Module 1: CHEMICAL THERMODYNAMICS

UNIT 1: ENERGY RELATIONSHIPS IN CHEMICAL REACTIONS

Contents

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; and
- iv. Differentiate between extensive and intensive variables, providing two examples each.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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 competition, 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 - Ijesha water fall in Osun State.
2. Controlled chemical reactions: You can determine the dissociation constant *(pKa),*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 heterogeneous, 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 heterogeneous 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.

i) **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.

ii) **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.

iii) **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 dependant variable. Others, on which it is dependent are called independent variables. For example, if you write the ideal gas equation as:

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

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

$$P = \frac{nRT}{V} \text{.......................................(i)}$$

then this 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 inside 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 given 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 will be 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 andB are two vessels containing different liquids, and C is an ordinary mercury thermometer. If A is inthermal 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 aphase in the system or the mass of the system. For a heterogeneous system made up of severalphases, the total value of an extensive property is equal to the sum of the contributions from itsvarious phases. Mass, volume, and energy are examples of extensive properties. Thus, if a systemat equilibrium consists of 0.100 kg of ice and 0.100 kg of liquid water at 273.15K, the total volumeof the system is the sum of the two volumes, each of which is directly proportional to its mass.

$$\text{Volume of 0.100 kg of ice} = \frac{\text{Mass of ice}}{\text{Density of ice}}$$

$$= \frac{0.100\ \text{kg.}}{917\text{kgm}^{-3}}$$

$$= 1.09 \times 10^{-4}\ \text{m}^3$$

$$\text{Similarly, the volume of 0.100 kg of water} = \frac{\text{Mass of water}}{\text{Density of water}}$$

$$= \frac{0.100\ \text{kg}\_\_}{1.00 \times 10^3\ \text{k/gm}^3}$$

$$= 1.00 \times 10^{-4}\ \text{m}\cdot$$

$$\textbf{Total volume} = (1.09 + 1.0) \times 10^{-4}\ \text{m}^3$$

$$= 2.09 \times 10^{-4}\ \text{m}^3$$

Intensive variables: An intensive property of a heterogeneous system is dependent 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 J t. 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) Surrounding 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) Ina closed system, heat neither leaves nor enters.
2. Define thermodynamics.
3. Differentiate between a closed, an open and isolated system.

1.9 References

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UNIT 2: WORK, HEAT AND HEAT CAPACITY

Contents

2.1 Introduction

In Unit 1of this course, we examined some terminology used in thermodynamics and the concept of thermodynamics itself in matter. In this un]t, 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:

- describe isothermal, adiabatic and cyclic processes;
- Differentiate between these types of processes;
- Explain the terms- work, heat and heat capacity; and
- Perform some calculations on work, heat and heat capacity.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
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3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

2.3 Types of process

When the system undergoes change from one thermodynamic state to final state due change in properties like temperature, pressure, volume etc, the system is said to have undergone thermodynamic process. Various types of thermodynamic processes are: isothermal process, adiabatic process, isochoric process, isobaric process and reversible process. These have been described below:

1) Isothermal process: When the system undergoes change from one state to the other, but its temperature remains constant, the system is said to have undergone isothermal process. For instance, in our example of hot water in thermos flask, if we remove certain quantity of water from the flask, but keep its temperature constant at 50 degree Celsius, the process is said to be isothermal process.

Another example of isothermal process is latent heat of vaporization of water. When we heat water to 100 degree Celsius, it will not start boiling instantly. It will keep on absorbing heat at constant temperature; this heat is called latent heat of vaporization. Only after absorbing this heat water at constant temperature, water will get converted into steam.

2) Adiabatic process: The process, during which the heat content of the system or certain quantity of the matter remains constant, is called as adiabatic process. Thus in adiabatic process no transfer of heat between the system and its surroundings takes place. The wall of the system which does not allows the flow of heat through it, is called as adiabatic wall, while the wall which allows the flow of heat is called as diathermic wall.

3) Isochoric process: The process, during which the volume of the system remains constant, is called as isochoric process. Heating of gas in a closed cylinder is an example of isochoric process.

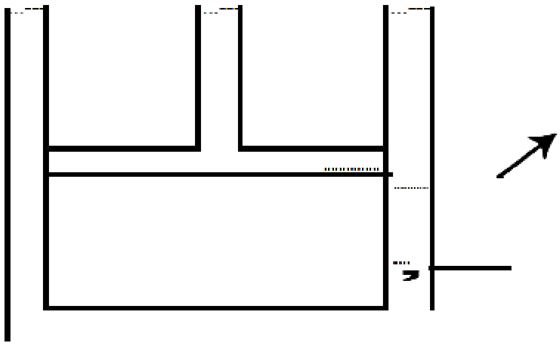
4) Isobaric process: The process during which the pressure of the system remains constant is called as isobaric process. Example: Suppose there is a fuel in piston and cylinder arrangement. When this fuel is burnt the pressure of the gases is generated inside the engine and as more fuel burns more pressure is created. But if the gases are allowed to expand by allowing the piston to move outside, the pressure of the system can be kept constant.

The constant pressure and volume processes are very important. The Otto and diesel cycle, which are used in the petrol and diesel engine respectively, have constant volume and constant pressure processes. In practical situations ideal constant pressure and constant pressure processes cannot be achieved.

5) Reversible process: In simple words the process which can be reversed back completely is called a reversible process. This means that the final properties of the system can be perfectly reversed back to the original properties. The process can be perfectly reversible only if the changes in the process are infinitesimally small. In practical situations it is not possible to trace these extremely small changes in extremely small time, hence the reversible process is also an ideal process. The changes which occur during reversible process are in equilibrium with each other.

A process is cyclic if the system (after any number of intermediate changes) returns to 1t’s original state.1he 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 affecting 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 pin 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 (Pext) infinitesimally, the gas can be compressed. On the other hand, by slightly decreasing the external pressure, the gas may be expanded.



Thus, if

Pext = p, the system is static and the piston does not move.

Put = p + dp, the gas is compressed and the piston moves downwards, infinitesimally slowly;

Pext= 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 recognize 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 Hp 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,
a) lg of ice will occupy .... space than lg of water (less/more)
b) 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 thecalorimeter 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 = Force x distance (x)
W = *F.x*..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 *Elt.*
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 lK. If, during the process, the volume of the system remains constant, then it is called *heat capacity at constant volume (Cv).* If the pressure remains unchanged, it is called *heat capacity at constant* *temperature (Cp).* For one mole of a pure substance, these are called molar heat capacity at constant pressure, C and molar heat capacity at constant volume (C.). 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, where as 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

$$dq_v = nC_vdT \ldots\ldots 2.2$$

$$dq_p = nC_pdT \ldots\ldots 2.3$$

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,

$$dq_v = \int_{T1}^{T2} nCvdT = nCv\int_{T1}^{T2} dT \ldots\ldots 2.4$$

$$dq_p = \int_{T1}^{T2} nCpdT = nCp\int_{T1}^{T2} dT \ldots\ldots 2.5$$

In later sections, we will study the use of CP and Cv in the calculation of energy changes. Let us give an example here for the calculation of n, Cp' T 1 and T2 are given.

Example 2.1

The equation for the molar heat capacity of butane is C = (19.41+0.233T) J mol·1K"1 Calculate the heat necessary to raise the temperature of 3.00 mol/J of butane from 298 K to 573 K at constant pressure.

Solution

We have to calculate qP as per Equation 2.5.

$$dq_p = \int_{T1}^{T2} nCpdT$$

where T_1= 298K , T2=573K and n = 3.00 mol

C*p* = (19.41 + 0.233) J/mol/K

$$CJ_P = \int_{298}^{573} 3.00(19.41 + 0.233T)dT$$

$$= 3.00 \times 19.41 \int_{298}^{573} dT + 3.00 \times 0.233^{J573}_{298}\ TdT$$

$$= \left[3.00 \times 19.41(573 - 298) + \frac{3.00 \times 0.233}{2}(573^2 - 298^2)\right] J$$

$$= 9.97 \times 10^4 J$$

$$= 99.7kJ$$

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

Exercise 2.2

The molar heat capacity of ethane at constant pressure is 2.6 J K-1 moi-1, Calculate the energy required to heat 3.00 mol of ethane from 305 K to 405 K at constant pressure.

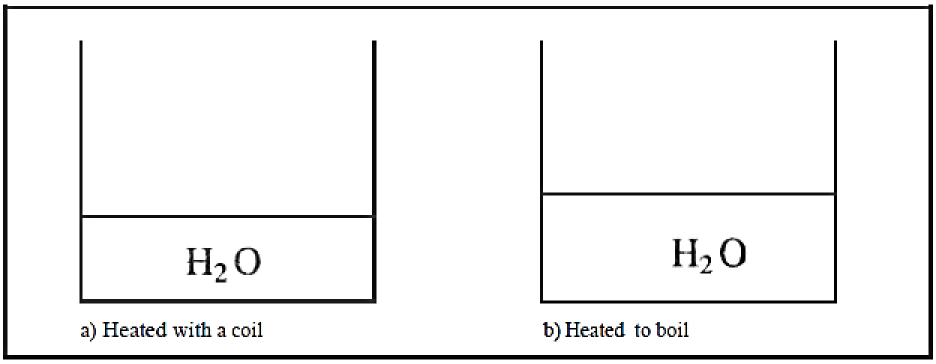
Hints: i) Use Equation 2.5

ii) Integration is to be done as per formula 1and I 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 ΔV = nR {T - T) 2.6 2 1
= nR ΔT (does not apply to Vander Waals equation) 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.



a) Heated with a coil b) Heated to boil

Fig. 2.2

Example 2.2

One mole of an ideal gas is heated at a constant pressure of 101.3K Nm^{-2} from 273 K to 373K.

a) Calculate, in Joules, the work involved.

b) If the gas expanded isothermally at 273 K from the pressure of 101.3I<Nm^{-2} to some pressure, P, what must be the pressure of the isothermal work that is equal to the work in (a) above?

