ratio of 1:10:100. Thus, we see that ion-atmosphere radius increases with dilution. Hence, it can be concluded that at very low concentrations or at infinite dilution, an ion would be free from inter-ionic interactions. The concepts developed so far form the basis for the theory of ionic solutions as given by Debye and Huckel. However, our immediate concern here is to study the effects of passage of current through an electrolyte solution but not the theory of electrolytic conductance. Next section is devoted to one these studies.

19.4 Faraday's laws of electrolysis

Now to the concept of electrolysis. We have learnt about electrolysis before. Is it a process or a product? How can you define electrolysis? Your answer should be as exact as the definition given in the next statement. A process in which a chemical change is brought about by the passage of electric current through a solution is called electrolysis. The apparatus in which electrolysis is carried out is known as an *electrolytic cell*. Now, can you consider a solution of an electrolyte into which two metal plates are dipped. What do we call these two plates? The metal plates do not chemically react with the solution. On connecting the plates to the two terminals of a battery, a current starts flowing through the solution due to movement of ions in solution. The negatively charged plate is called *cathode* and the positively charged plate is called *anode*. The ions which

move towards cathode and anions are known as *cations* and *anions* respectively. The combined name for the two plates is *electrodes*. As the ions reach the two electrodes, a chemical reaction takes place at each electrode; *oxidation* at the anode and *reduction* at the cathode. Suppose that an electric current is passed through a solution of copper (II) tetraoxosulphate (VI) into which two copper electrodes are dipped. Make an attempt to write down the reactions that are likely to occur. Is your answer very close to the two reactions below. If not, you need to master electrolytic reactions of solutions very well. The following reactions occur at the electrodes:



The battery pushes electrons to one electrode and takes away from the other. In other words, electrons are transferred between the electrodes and ions. The current in the solution is due to the migration of ions. When a current (I) is passed through an electrolyte solution for a time t, then the quantity of electric current (Q) passed through is given by the product of current and time.

$$Q = It \quad \dots\dots\dots (19.4)$$

The units of quantity of electricity, current and time are coulomb (C), ampere (A) and second(s) respectively.

An electrolytic cell designed to measure the quantity of electric current that has passed through the solution is called a *coulometer* (see: Example 19.1). For example, a silver coulometer uses platinum electrodes and a solution of silver nitrate as electrolyte. On electrolysis the following reaction occurs at the cathode and silver gets deposited.



By measuring the increase in mass of the cathode, one can calculate the quantity of electric current that was passed during electrolysis. To understand the calculation involving coulometer, we must study Faraday's laws of electrolysis.

In 1813, Faraday made certain useful observations on the decomposition of electrolyte solutions by the passage of electric current. These are known as *Faraday's laws of electrolysis*. These laws are stated as follows:

1. *The mass (w) of a product formed at an electrode is directly proportional to the quantity of electricity (q) passed i.e.*

$$W \propto q \quad \dots\dots\dots (19.6)$$

2. *The masses of different products (or W₁ and W₂) for two substances and 2) formed at the electrodes by the passage of the same quantity of electricity are directly proportional to their equivalent weights.*

Thus the quantity of electricity that has passed through the electrolytic cell can be measured by the extent of the chemical reaction which has taken place in cell or vice-versa.

In order to appreciate these laws, we must explain the term faraday. The quantity of electricity carried by 1 mole of electrons is called faraday and given the symbol, F. The charge on one electron is $1.602 \times 10^{-19} \text{C}$. Hence, the charge on one mole of electrons would be

$$1.602 \times 10^{-19} \times 6.022 \times 10^{23} \text{C} \text{ or } 96,489 \text{C}$$

It is usual to approximate one faraday as being equal to 96500 C.

Consider an electrode reaction;



The quantity of electricity required for the deposition of 1 mole of X will be equal to nF, where n is the number of moles of electrons required for the reaction. Let M be the mass of 1 mole atoms of an element X. Therefore, for the deposition of M kg (or 1 mole) of the element, we require nF or n x 96500 C of electricity. We can express this as follows:

n x 96500 C of electricity deposits **M** kg (or **1** mole) of an element.

Hence, q coulomb of Electricity deposits $\frac{M \cdot q}{n \cdot 96500}$ kg of the element

$$= \frac{M \cdot q}{n \cdot 96500} \text{ kg} \quad \dots\dots\dots (19.7)$$

Substitution the value of q from Equation 19.4 into Equation 19.7 we get.

$$W = \frac{M \cdot I \cdot t}{n \cdot 96500} \quad \dots\dots\dots (19.8)$$

This equation is useful in calculating the mass of an element deposited by the passage of known quantity of current. Let us make use of Equation 19.8 in solving a problem.