Solution

$$W = nR(T2 - Td$$

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

$$= 8314\,J\,\text{mor}^{1}$$

b) $$W = \int_{V_1}^{v_2} nRT\frac{dv}{v}$$

$$= nRT\ln\frac{v2}{v1}\,(1\text{ mole})$$

$$8314\}/\text{mole} = \frac{8314\text{ Joules}}{\text{K-mol}} \times \frac{273\,\text{KIn}\,(1013 \times 10^{3})}{P}$$

Since n = 1 mole, then we have

$$= RT\ln\frac{v2}{Vt}$$

It is known that: $P_1V_1 = P_2V_2$

VW!can now have $W = Rl'\ln P.JP_2$

$$\text{t.e. } \frac{1\backslash}{\;} = \frac{v2}{V.}$$

$$831.4\}/\text{molD}\ \frac{8314\text{Joules}}{\text{Kmol}}\ )(\ \frac{273\,\text{KIn}\,(101.3 \times \text{to}')}{p}$$

$$P\ a\ S.31^{4}\frac{\text{Joules}}{\text{Kmol}}\ )(\ 273\,\text{KIn}\,(101.3\ )(\ 1o' \xrightarrow[m-]{} \text{mol}\quad 83tAJ$$

$$P\ a\ 273\ln 101.3\ )(\ \text{to}'\,\overset{N}{rd}$$

$$P\ a\ 273\ )(2.3031cJs\ 101.3)(1o',^{N}$$

$$-6.37\ )(10^{7}\ \text{Nm}$$

2.5 Conclusion

In this unit, we listed different processes and described each of them. In add1lion, the various types 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 1mole 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 x w-s m3 to 8.00 x 10-3 m3against a constant pressure of 1.00 x l0^5 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 CP for water= 75.2 J molK$^{\cdot 1}$.

3. Calculate the heat required to increase the K at constant pressure. Cp for methane = 35.3 J mot·• K·' temperature of 1.00 mol of methane from 298 K to 398.

2.8 References

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UNIT 3: THE FIRST LAW OF THERMODYNAMICS

Contents

3.1 Introduction

In Unit 1, we discuss some thermodynamics terminology. In this unit, we will still proceed to make some detail to see how thermodynamics will be explained, with particular reference to isotheral process.

3.2 Objectives

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

- State the first law of thermodynamics
- Understand isothermal processes.
- Calculate the work done on an ideal gas system.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
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4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

3.3 The first law of thermodynamics

The first law of thermodynamics was first stated in 1840, by Mcyer and Helmholtz in Germany, Joule in England, and Colding in Denmark. This law is also known as the *Law of Conservation ofEnergy.* 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. If, on the other hand, the system interacts with the surroundings, then the energy may change but then there will also be an equal and opposite change by the energy *or* the surroundings.

Internal energy

In thermodynamics, the **internal energy** of a system is energy contained within the system, excluding the kinetic energy of motion of the system as a whole and the potential energy of the system as a whole due to external force fields. It keeps account of the gains and losses of energy of the system that are accounted for by its internal state.

The internal energy of a system can be changed by transfers: as heat, as work, or with matter. When matter transfer is prevented by impermeable containing walls, the system is said to be closed. Then the first law of thermodynamics states that the increase in internal energy is equal to the total heat added plus the work done on the system by its surroundings. If the containing walls pass neither matter nor energy, the system is said to be isolated. Then its internal energy cannot change. In a sense, the first law of thermodynamics may be regarded as establishing the existence of the internal energy.

The internal energy is one of the two cardinal state functions of the state variables of a thermodynamic system.

Internal energy of the ideal gas

Thermodynamics often uses the concept of the ideal gas for teaching purposes, and as an approximation for working systems. The ideal gas is a gas of particles considered as point objects that interact only by elastic collisions and fill a volume such that their free mean path between collisions is much larger than their diameter. Such systems are approximated by the monatomic gases, helium and the other noble gases. Here the kinetic energy consists only of the translational energy of the individual atoms.

Monatomic particles do not rotate or vibrate, and are not electronically excited to higher energies except at very high temperatures.

Therefore internal energy changes in an ideal gas may be described solely by changes in its kinetic energy. Kinetic energy is simply the internal energy of the perfect gas and depends entirely on its pressure, volume and thermodynamic temperature.

The internal energy of an ideal gas is proportional to its mass (number of moles) N and to its temperature T

$U = cNT;$

Where *c* is the heat capacity (at constant volume) of the gas. The internal energy may be written as a function of the three extensive properties *S*, *V*, *N* (entropy, volume, mass) in the following way:

$$U(S,V,N) = const \cdot e^{\frac{S}{cN}} V^{\frac{-R}{c}} N^{\frac{R+c}{c}},$$

Where *const*is an arbitrary positive constant and where *R* is the Universal Gas Constant. It is easily seen that *U* is a linearly homogeneous function of the three variables (that is, it is *extensive* in these variables), and that it is weakly convex. Knowing temperature and pressure to be the derivatives $T = \frac{\partial U}{\partial S}, p = -\frac{\partial U}{\partial V},$ the Ideal Gas Law *pV=RNT* immediately follows.

Internal energy of a closed thermodynamic system

This above summation of all components of change in internal energy assume that a positive energy denotes heat added to the system or work done on the system, while a negative energy denotes work of the system on the environment.

Typically this relationship is expressed in infinitesimal terms using the differentials of each term. Only the internal energy is an exact differential. For a system undergoing only thermodynamics processes, i.e. a closed system that can exchange only heat and work, the change in the internal energy is

$$du = \delta Q + \delta W$$

which constitutes the first law of thermodynamics. It may be expressed in terms of other thermodynamic parameters. Each term is composed of an intensive variable (a generalized force) and its conjugate infinitesimal extensive variable (a generalized displacement).

For example, for a non-viscous fluid, the mechanical work done on the system may be related to the pressure *p* and volume *V*. The pressure is the intensive generalized force, while the volume is the extensive generalized displacement:

$$\delta W = -pdV$$

This defines the direction of work, *W*, to be energy flow from the working system to the surroundings, indicated by a negative term. Taking the direction of heat transfer *Q* to be into the working fluid and assuming a reversible process, the heat is

$$\delta Q = TdS$$

T is temperature
S is entropy

and the change in internal energy becomes

$$dU = TdS - pdV$$

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 *Pat'* which is slightly less than the gas pressure. The gas will expand against an opposing force, which is given by, ·

$F = PA$ 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,

$dw' = Fdx= Pu,Adx$...............................3.5

But *Adx is* the change in volume of the gas, *dV.* Hence,

$dw' = P,r,dV$.................................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

$dw= -PuflV$................................3.7

Equation 3.7 is a general expression useful in calculating pressure- volume work, when its isothermal or adiabatic process. It can be seen that *dw*is negative when the gas expand and positive when the gas contracts, *(dV*= +n in expansion and *dV*= we 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 (Pz. 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 V2 respectively. The total work done, W, on the system is obtained by integrating Equation 3.7.

$$W = -\int_{V_1}^{V_2} P_{ext} dV = -P_{ext}\int_{V_1}^{V_2} dV \qquad \text{.....} \; 3.8$$

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

The symbol, dV, 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 10m3 to 12m3, against a constant pressure of 1bar at 298K. What is the work done on the gas?

Solution

We have to calculate work done under constant pressure using Equation 3.8. Hence,
W=-Pex1 (V2-Vd= [-1 x 10 Pa x (12m3 -10m3]
= -2 x 10^S Pam^3 because 1bar= 1x $l0^5$
= -2 x 10^5 J because 1Pa m^3 = 1J

It can be seen that work done on the system is negative. This means that the system has actually done work equal to 2 x l0 SJ 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 (Pm) is only infinitesimally different from the gas pressure (P) inside a cylinder. In such a case, *P, x,* = *P* and hence, Equation 3.7 can be written as,
dw= -PdV...............................3.9
The total work done, W, as the gas expands isothermally and reversibly from a volume *V 1* to a volume V is then given by integrating Equation 3.9 within limits V1and *V*2

$$W = \int_1^2 PdV \qquad \text{.....3.10}$$

Let us assume that the gas behaves ideally. Hence,

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

Using Equation 3.10, we have

$$W = -\int_{V1}^{V2} \frac{nRT}{V} dV$$

$$= -nRT \int_{V1}^{V2} \frac{dV}{V} \qquad 3.11$$

$$= -nRT\ In \frac{V2}{V1} = nRT\ In \frac{V1}{V2} \qquad 3.12$$

Hence ,$W = -2.303\ nRT\ log \frac{V2}{V1} = 2.303\ nRT\ log \frac{V1}{V2}$ 3.13

It is seen that if $V_1$is less than V, 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 (P1 and P2 of the gas. For an ideal gas temperature,

$$P_1V_1 = P_2V_2 \qquad \text{..............................3.14}$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \qquad \text{..........................3.15}$$

Using Equations 3.13 and 3.15

$$W = -2.303\, nRT \log\frac{11}{12} \qquad \text{..........................3.16}$$

$$= 2.303\, nRT \log\frac{12}{11} \qquad \text{..........................3.17}$$

Let us illustrate the use of Equations 3.16. and 3.17

Example 3.2

An ideal gas initially at 3.00 x 102 K and 3.00 x 105 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 x 106 Pa?

Solution

P_1= 3.00 x 105 Pa; P = 6.00 x 106 Pa
R = 8.314 mo1^{-1}K^{-1}*T*= 3.00 x 102 K

We have to calculate the value of n (the amount of the gas). In order to use Equation3.17, the value of *n* can be found from the initial conditions using the ideal gas equation.

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

Substituting the values in Equation 3.17

$W = 2.303 \times 1.00 \times 10^2 mol \times 8.314\ J\ mol^{-1} \times 3.00 \times 10^2\ K \log\frac{6.00\times10^6}{3.00\times10^5}$

$2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times (6.7782-5.4771)$ J [step ii]
$2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times 1.3011$ J [step iii]
W = 7.47 x 10S 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 thermo dynamics. 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 $dw = -P.,.\ \mathrm{d}V$

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 12.48J mol^{-1}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: HEAT OF REACTION AND HESS'S LAW

Contents

4.0 Introduction

In the previous units of this course, you learnt that the first law of thermodynamics is the same as the law of conservation of mass and here we are going to discuss about heat of reactions.

4.1 Objectives

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

- define the heat of reaction;
- explain the heat change at constant volume;and
- calculatethe internal energy of a system.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

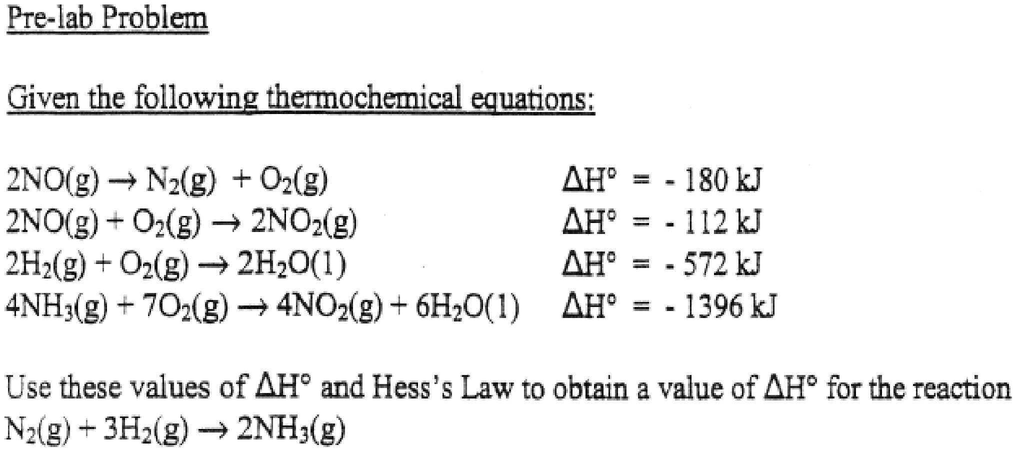
4.2 Heat of Reaction

One sign that a chemical reaction is taking place is the observation of a temperature change. The temperature change is brought about by the emission of heat from the system to the surroundings, or the absorption of heat by the system from the surroundings. These are referred to as endothermic and exothermic processes, respectively. The measurement of the heat given off or absorbed is important because these changes reflect changes in the energy states of the molecules involved in the chemical reaction. In a chemical reaction, chemical bonds are broken, which requires energy, and new chemical bonds are formed, which is accompanied by the release of energy. The heat given off or absorbed in a chemical reaction is called the heat of reaction (or enthalphy of reaction, ΔH).

Sometimes a heat of a reaction for a particular reaction is difficult to measure directly. Hess's Law (also called the Law of Constant Heat Summation) provides a method for obtaining heats of reaction for reactions that cannot be easily measured.

Hess's Law: If a process can be considered to occur in stages or steps (Either actually or hypothetically) the enthalpy change for the overall process can be obtained by summing the enthalpy changes for the individual steps.

In this experiment you will measure the heat of reaction for the reaction between magnesium and hydrochloric acid. You will then measure the heat of reaction for the reaction between magnesium oxide and hydrochloric acid. Finally, these two heats of reaction along with the heat of formation for water, and Hess's Law will be used to determine the heat of formation of magnesium oxide.



Pre-lab Problem

Given the following thermochemical equations:

$2NO(g) \rightarrow N_2(g) + O_2(g)$ $\Delta H^\circ = -180\ kJ$
$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta H^\circ = -112\ kJ$
$2H_2(g) + O_2(g) \rightarrow 2H_2O(1)$ $\Delta H^\circ = -572\ kJ$
$4NH_3(g) + 7O_2(g) \rightarrow 4NO_2(g) + 6H_2O(1)$ $\Delta H^\circ = -1396\ kJ$

Use these values of ΔH° and Hess's Law to obtain a value of ΔH° for the reaction
$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

4.3 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. Then,

$dE = dq - PdV$............................4.1
or$dq = dE + PdV$· ·····-········· ··4.2

If the process is carried out at constant volume, then,
$dV = PdV = O$
Hence, $dq = dH$.........................4.3
For finite changes in internal energy, Equation 4.3becomes
$q = \Delta E$
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 react reaction. From Equations 4.2 and 4.3,

$dE = CpdT = n\,CpdT$.........................4.4

This holds good for n mol of an ideal gas. Equation 4.4 can be written as,
$=[\Delta E]_v$....................... 4.5

i.e. heat capacity at constant volume equal to change in internal energy for lK rise in temperature, at constant volume.

In order to obtain ΔE when an ideal gas is heated from temperature T_1 to T_2at constant volume the integrated form of Equation 4.4 is to be used.

$$E = \int_{T1}^{T2} CvdT = \int_{T1}^{T2} nCpdT$$

Hence, by knowing Cp, over the temperatures $T_2$and T_1, it is possible to obtain the value of E. We have defined Cv, through Equation 4.4, what about Cp? Is there some thermodynamic property to which $C_P$can be retained m a similar way? For this purpose, we shall define the enthalpy in Unit 5.

4.4 Summary

You learnt in this unit that the heat released or absorbed in a chemical reaction is called heat of reaction or enthalpy of reaction represented by ΔH^0. You also learnt that heat absorbed by a system at constant volume is exactly equal to its internal energy change.

4.5 Tutor-marked Assignment

1. Calculate the change in internal energy of an ideal gas undergoing isothermal reversible 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 at constant volume. In the next unit, we shall continue with topics in thermodynamics by examining the concept of enthalpy and enthalpy changes.

4.6 Reference

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

UNIT 5: ENTHALPY CHANGES

Contents

5.1 Introduction

In the previous units of this course, we stressed the importance of energy inchemical 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-Thompson effect.

5.2 Objectives

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

- define the term *enthalpy;*
- state the significance of enthalpy and enthalpy change of a system;
- derive the relationships between c and c of an ideal gas; and
- explain the joule-Thompson effect.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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,

$$dV=O$$

And this means, therefore, that

$$W= PdV=O \text{ .... } 5.1$$

Therefore,

$q=dE$(internal energy) 5.2

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

W = PdV.. 5.3

$dE= q$ - W = q -PdV

q_1 =$dE+ PdV$.. 5.4

q_1 =E+ PdV.. 5.4

(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 + PdVdepends on the initial and final states of the system but the not on the path.

$E + PdV$is called **enthalpy** 5.6

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

$H= E +PV$ ··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, 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,

$\Delta H=H_2 - H_1$ 5.8

$= (E_2 + P_2V_2)-(E_1+ P_1V_1)$

$= \Delta E + (P_2V_2 - P_1V_1)$ 5.9

In the case of a constant pressure process P,=P2 = P. Equation 5.9 can be written as,

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

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

$qP = \Delta E + P\Delta V$ ....•.......•............................5.11

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

The subscript p in qPstands for the constant pressure condition.

In other words, the enthalpy change is 3qual to the heat absorbed by the system at constant pressure.

For a small change in enthalpy, we can write

$dqP = dH$.. 5.13

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

$dH = CvdT = nCpdT$...................5.14

In order to obtain .1H value when an ideal gas is heated from temperature $T_1$to T_2at constant pressure, the integrated form of Equation 5.14 is to be used.

ΔH= $\int_{T1}^{T2} CpdT$= $\int_{T1}^{T2} nCpdT$.................................. 5.15

Consider a change in state of a system of

Initial state, H1= f1 + P1V1
Final state, $H2 = E2 + P2V2$ ·
And H_2- H_1 = $dH = dE + d(PV)$

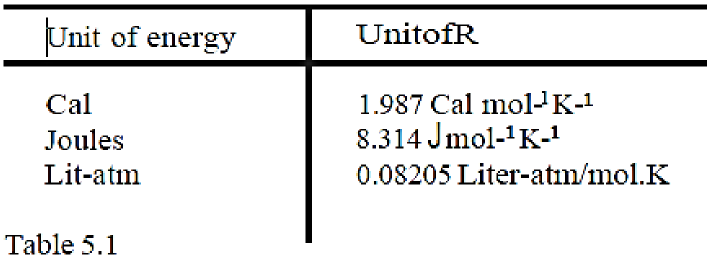
At constant pressure

$$dH=dE+PdV$$

For an ideal gas,

$dH= dE+ dnRT$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	UnitofR
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 1moleof water at101.3 KN m- 2 pressure at 373.15K.
a) What are the *dH*and *dE*for the process?
b) 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 kNm-2?