Example 19.1

A current of 5.0×10^{-3} A is passed for 100 minutes through a silver coulometer. Calculate the mass of silver deposited on the cathode. Atomic mass of Ag = 107.9 (or $M = 0.1079 \text{ kg mol}^{-1}$)

Solution

Substituting the values in Equation 19.8 we get

$$\frac{0.1079 \text{ kg mol}^{-1} \times 5.0 \times 10^{-3} \text{ A} \times (100 \times 60) \text{ s}}{1 \times 96500 \text{ C mol}^{-1}}$$

(n = 1, since 1 mole of Ag⁺ ions needs 1 mole of electrons)
= 0.4×10^{-3} kg

Exercise 19.1

A current is passed through an electrolytic cell containing molten magnesium chloride, how long would it take to prepare a mole of magnesium metal?

Hint: $\text{Mg}^{2+} + 2e^{-} \rightarrow \text{Mg}$

19.5 Conclusion

In this unit, we have discussed the behaviour of electrolytes in solution under the influence of an electric field. Since the ions produced by the dissolution of an electrolyte are charged particles, these are bound to interact with each other. However, these interaction will not be as strong as in the solid state due to the thermal motion of the ions. At the same time, the ions will interact with polar molecules of the solvent, water. After explaining the nature of these interactions, we then analysed in brief as to what happens to these solutions at the electrodes when we passed electric current through them. This has been summarised up in the two laws of Faraday.

19.6 Summary

- At the end of this unit, you have learnt that:
- i) interactions occur between ions in solutions and between ions and solvent;
 - ii) there are the ion-ion and ion-solvent interactions;
 - iii) solvent molecules so held by the central ion are known to form the first solvation shell;
 - iv) faraday is the quantity of electricity carried by 1 mole electrons.

19.7 References

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Sharma, K. L. and K. Sharma, (1997), *A Textbook of Physical Chemistry; 3rd Revised Edition*, New Delhi, Vikas Publishing House NT210.

Unit 20: Electrolytic conductance

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- 20.1 Introduction
- 20.2 Objectives
- 20.3 Electrolytic conductance
- 20.4 Molar and equivalent conductance
- 20.5 Molar conductance at infinite dilution
- 20.6 Conclusion
- 20.7 Summary
- 20.8 Tutor-marked assignment
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20.1 Introduction

In Unit 19, we talked about electrolysis and some interactions possible in an electrolyte solution. In this last unit, we shall examine the electrolytic conductance of solutions. There are some useful applications of conductance. We may not be able to cover this in this unit. Meanwhile, it is important to you know that other aspects of electrochemistry will be covered in other physical chemistry courses you will take later in this programme.

20.2 Objectives

By the end of this unit, you should be able to:

- i) define electrolytic conductance;
- ii) define specific and molar conductance of a solution
- iii) describe the dependence of conductance on concentration.

20.3 Electrolytic conductance

The Ohm's law can be used to determine the *resistance* of an electrolytic conductor to current passing through it. It is usual, however, to talk about the *conductance* in place of resistance. Conductance is the *reciprocal* of the electric resistance.

The resistance of any conductor is directly proportional to its length and inversely to its cross-sectional area (A). It can be expressed as,

$$R = \frac{\rho l}{A} \quad \text{or} \quad R = \rho \frac{l}{A} \quad \text{..... (20.1)}$$

The proportionality constant, ρ , is known as its *electrical resistivity*. The unit of resistance is ohm (W) while the unit of resistivity is ohm metre (Wm). The electrical conductance is defined as the inverse of electrical resistance. Similarly, *conductivity* or *specific conductance* (k) of a material is defined as the reciprocal of its electrical resistivity. Hence,

$$R = \frac{l}{kA} \quad \text{..... (20.2)}$$
$$\therefore k = \frac{1}{AR}$$

Since the resistance is expressed in ohm, the reciprocal of ohm (Ω^{-1}) was earlier used as the unit for conductance. However, in SI system, the unit for conductance is siemens and its given the symbol S. Hence, the unit for conductivity will be $S \text{ m}^{-1}$ ($1 \text{ S} = 1 \Omega^{-1}$).

For the measurement of electrical resistance (R_x) of a sample, we use a set-up known as Wheatstone bridge. It consists of two wires R_1 , R_2 of known resistance values, and a third resistance, R_x , the value of which can be adjusted. These are all connected to a battery source, E , as shown in Fig. 20.1. R_x is adjusted until points a and b are exactly at the same potential. There will be no deflection in the ammeter.