Solution

a) *dH and dE*
$PV = P(V_2 – V_1)$
$PV = RT$
= 8.314J $mol^{-1}K^{-1}$(373.15 K)
= 3 102.3 $Jmol^{-1}$
= 3.102 kJ mol^{-1}
$dH=dE+PdV$
dE= 40.59-3.102 kJ mol^{-1}
=37.49 kJ mol^{-1}

b) dH= -(q),

=-40.59 kJ mol^{-1}

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

Therefore, $dE= dH-RT$

=-40.59 kJ moi^{-1}-(-3.102 kJ moi-1)

=-40.59 +3.102 kJ mol^{-1}

=-37.49 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*i* is given a positive sign. In exothermic processes (in which heat is evolved),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 CP and CV 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,

$$H = E + PV = E + RT \quad \text{...} 5.16$$

On differentiating, we get

$dH= dE+ RdT$(because R is a constant)

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

$CiT= C,dT+ RdT$

cp= c.+R...5.17

And hence, CP -C, = R 5.18

Also, for n mole, C_P–Cv = nR... 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 realize 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 defined 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.......... ....5.20

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

$dE= CvT$

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,

$C.dT=-PdV$......................•...................................... 5.21

For one mole of an ideal gas,

$P = -\frac{RT}{v}$

Using this relationship in Equation 5.21, we get

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 = $-P\Delta V$ 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.

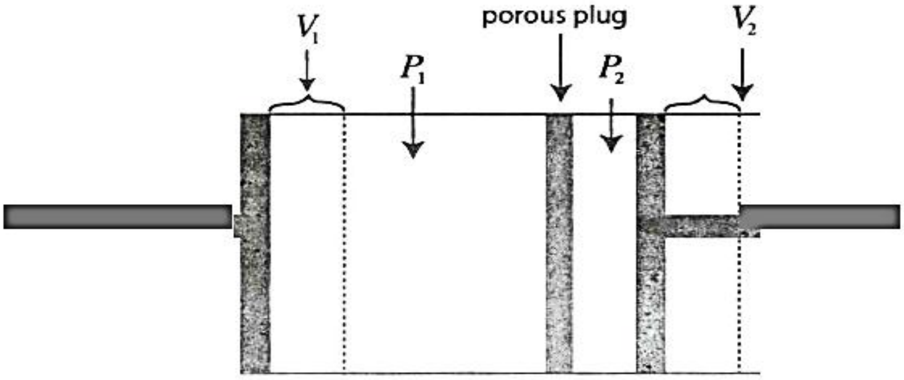
Using Equation 5.32 in Equation 5.31, derive an equation 5.33. Your instructor will lead you. Hence, Equation 5.33 is useful in calculating the final temperature of an ideal gas undergoing adiabatic irreversible expansion while Equation 5.26 or 5.28 is of help in an adiabatic reversible process.

Exercise 5.1

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

5.6 The Joule-Thomson effect

It was mentioned earlier that the internal energy of an ideal gas is independent of pressure or volume. This, however, is not truth 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 in wards so that, without changing the value of P_1a volume $V_1$of gas is introduced through the plug into the other compartment piston and also in volume increase. Let the final volume be V_2. Accurate temperature measurements are made in both compartments.



The net work done on the system is given by

$$W = -(P_2V_2 + P_1V_1) = P_1V_1 - P_2V_2 \quad \text{••••••••••••••••••••••••••••••••••} \quad 5.34$$

It should be remembered that $P_2V_2$is the work done by the system and $P,V,$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,

$$dE = W = (P_1V_1 - P_2V_2) \quad \text{..} \quad 5.35$$

$$\text{or} \, dE + (P_2V_2 - P_1V_1) = 0 \quad \text{...} \quad 5.36$$

Using Equation 5.9, dE+ $(P2V2 - P,V,) = \Delta H$

From Equations 5.9 and 5.36, we note that

$$\Delta H = O \quad \text{...} \quad 5.37$$

Hence, in the Joule-Thomson experiment, $\Delta H = 0$ 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_{JT}, as

$$= (\partial T/\partial P)_H \text{ ....} 5.38$$

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 is 0 is called the inversion temperature (T,) 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 other 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 as 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 above the upper inversion temperature; differ from those of other gases because they are
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 3/2nRT. Find its *CP* and Co 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

Contents

6.1 Introduction

The branch of science dealing with heat changes during chemical reactions is known as Thermochemistry.

In this unit, we shill 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:
- define the standard enthalpy of formation.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

6.3 Standard Enthalpy of Formation

The **standard enthalpy of formation** or **standard heat of formation** of a compound is the change of enthalpy during the formation of 1 mole of the compound from its constituent elements, with all substances in their standard states at 1 atmosphere (1 atm or 101.3 kPa). Its symbol is $\Delta H_f^\ominus$ or $\Delta_f H^\ominus$. The superscript theta (zero) on this symbol indicates that the process has occurred under standard conditions at the specified temperature (usually 25 degrees Celsius or 298.15 K). Standard states are as follows:

1. For a gas: the standard state is a pressure of exactly 1 atm
2. For a solute present in an ideal solution: a concentration of exactly one mole/liter (M) at a pressure of 1 atm
3. For a pure substance or a solvent in a condensed state (a liquid or a solid): the standard state is the pure liquid or solid under a pressure of 1 atm
4. For an element: the form in which the element is most stable under 1 atm of pressure. One exception is phosphorus, for which the most stable form at 1 atm is black phosphorus, but white phosphorus is chosen as the standard reference state for zero enthalpy of formation.

For example, the standard enthalpy of formation of carbon dioxide would be the enthalpy of the following reaction under the conditions above:

$$\mathbf{C_{(s,graphite)} + O_{2(g)} \rightarrow CO_{2(g)}}$$

All elements are written in their standard states, and one mole of product is formed. This is true for all enthalpies of formation.

The standard enthalpy of formation is measured in units of energy per amount of substance, usually stated in kilojoule per mole (kJ mol^{-1}), but also in calorie per mole, joule per mole or kilocalorie per gram (any combination of these units conforming to the energy per mass or amount guideline). In physics the energy per particle is often expressed in electron volts which corresponds to about 100 kJ mol^{-1}.

All elements in their standard states (oxygen gas, solid carbon in the form of graphite, etc.) have a standard enthalpy of formation of zero, as there is no change involved in their formation.

The formation reaction is a constant pressure and constant temperature process. Since the pressure of the standard formation reaction is fixed at 1 atm, the standard formation enthalpy or reaction heat is a function of temperature. For tabulation purposes, standard formation enthalpies are all given at a single temperature: 298 K, represented by the symbol ΔH_{f298}

The standard enthalpy of formation is equivalent to the sum of many separate processes included in the Born-Haber cycle of synthesis reactions. For example, to calculate the standard enthalpy of formation of sodium chloride, we use the following reaction:

$$\mathbf{Na_{(s)} + (1/2)Cl_{2(g)} \rightarrow NaCl_{(s)}}$$

This process is made of many separate sub-processes, each with its own enthalpy. Therefore, we must take into account:

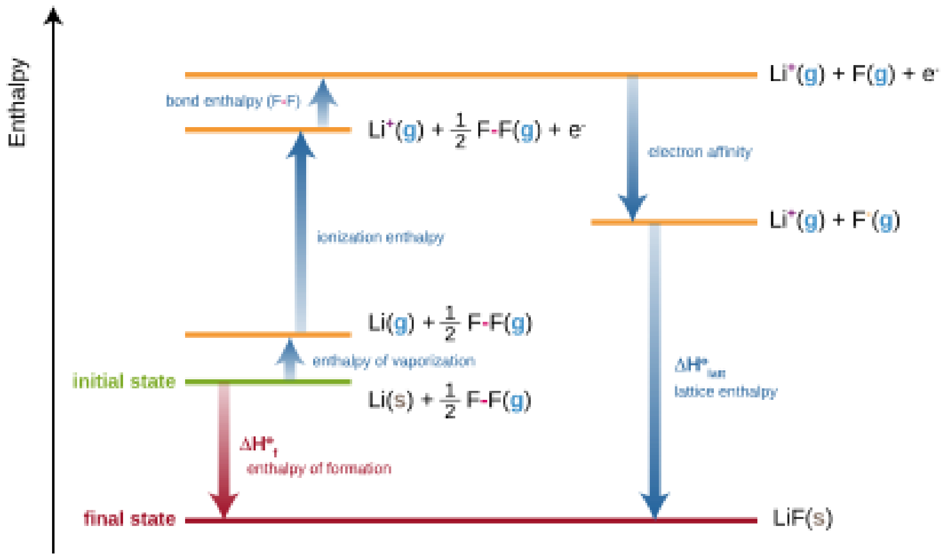


Fig 1: Standard enthalpy change of formation in Born-Haber diagram for lithium fluoride.

1. The standard enthalpy of atomization of solid sodium
2. The first ionization energy of gaseous sodium
3. The standard enthalpy of atomization of chlorine gas
4. The electron affinity of chlorine atoms
5. The lattice enthalpy of sodium chloride

The sum of all these values will give the standard enthalpy of formation of sodium chloride.

Additionally, applying Hess's Law shows that the *sum* of the individual reactions corresponding to the enthalpy change of formation for each substance in the reaction is equal to the enthalpy change of the overall reaction, regardless of the number of steps or intermediate reactions involved. This is because enthalpy is a state function. In the example above the standard enthalpy change of formation for sodium chloride is equal to the sum of the standard enthalpy change of formation for each of the steps involved in the process. This is especially useful for very long reactions with many intermediate steps and compounds.

Chemists may use standard enthalpies of formation for a reaction that is hypothetical. For instance carbon and hydrogen will not directly react to form methane, yet the standard enthalpy of formation for methane is determined to be -74.8 kJ mol^{-1} from using other known standard enthalpies of reaction with Hess's law. That it is negative shows that the reaction, if it were to proceed, would be exothermic; that is, it is enthalpically more stable than hydrogen gas and carbon.

It is possible to predict heat of formations for simple unstrained organic compounds with the Heat of formation group additivity method.