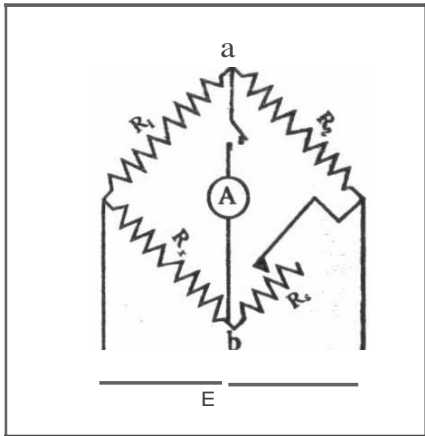


Fig. 20.1 Wheatstone bridge

Under these conditions, the following relation will hold good:

$$\frac{R_1}{R_2} = \frac{R_3}{R_x}$$

$$\text{Or } R_x = R_3 \frac{R_2}{R_1}$$

For finding the resistance of a solution (R_c), we make slight alterations in the Wheatstone bridge described above. Instead of a battery, we use an alternating current source to prevent electrolysis. The electrolysis that occurs when current passes in one direction is reversed when it passes in the other direction. The direction of current changes so rapidly that the build-up of charges at the electrode is not possible. Finally, instead of an ammeter, we use an alternating current detector.

At the balance point,

$$R_c = R_s \frac{R_2}{R_1} \quad \dots \dots \dots (20.4)$$

The relationship between specific conductance and resistance is given as

$$k = \frac{1}{AR}$$

i.e. $k = \text{cell constant} \times \frac{1}{R}$

where cell constant is the ratio $\frac{l}{A}$; it is a constant as far as the same cell is used for measurements. Since the conductivity of certain standard solutions have been carefully measured, we could use such a solution in a cell and measure its resistance. Thus knowing k and R we can calculate the value of k , the cell constant. Once k is determined, we can use the same cell for the measurement of conductivity of other electrolyte solutions. Using these ideas, work out the following exercise.

Exercise 20.1

A conductance cell filled with 0.20 M KCl has a resistance of 195.96 Ω at 298 K. When filled with a 0.050 M AgNO_3 solution, it has a resistance of 94.2 Ω . The specific conductance of 0.020 M KCl is 0.2768 S m^{-1} . What is the specific conductance of 0.050 AgNO_3 solution?

20.4 Molar and equivalent conductance

In order to compare the conductivities of different electrolytes, we must use the same concentration. This is because the conductivity of the solution depends on the number of ions present. Therefore, instead of specific conductance, we use molar conductivity, Λ_m which is the conductivity per unit molar concentration and is given by the expression:

$$\Lambda_m = \frac{\kappa}{C} \quad \dots\dots\dots (20.6)$$

where C is in mol m^{-3} units. The molar conductivity is usually expressed in $\text{S m}^2 \text{mol}^{-1}$ or $\text{S cm}^2 \text{mol}^{-1}$. It may be remembered that, $\text{S m}^2 \text{mol}^{-1} = 10000 \text{S cm}^2 \text{mol}^{-1}$.

It might be thought that Λ_m should be a quantity independent of concentration. However, it is an experimental fact that Λ_m for NaCl, KBr, etc. in aqueous solution does vary with concentration. This is due to the ionic interactions, which change with concentration. This, in turn, affects the conductivity, κ .

If we plot the molar conductivities of a large number of electrolytes against the concentrations we find that these fall into two distinct categories. In one class of electrolytes, there is a small decrease in molar conductivities with the decrease in concentration. Such electrolytes are called *strong electrolytes*. Since these electrolytes dissociate almost completely even in concentrated solution, the number of ions do not change much with concentration. The conductivity should not vary much since it is directly related to the number of ions present in solution. The minor changes observed are due to interionic interactions. The second class of compounds, known as *weak electrolytes* are those where ionisation is incomplete. The ionisation will increase with dilution, and hence the molar conductivity increases with dilution. Thus, the conductivity is directly proportional to the degree of dissociation of a weak electrolyte.

Example 20.1

At 298 K, the resistance of 2.00×10^{-2} M KCl is 195.96 Ω and that of 2.50×10^{-3} M K_2SO_4 is 775.19 Ω . The specific conductance (κ) of 2.00×10^{-2} M KCl at 298 K is 0.2768 S m^{-1} . Calculate the molar conductivity of K_2SO_4 solution.

Solution

First, we have to find out the cell constant. Using the equation $\kappa_{\text{cell}} = \kappa \times R$.