6.4 Standard Enthalpy of Reaction

Standard enthalpies of formation are used in thermochemistry to find the standard enthalpy change of any reaction. This is done by subtracting the sum of the standard enthalpies of formation of the reactants (each being multiplied by its respective stoichiometric coefficient, ν) from the sum of the standard enthalpies of formation of the products (each also multiplied by its respective stoichiometric coefficient), as shown in the equation below:

$$\Delta H^\circ = \Sigma(\nu \times \Delta H_\mathrm{f}^\circ)\ \text{(products)} - \Sigma(\nu \times \Delta H_\mathrm{f}^\circ)\ \text{(reactants)}$$

This calculation has a tacit assumption of ideal solution between reactants and products where the enthalpy of mixing is zero.

For example, for the reaction $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$:

$$\Delta H_\mathrm{r}^\circ = [(1 \times \Delta H_\mathrm{f}^\circ{}_{(\mathrm{CO2})}) + (2 \times \Delta H_\mathrm{f}^\circ{}_{(\mathrm{H2O})})]\ \text{(products)} - [(1 \times \Delta H_\mathrm{f}^\circ{}_{(\mathrm{CH4})}) + (2 \times \Delta H_\mathrm{f}^\circ{}_{(\mathrm{O2})})]\ \text{(reactants)}$$

If the standard enthalpy of the products is less than the standard enthalpy of the reactants, the standard enthalpy of reaction will be negative. This implies that the reaction is exothermic. The converse is also true; the standard enthalpy of reaction will be positive for an endothermic reaction.

6.5 Thermochemical Equations

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

$H_2\,(g) + O_2\,(g) \rightarrow H_2O \quad \Delta H = -255\ \mathrm{kjmol^{-1}}$
$C\ (\text{graphite}) + O_2\,(g) \rightarrow CO_2\,(g) \quad \Delta H = 3935\ \mathrm{kjmol^{-1}}$

are thermochemical equations. In such equations, s, I 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

For the reaction given below, calculate H^0 at 298.15K.
$C_3H_6\,(g) + 2O_2\,(g) \rightarrow 3CO_2\,(g) + 3H_2O(1)$

Solution
Given that: 6.f1° values of propene, carbon dioxide and water at 298.15 K are 20.42,-393.5 and -285.8 kJ mol^{-1} respectively.

From Equations 6.18 and 6.20,6.rH" = (36.rH"(C) + *36.tlf'* (H20))=- (6.tH 0 (C3)+6.tH( ))
=3 *x* (-393.5) + 3 *x* (-285.8)- (1 *x* 20.42) (since the standard enthalpy of formation of oxygen is zero).

$\Delta H^0 = -2\ 058$ kJ

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 ΔH^0 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,
C2H6 (g) + O_2 (g) → 2CO2 (g) + $3H_2O(1)$
in terms of the standard enthalpies of formation of the components.

6.6 Conclusion

In this unit, some of the aspects of thermochemistry have been discussed. Specifically, enthalpy change has been studied. 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.

6.7 Summary

In this unit, you have learnt that:
i) enthalpy change (6.H) is the heat absorbed in a process occurring at constant pressure;
ii) the enthalpy change which occurs when 1mole of a compound in its standard state is formed from its elements in their standard states is called the standard enthalpy of formation.

6.8 Tutor-marked assignment

1. For the reaction Fe (s) + 3H (g) → 2Fe(s) + 3O(1), ΔH^0 at 298 K is -35.1kJ. What will be the enthalpy of reaction at 375 K,if the difference between the sum of the Cp's of the products and of the reactants is 85.7 JK-1 and it is independent of 36 temperature?
2. Using Table 6.1 for the standard enthalpies of formation for CO_2 (g) and H_2(l), calculate the standard enthalpy of formation for naphthalene, if the standard enthalpy of combustion is -5153 kJ mol-1
3. The standard enthalpy of formation of H_2 (1) at 298 K is -285.8 kJ mol-1 Calculate the standard internal energy change [ΔH^0 (Hp)] for the formation of water at 298 K.
4. Calculate the standard enthalpy of formation of PCI5(s), using the following data:
   P(s) +1.5 C (g) PC (l) A, HO = -318 kJ
   $PC1_3(1)$+ Cl (g) $PC1_5(s)$ A,H = -137 kJ

6.9 Reference

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

UNIT 7: ENTHALPY CHANGES IN DIFFERENT PROCESSES AND REACTIONS

Contents

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:

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

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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
C (graphite) + 0_2(g) → CO_2(g) H_1 = -393.5HkJ
C (diamond)+ 02(g) → CO_2(g) , H_2 = -395.4 kJ

Solution

Subtracting, we get
C (graphite)-C (diamond) = 0 or C (graphite) = C (diamond), and H =,H
= -393.5kJ-(-395.4 kfl = 1.9 kJ

Hence, we can write

C (graphite)C (diamond) a, H= 1.9 kj

Example 7.2

Carbon(s) reacting with H (g} to give CH_4 (g)

Solution

C(s)(granite) + 2H → CH_4(g). (It is important to note m at side products are formed}
Hence, we can perform an oxidation action on granite, which can occur easily and also another oxidation reaction on hydrogen;

1. C(s) + O_2(g)→CO_2(g) $\Delta H = -\ 393.3$kj mol^{-1}

In excess oxygen the reaction goes to completion

2. H_2(g) + 1/2 O_2(g) → H_2O(l) $\Delta H = -\ 2855$kj mol^{-1}

It is possible for *us* to burn CH_4 in O_2(g).

3. CH_4(g) + $2O_2$(g) → CO_2(g) + $2H_2O$(l) $\Delta H = -\ 889.5$kj mol^{-1}

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

4 2H:(g) + 0(g) 2H/.){1) M1 = 2 (-28.'>.5) kJ mol :

If we add Equations 1 and 4, and subtract Equation 3 from it, we come up with a final formular

(granite)+ O_2(g) → CH_4 (g).

Therefore, ΔH =-393 3 kJ/mol + 2 (-2855kJ/mol) - (-*8895* kJ/mol)
= -74.8 kJ/mol

This is the heat of formation of CH_4(g). The standard enthalpy for compounds is also called heat of formation since the compounds are formed from the elements.

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 neutralization.

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 (ΔH, The final oxidation product ofa compound containing only C, H, 0 and N are CO_2(g), H_2(l) and N_2(g). lf a compound also contains O, Br, Cl, F, S and P, the final products include the aqueous solutions of HO, HBr, H_2, HF, SO and $HP0_4$ at infinite dilution. Thus, the enthalpy of combustion for methanol and urea are represented by the reactions:

$$C + 1.5O_2(g) \rightarrow CO_2(g) + O(g) \qquad \Delta H = -726.1 \text{ kJ mor1}$$

$$CO(NH_2)_2(s) + 1.5\,O_2(g) \rightarrow CO_2(g) + 2H_2O(l) + N_2(g) \qquad \Delta H = -633.4 \text{ kJ/mol}$$

The enthalpy of combustion is quite useful in determining the enthalpies of formation of those substances, which are difficult to mea5.ure experimentally. Here again, we make use of Hess's law.

Enthalpy change of solution

The **enthalpy of solution**, **enthalpy of dissolution**, or **heat of solution** is the enthalpy change associated with the dissolution of a substance in a solvent at constant pressure resulting in infinite dilution.

The enthalpy of solution is most often expressed in kJ/mol at constant temperature. The energy change can be regarded as being made of three parts, the endothermic breaking of bonds within the solute and within the solvent, and the formation of attractions between the solute and the solvent. An ideal solution has an enthalpy of solution of zero. For a non-ideal solution it is an excess molar quantity.

Energetics

Dissolution by most gases is exothermic. That is, when a gas dissolves in a liquid solvent, energy is released as heat, warming both the system (i.e. the solution) and the surroundings. The temperature of the solution then decreases to that of the surroundings. The equilibrium, between the gas as a separate phase and the gas in solution, will therefore (by Le Châtelier's principle) shift to favour the gas going into solution as the temperature is decreased. Thus, decreasing the temperature increases the solubility of a gas. When a saturated solution of a gas is heated, gas comes out of solution.

Steps in dissolution

Dissolution can be viewed as occurring in three steps:

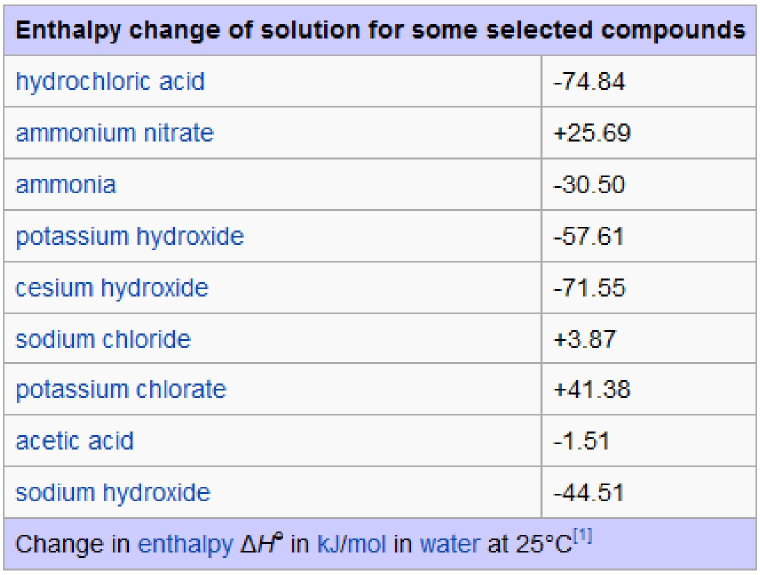
1. Breaking solute-solute attractions (endothermic), see for instance lattice energy in salts.
2. Breaking solvent-solvent attractions (endothermic), for instance that of hydrogen bonding
3. Forming solvent-solute attractions (exothermic), in solvation.