Substituting the given values for 2.0×10^{-2} M KCl, we get,

$$\begin{aligned} \kappa_{\text{cell}} &= 0.2768 \text{ S m}^{-1} \times 195.96 \text{ } \Omega \\ &= 54.24 \text{ m}^{-1} \end{aligned}$$

Next, we have to calculate the κ of K_2SO_4 solution.

$$\begin{aligned} \kappa &= \frac{\kappa_{\text{cell}}}{R} = \frac{54.24 \text{ m}^{-1}}{775.19 \text{ } \Omega} \\ &= 0.06997 \text{ S m}^{-1} \end{aligned}$$

The concentration of K_2SO_4 is given in molarity. Hence, its concentration in mol m^{-3} units may be obtained by

$$\begin{aligned} C &= 1000 \times 2.50 \times 10^{-3} \text{ mol m}^{-3} \\ &= 2.50 \text{ mol m}^{-3} \end{aligned}$$

We can calculate Λ_m using

$$\Lambda_m = \frac{k}{C} = \frac{0.06997}{2.50} \text{ Sm}^2 \text{ mol}^{-1}$$

$$= 0.0285 \text{ m}^2 \text{ mol}^{-1}$$

20.5 Molar conductance at infinite dilution

We have already seen that the molar conductance of an electrolyte increases with decreasing concentrations. This is also shown from the values given in Table 20.1.

Table 20.1 Molar conductance at 298 K

M	Concentration		$\Lambda_m/\text{Sm}^2 \text{ mol}^{-1}$	
	HCl	KCl	CH_3COOH	AgNO ₃
1.000	0.3328	0.11119	—	—
0.100	0.03913	0.01289	0.00052	0.011
0.010	0.04120	0.04120	0.00162	0.0108
0.001	0.04214	0.01469	0.0486	0.01305
0.0005	0.04227	0.01478	0.01350	0.01314

Moreover, as a consequence of interionic interactions, every ion in solution has a diffused ionic atmosphere of opposite charges. The interionic forces would least affect the motion of an ion under the influence of an electric field when the solution is very dilute. Indeed, the value of molar conductance extrapolated to zero concentration should be independent of interionic interactions. This is called *limiting molar conductivity* or *molar conductance at infinite dilution* and given the symbols Λ_m^∞ . Kohlrausch gave an empirical formula on the basis of his experimental results, which connects the molar conductivities with concentration, for strong electrolytes:

$$\Lambda_m = \Lambda_m^\infty - AC^{\frac{1}{2}}$$

Where Λ_m^∞ is constant; its value depends on the nature of the electrolyte rather than on the identity of the specific ions. For example, electrolytes of the type KCl, NaOH, NaCl, etc. have the same value of Λ_m^∞ whereas BaCl₂, CuSO₄, etc. have a different value.

Kohlrausch's law of independent migration of ions

On the basis of conductivity measurements on a series of strong electrolytes, Kohlrausch discovered that the molar conductance at infinite dilution is the sum of the contributions from each ion. It is known as the law of independent migration (or mobility) of ions. This law can be expressed as

$$\Lambda_m^\infty = \nu_+ \lambda_{+}^\infty + \nu_- \lambda_{-}^\infty \quad \dots (20.8)$$

Where ν_+ and ν_- are numbers of cations and anions per formula unit, respectively and λ are the corresponding molar conductivities of the ions at infinite dilution. For example, Table 3.2 gives

values for a number of salts. If you compare the values for any pair of salts having a common ion, it always shows a constant difference between Λ_m^∞ values. These values can be explained if we assume that Λ_m^∞ is the sum of two terms, one arising due to cation and the other due to anion. Thus the first set of values gives the difference due to the different contributions of K⁺ and Na⁺, the second due to K⁺ and Li⁺ and the third due to Cl⁻ and NO₃⁻;

Table 20.2 Λ_m^∞ values for some electrolytes

Electrolyte	$\frac{\Lambda_m^\infty}{S\ m^2\ mol^{-1}}$	Electrolyte	$\frac{\Lambda_m^\infty}{S\ m^2\ mol^{-1}}$	Electrolyte	$\frac{\Lambda_m^\infty}{S\ m^2\ mol^{-1}}$
KOH	0.01498	KOH	0.02715	KNO ₃	0.01450
NaOH	0.01264	NaOH	0.02481	NaNO ₃	0.01216
Difference	0.00234		0.00234		0.00234
KCl	0.01498	KNO ₃	0.01450	KClO ₄	0.01400
LiCl	0.01150	LiNO ₃	0.01101	LiClO ₄	0.01051
Difference	0.00348		0.00349		0.00349
LiCl	0.01150	KCl	0.01498	NaCl	0.00349
LiNO ₃	0.01101	KNO ₃	0.01450	NaNO ₃	0.01216
Difference	0.00049		0.00048		0.00048