The value of the enthalpy of solution is the sum of these individual steps. Dissolving ammonium nitrate in water is endothermic. The energy released by solvation of the ammonium ions and nitrate ions is less than the energy absorbed in breaking up the ammonium nitrate ionic lattice and the attractions between water molecules. Dissolving potassium hydroxide is exothermic, as more energy is released during solvation than is used in breaking up the solute and solvent.

Dependence on the nature of the solution

The enthalpy of solution of an ideal solution is zero by definition. For non-ideal solutions of electrolytes it is connected to the activity coefficient of the solute(s) and the temperature derivative of the relative permittivity.

$$H_{dil} = \sum_i \nu_i RT ln\gamma_i (1 + \frac{T}{\epsilon}\frac{\partial \epsilon}{\partial T})$$



Enthalpy change of solution for some selected compounds	
hydrochloric acid	-74.84
ammonium nitrate	+25.69
ammonia	-30.50
potassium hydroxide	-57.61
cesium hydroxide	-71.55
sodium chloride	+3.87
potassium chlorate	+41.38
acetic acid	-1.51
sodium hydroxide	-44.51
Change in enthalpy ΔH^o in kJ/mol in water at 25°C[1]	

Enthalpy of neutralization

The **enthalpy of neutralization** (**ΔH_n**) is the change in enthalpy that occurs when one equivalent of an acid and one equivalent of a base undergo a neutralization reaction to form water and a salt. It is a special case of the enthalpy of reaction. It is defined as the energy released with the formation of 1 mole of water.

When a reaction is carried out under standard conditions at the temperature of 298 K (25 degrees Celsius) and 1 atm of pressure and one mole of water is formed it is called the *standard enthalpy of neutralization* ($\Delta H_n^{\ominus}$).

The energy (Q) released during a reaction is

$$Q = mc_p\Delta T$$

where$m$ is the mass of the solution, c_p is the specific heat capacity of the solution, and ΔT is the temperature change observed during the reaction. From this, the standard enthalpy change (ΔH) is obtained by division with the amount of substance (in moles) involved.

$$\Delta H = -\frac{Q}{n}$$

The standard enthalpy change of neutralization for a strong acid and base is -55.8 kJ/mol.

The standard enthalpy of neutralization for organic acids is slightly less exothermic than that of mineral acids because of the partially ionizing property of weak organic acids. The bond between the proton and its conjugate base requires energy to be broken, hence the lower measured value enthalpy change.

For weak acids and bases, heat of neutralization is different because they are not dissociated completely and during dissociation some heat is absorbed - total heat evolved during neutralization will be smaller, e.g.

$$HCN + NaOH \rightarrow NaCN + H_2O; \Delta H = -12kJ/mol$$

Heat of ionization in this reaction is equal to (–12 + 57.3) kJ/mol = 45.3 kJ/mol

Enthalpy change of a reaction of neutralization an acid and a base

When a powerful acid and a powerful base react, enthalpy change is unique. It may be more clear in the example below,

$$NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$$

when we consider the above reaction it is clear the only reaction we can see inside this is,

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

Enthalpy change of this reaction is -57.7 kJ mol^{-1} when a weak acid reacts with a powerful base the enthalpy change must be a lesser enthalpy change than -55.8 kJ mol^{-1}, as weak acids in solution do not fully dissociate to their respective anions and cations. To dissociate these bonds some amount of energy is needed; the enthalpy change reduces.

***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· and 9.2 kJmol^{-1}.Calculate the standard enthalpy of the reaction:

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

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).

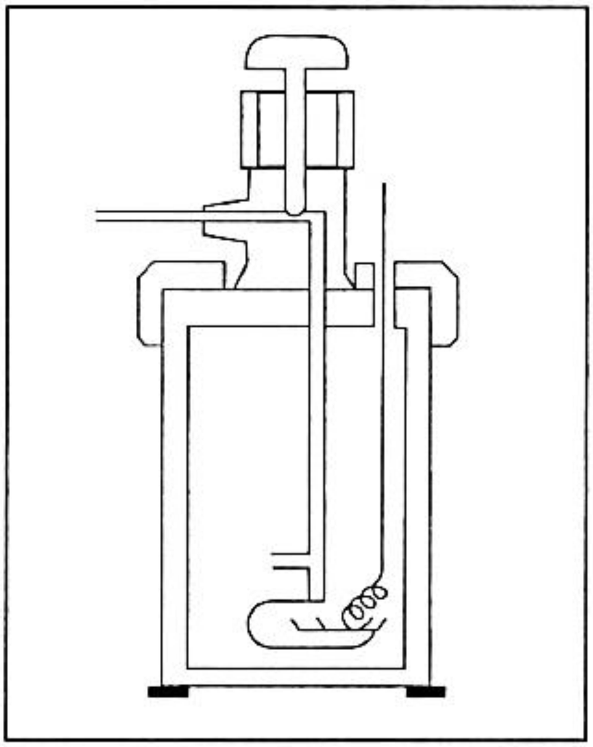


Fig. 7.1 The Bomb calorimeter

The method involves the combustion of a definite amount of substance m 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 taken before and after the combustion, using a sensitive thermometer. The heat capacity of the calorimeter, the amount of substance taken and the temperature readings, the enthalpy of combustion can now 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.

7.7 Summary

In this unit, you have learnt that the enthalpy changes in various processes are determined by using calorimeters; we learnt to determine the enthalpies of reaction and processes which cannot be determined

7.8 Tutor-marked assignment

Calculate the standard enthalpy of formation *cf*PC1 (s), using the following data
P(s) +1.5 Cl (g) → PC1 (1) ΔH^o = -318 kJ
PC1 (1) + C (g) → PCI (s) ΔH^o = -137 kj

7.9 Reference

IGNOU (1993), *Chemical thermodynamics: physical Chemistry CHE-04,* New Delhi.

MODULE 3: KINETICS AND EQUILIBRIUM

UNIT 8: REVERSIBLE AND IRREVERSIBLE REACTIONS

Contents

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:

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

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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 exam pies 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 recognize 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 ware 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 thecylinder 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 x l0^{5} Pa and 1litre at the initial condition, with initial temperature T. If it is expanded isothermally at 1.0132 x l0^{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 10.130x l0^{5} while the final temperature will be 0.Then, we can say

q = PdV = 0 (10-1) litre I= 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 x l0^{5} Pa pressure in form of rings. When the gas expands at 1.013 x l0S Pa, it then stops. Then,.

q = PdV = (1.013 x l0^{5} Pa) (0.01m^{3} -0.001m^{3}) = 10.02 x 10^{13} Pa

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 litre, then,

$$q = (P_1dV_1 + P_2dV_2 + P_3dV_3 + P_4dV_4).$$

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

$q_{irreversible} = \int_{i=1}^{n} (PdV1)$ ……………………......................................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 qrev and w.

Solution

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

$$=\int_{V1}^{V2} P2dV \text{ ....8.2}$$

where P_2 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$P_2 = P + dP$ (sliding forward and back easily).Then, we can have

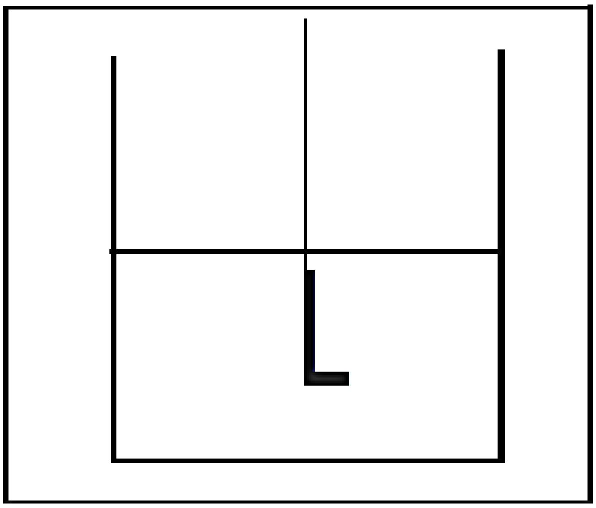


Fig. 8.1

$$q = \int_{V1}^{V2}(P + dP)dV \text{ .... 8.3}$$

Expanding this, we get

$$q = \int_{V1}^{V2}(PdV + dPdV) \qquad \text{ .... 8.4}$$

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

$$q = \int_{V1}^{V2} PdV$$

For ideal gas, we know that

$$PV = nRT \text{ .... 8.5}$$

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

Substituting, we can have

$$q = nRT \int_{V1}^{V2} dV /V$$

q = nRT $\int_{V1}^{V2} dlnV$

q = nRT $\int_{V1}^{V2} dV2/V1$.. 8.6

Work can be represented *as*

w_{irrev} =nRTlogV_2/V_1 =W_{rev} ·······•••···· ·········……………………………….*8.1*

Let us also consider a reversible process and an irreversible process in which 4E is the same. No matter how we carry out the process (reversible or irreversible), 4E depends only upon the initial and final states of the system.

ΔE = q + w, for reversible process 8.8

and E = q_{irrv}, + W_{irrv} for irreversible process 8.9

and so, q + w = q_{irrv} + W_{irrv} 8.10

We know that the work done by a system under reversible conditions work done is larger than the work done by a system under irreversible conditions (Wirr),

i.e. –W > -W_{irrv} 8.11
Hence, W <W_{irrv}................... . ...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,.._. orq;,m, is not equal to zero. Using Equations 8.10 and 8.12,we can write

$q_{rev}>q_{irrv}$.. 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 E, 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 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 = -(w1 + w2 + ...)-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,<L' 'h ..., etc, are the heat absorbed by the system and w1 w2 • ••, etc, are the work done on the system.
Using Example 8.2, you can understand the validity of Equations 8.12 and-8.13.

Example8.2

1.00 x 102 mol of an ideal gas at 3.00 x 102K temperature and 6.00 x1()6 Pa pressure occupies 4.16 x 1CT2m3 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 10^5 Pa:

a) isothermal reversible conditions
b) isothermal irreversible conditions.