Ostwald's dilution law

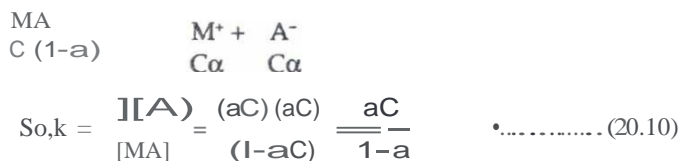
In the case of weak electrolytes, it is not possible to obtain the limiting molar conductance value, Λ_m^∞ by extrapolation of molar conductance value to zero concentration since increase in molar conductance and the experimental measurements become unreliable. This can be seen from the values given for acetic acid in Table 20.1. For weak electrolytes, Ostwald derived a relationship between the molar conductivity and the limiting molar conductance. This relationship is known as Ostwald's dilution law.

The molar conductivity of weak electrolytes can be expressed as the product of degree of ionisation of the electrolyte and its limiting molar conductance:

$$\Lambda_m = a \cdot \Lambda_m^\infty \quad \dots\dots\dots (20.9)$$

where a is the degree of ionisation.

If C is the molar concentration of the electrolyte, we can express the ionisation of a weak electrolyte as follows:



Equation (20.10) can be rearranged as

$$\frac{1-a}{a^2 C} = K$$

$$1 = a^2 C K \quad (\text{multiplying both sides of the equation by } a^2 C)$$

$$\Rightarrow \frac{1}{a^2} - \frac{1}{a} = K C$$

$$\Rightarrow \frac{1}{a} = 1 + K C \quad \dots\dots\dots (20.11)$$

But from Equation 20.9, we know that

$$\frac{\Lambda_m}{\Lambda_m^\infty} = a$$

Substituting the value of α in Equation 20.11, we get,

$$\lambda_m^0 = \frac{C_m}{1 + K_m C_m}$$

Dividing throughout by C_m we get,

$$\frac{\lambda_m^0}{C_m} = \frac{1}{1 + K_m C_m} \quad \dots\dots\dots (20.12)$$

It is found that for concentrations higher than 0.1 mol dm⁻³, Ostwald's law is not followed strictly. We can use Kohlrausch's law of independent mobility of ions to calculate indirect λ_m^0 value for weak electrolytes as illustrated by the following example.

$$\lambda_m^0(\text{CH}_3\text{COOH}) = \lambda_m^0(\text{CH}_3\text{COONa}) + \lambda_m^0(\text{HCl}) - \lambda_m^0(\text{NaCl})$$

Notice that all the terms on the right hand side are for strong electrolytes and are known; thus, we can calculate the value for this weak electrolyte, CH₃COOH, as shown below:

The values of molar conductance at infinite dilution for sodium acetate, hydrochloric acid and sodium chloride are 0.009101, 0.04261 and 0.01264 S m² mol⁻¹, respectively.

$$\begin{aligned} \text{Hence, } \lambda_m^0(\text{CH}_3\text{COOH}) &= [(0.009101 + 0.04261) - 0.01264] \text{ S m}^2 \text{ mol}^{-1} \\ &= 0.03907 \text{ S m}^2 \text{ mol}^{-1}. \end{aligned}$$

20.6 Conclusion

The electrical conductance has been discussed. Though we have not been able to cover the conductance methods of acid-base and precipitation titrations, we have discussed molar equivalent conductance. In another course, we should be examining other aspects of electrochemistry.

20.7 Summary

In this unit, you have learnt that:

- i) for weak electrolytes, their ionisation is incomplete;
- ii) electrical conductance is defined as the inverse of electrical resistance;
- iii) conductivity of a solution depends on the number of ions present;
- iv) ionisation increases with dilution and the molar conductivity increases with dilution too;
- v) conductivity is directly proportional to the degree of dissociation of a weak electrolyte.

20.8 Tutor-marked assignment

1. Identify which of the following are true or false
 - a) Electrical conductance is the inverse of electrical resistance
 - b) No relationship exists between specific conductance and resistance
 - c) Molar conductivity is expressed as λ_m^0/C .

20.9 References

IGNOU (1997) *Chemical Equilibria and Electrolysis-Physical Chemistry 4 CHE -04*.
 Sharma, K. L. and K. Sharma, (1997), *A Textbook of Physical Chemistry, 3rd Revised Edition*, New Delhi, Vikas Publishing House.