Solution

In an isothermal process, for an ideal gas,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

$q_{rev} = -W_{rev} = -2.303nRT \log V_2/V_1$

$q_{rev} = 2303nRT\log 0.832m^3/4.16 \times 10^{-2}m^3$

$= 2.303 \times 1.00 \times 102\ mol \times 8.314\ molK\text{-}^{1\cdot} \times 3.00 \times 102\ K \log 0.832m^3/4.16 \times 10^{-2}m^3$

$= 7.47x\ l0^5$ J

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

$q_{irrv} = w_{irrv} = P_{et} (V_2-V_1)$

= 3.00 x $l0^5$ Pa (0.832 m3 -0.0416m3

= 3.00 x $l0^5$ X 0.7904 J

= 2.37 x $l0^5$ J

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

$W_{rev} = -7.47 \times l0^5$ J; $W_{irrv} = -2.37 X\ l0^5$ J

Hence, $W_{rev}<W_{irrv}$ as shown in Equation 8.12

w= 7.47 x $l0^5 q_{irrv}$ = 2.37 X $l0^5$ J

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

8.4 The Carnot cycle

The **Carnot cycle** is a theoretical thermodynamic cycle proposed by Nicolas Léonard Sadi Carnot in 1824 and expanded upon by others in the 1830s and 1840s. It provides an upper limit on the efficiency that any classical thermodynamic cycle can achieve during the conversion of thermal energy into work, or conversely, the efficiency of a refrigeration system in creating a temperature difference (e.g. refrigeration) by the application of work to the system. It is not an actual thermodynamic cycle but is a theoretical construct. Every single thermodynamic system exists in a particular state. When a system is taken through a series of different states and finally returned to its initial state, a thermodynamic cycle is said to have occurred. In the process of going through this cycle, the system may perform work on its surroundings, thereby acting as a heat engine. A system undergoing a Carnot cycle is called a Carnot heat engine, although such a “perfect” engine is only a theoretical construct and cannot be built in practice.

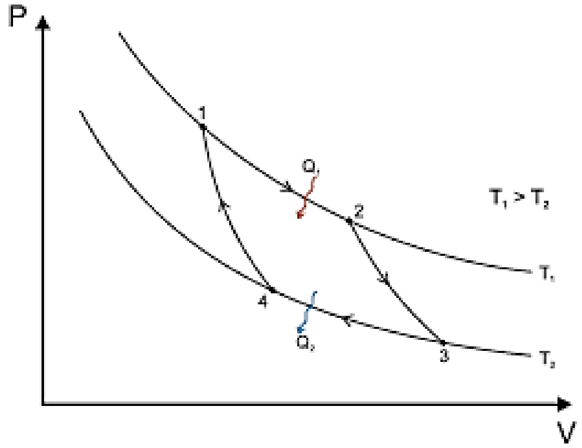


Figure 8.2: A Carnot cycle illustrated on a PV diagram to illustrate the work done.

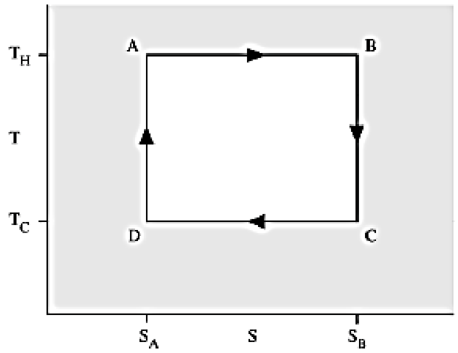


Figure 8.3: A Carnot cycle acting as a heat engine, illustrated on a temperature-entropy diagram. The cycle takes place between a hot reservoir at temperature TH and a cold reservoir at temperature TC. The vertical axis is temperature, the horizontal axis is entropy.

The Carnot cycle when acting as a heat engine consists of the following steps:

1. **Reversible isothermal expansion of the gas at the “hot” temperature, *T1* (isothermal heat addition or absorption).** During this step (1 to 2 on Figure 8.2,A to B in Figure 8.3) the gas is allowed to expand andit does work on the surroundings. The temperatureof the gas does not change during the process, andthus the expansion is isothermal. The gas expansionis propelled by absorption of heat energy Q1 and ofentropy $\Delta S = Q1/T1$ from the high temperature reservoir.

2. **Isentropic (reversible adiabatic) expansion ofthe gas (isentropic work output).** For this step (2 to 3 on Figure 8.2, B to C in Figure 8.3) the mechanisms of the engine are assumed to be thermally insulated, thus they neither gain nor lose heat. The gas continues to expand, doing work on the surroundings, and losing an equivalent amount of internal energy. The gas expansion causes it to cool to the "cold" temperature, T_2. The entropy remains unchanged.

3. **Reversible isothermal compression of the gas at the "cold" temperature, *T2*. (isothermal heat rejection)** (3 to 4 on Figure 8.2, C to D on Figure 8.3)Now the surroundings do work on the gas, causing an amount of heat energy Q2 and of entropy $\Delta S = Q2/T2$ to flow out of the gas to the low temperaturereservoir. (This is the same amount of entropyabsorbed in step 1, as can be seen from the**Clausius inequality**.)

4. **Isentropic compression of the gas (isentropic work input).** (4 to 1 on Figure 8.2, D to A on Figure8.3) Once again the mechanisms of the engine are assumedto be thermally insulated. During this step, the surroundings do work on the gas, increasing itsinternal energy and compressing it, causing the temperature to rise to *T1*. The entropy remains unchanged.At this point the gas is in the same stateas at the start of step 1.

8.4.1 The pressure-volume graph

When the Carnot cycle is plotted on a pressure volume diagram, the isothermal stages follow the isotherm lines for the working fluid, adiabatic stages move between isotherms and the area bounded by the complete cycle path represents the total work that can be done during one cycle.

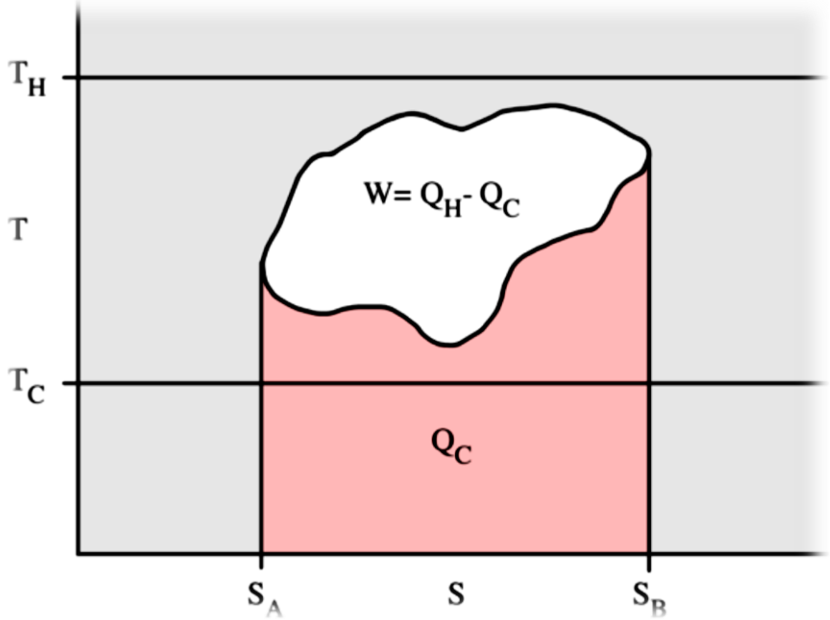


Figure 8.4: Carnot graph

8.4.2 Properties and significance

A generalized thermodynamic cycle will take place between a hot reservoir at temperature, TH and a cold reservoir at temperature TC. By the second law of thermodynamics, the cycle cannot extend outside the temperature band from TC to TH. The area in red QC is the amount of energy exchanged between the system and the cold reservoir. The area in white W is the amount of work energy exchanged by the system with its surroundings. The amount of heat exchanged with the hot reservoir is the sum of the two. If the system is behaving as an engine, the process moves clockwise around the loop, and moves counter-clockwise if it is behaving as a refrigerator. The efficiency to the cycle is the ratio of the white area (work) divided by the sum of the white and red areas (heat absorbed from the hot reservoir).

8.4.3 The temperature-entropy diagram

The behaviour of a Carnot engine or refrigerator is best understood by using a temperature-entropy diagram (TS diagram), in which the thermodynamic state is specified by a point on a graph with entropy (S) as the horizontal axis and temperature (T) as the vertical axis. For a simple system with a fixed number of particles, any point on the graph will represent a particular state of the system. A thermodynamic process will consist of a curve connecting an initial state (A) and a final state (B). The area under the curve will be:

$$Q = \int_A^B T\,dS$$

which is the amount of thermal energy transferred in the process. If the process moves to greater entropy, the area under the curve will be the amount of heat absorbed by the system in that process. If the process moves towards lesser entropy, it will be the amount of heat removed. For any cyclic process, there will be an upper portion of the cycle and a lower portion. For a clockwise cycle, the area under the upper portion will be the thermal energy absorbed during the cycle, while the area under the lower portion will be the thermal energy removed during the cycle. The area inside the cycle will then be the difference between the two, but since the internal energy of the system must have returned to its initial value, this difference must be the amount of work done by the system over the cycle. Referring to figure 8.2, mathematically, for a reversible process we may write the amount of work done over a cyclic process as:

$$W = \oint PdV = \oint (dQ - dU) = \oint (T\,dS - dU)$$

Since *dU*is an exact differential, its integral over any closed loop is zero and it follows that the area inside the loop on a T-S diagram is equal to the total work performed if the loop is traversed in a clockwise direction, and is equal to the total work done on the system as the loop is traversed in a counterclockwise direction.

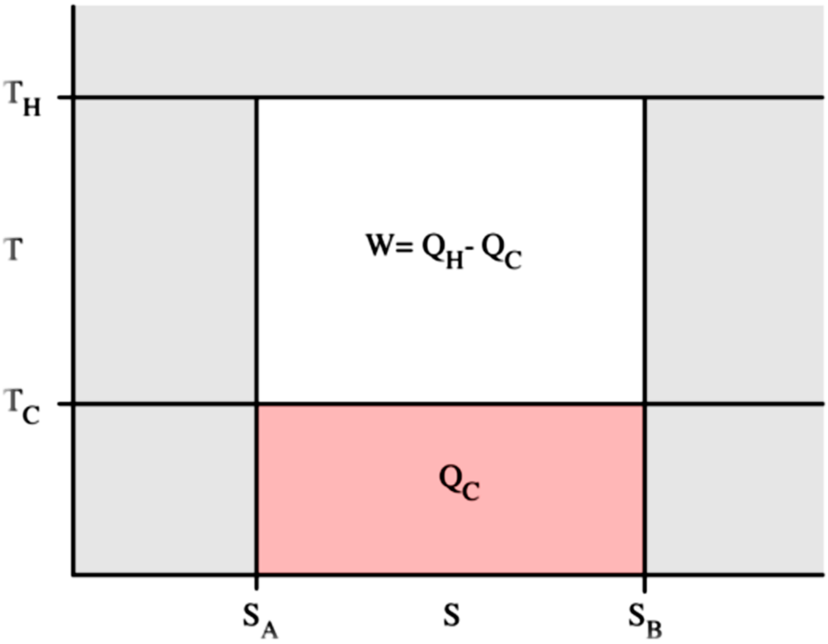


Figure 8.5: A Carnot cycle taking place between a hot reservoir at temperature TH and a cold reservoir at temperature TC.

Evaluation of the above integral is particularly simple for the Carnot cycle. The amount of energy transferred as work is

$$W = \oint PdV = \oint Tds = (T_H - T_C)(S_B - S_A)$$

The total amount of thermal energy transferred from the hot reservoir to the system will be

$$Q_H = T_H(S_B - S_A)$$

and the total amount of thermal energy transferred from the system to the cold reservoir will be

$$Q_C = T_C(S_B - S_A)$$

The efficiency is defined to be:

$$\eta = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H}$$

where
W is the work done by the system (energy exiting the system as work),
QC is the heat taken from the system (heat energy leaving the system),
QH is the heat put into the system (heat energy entering the system),
TC is the absolute temperature of the cold reservoir, and
TH is the absolute temperature of the hot reservoir.
SB is the maximum system entropy
SA is the minimum system entropy

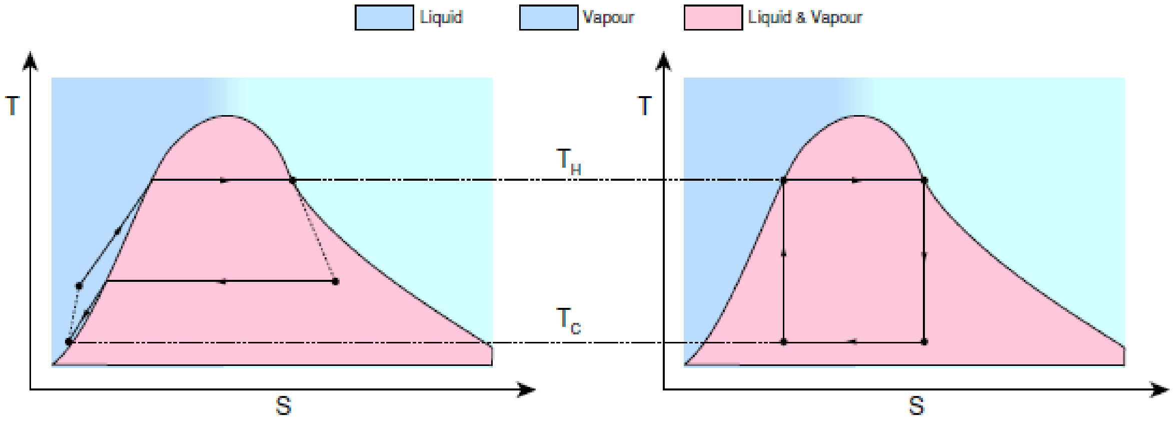
This definition of efficiency makes sense for a heat engine, since it is the fraction of the heat energy extracted from the hot reservoir and converted to mechanical work. A Rankine cycle is usually the practical approximation.

8.4.4 The Reversed Carnot cycle

The Carnot heat-engine cycle described is a totally reversible cycle. That is, all the processes that comprise it can be reversed, in which case it becomes the Carnot refrigeration cycle. This time, the cycle remains exactly the same except that the directions of any heat and work interactions are reversed. Heat is absorbed from the low-temperature reservoir, heat is rejected to a high temperature reservoir, and a work input is required to accomplish all this. The P-V diagram of the reversed Carnot cycle is the same as for the Carnot cycle except that the directions of the processes are reversed.

8.4.5 Carnot's theorem

It can be seen from the above diagram, that for any cycle operating between temperatures *TH* and *TC* , none can exceed the efficiency of a Carnot cycle.



A real engine (left) compared to the Carnot cycle (right). The entropy of a real material changes with temperature. This change is indicated by the curve on a T-S diagram. For this figure, the curve indicates a vapor-liquid equilibrium. Irreversible systems and losses of heat (for example, due to friction) prevent the ideal from taking place at every step.

Carnot's theorem is a formal statement of this fact: *No engine operating between two heat reservoirs can be more efficient than a Carnot engine operating between those same reservoirs.* Thus, Equation 3 gives the maximumefficiency possible for any engine using the correspondingtemperatures. A corollary to Carnot's theorem statesthat: *All reversible engines operating between the same heat reservoirs are equally efficient.* Rearranging the rightside of the equation gives what may be a more easily understoodform of the equation. Namely that the theoreticalmaximum efficiency of a heat engine equals the differencein temperature between the hot and cold reservoirdivided by the absolute temperature of the hot reservoir.To find the absolute temperature in kelvin, add 273.15degrees to the Celsius temperature. Looking at this formula *a*n interesting fact becomes apparent. Lowering thetemperature of the cold reservoir will have more effecton the ceiling efficiency of a heat engine than raising thetemperature of the hot reservoir by the same amount. Inthe real world, this may be difficult to achieve since the cold reservoir is often an existing ambient temperature.

In other words, maximum efficiency is achieved if and only if no new entropy is created in the cycle, which would be the case if e.g. friction leads to dissipation of work into heat. In that case the cycle is not reversible and the Clausius theorem becomes an inequality rather than equality. Otherwise, since entropy is a state function, the required dumping of heat into the environment to dispose of excess entropy leads to a (minimal) reduction in efficiency. So Equation 3 gives the efficiency of any reversible heat engine.

In mesoscopic heat engines, work per cycle of operation fluctuates due to thermal noise. For the case when work and heat fluctuations are counted, there is exact equality that relates average of exponents of work performed by any heat engine and the heat transfer from the hotter heat bath. This relation transforms Carnot's inequality into an exact equality that applies to an arbitrary heat engine coupled to two heat reservoirs and operating at an arbitrary rate.

8.4.2 Efficiency of real heat engines

Carnot realized that in reality it is not possible to build a thermodynamically reversible engine, so real heat engines are even less efficient than indicated by Equation 3. In addition, real engines that operate along this cycle are rare. Nevertheless, Equation 3 is extremely useful for determining the maximum efficiency that could ever be expected for a given set of thermal reservoirs. Although **Carnot's cycle** is an idealisation, the expression of Carnot efficiency is still useful. Consider the average temperatures,

$$\langle T_H \rangle = \frac{1}{\Delta S} \int_{Q_{in}} T dS$$

$$\langle T_C \rangle = \frac{1}{\Delta S} \int_{Q_{out}} T dS$$

at which heat is input and output, respectively. Replace *TH* and *TC* in Equation (3) by ⟨*TH*⟩ and ⟨*TC*⟩ respectively. For the Carnot cycle, or its equivalent, the average value ⟨*TH*⟩ will equal the highest temperature available, namely *TH*, and ⟨*TC*⟩ the lowest, namely *TC*. For other less efficient cycles, ⟨*TH*⟩ will be lower than *TH*, and ⟨*TC*⟩ will be higher than *TC*. This can help illustrate, for example, why a reheater or a regenerator can improve the thermal efficiency of steam power plants—and why the thermal efficiency of combined-cycle power plants (which incorporate gas turbines operating at even higher temperatures) exceeds that of conventional steam plants. The first prototype of the diesel engine was based on the Carnot cycle.

8.5 Conclusion

In this unit, *we* described reversible, irreversible processes, we sho*w* how q =-w for isothermal reversib1e expansion. We also described the Carnot cycle and show its efficiency.

8.6 Summary

In this unit, you have learnt that:

i) The work done by a system is maximum when reversible path is adopted.
ii) q =-w for isothermal reversib1e expansion.

iii) Carnot engine are separate in reversible cycle, thus no engine operating between two heat reservoirs can be more efficient that a Carnot engine operating between those same reservoirs.

8.7 Tutor-marked assignment

1. If the efficiency of a Carnot engine is20%and the temperature of the sink is 3.00x102K.Calculate the temperature of the source.
2. A Carnot engine works between 5.00 x 102 K and 3.00 x102 K. Calculate the minimum amount of heat that must be absorbed by the engine from the source at 5.00 x 102 Kin order to obtain 1.50 kJ of work.

8.8 References

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UNIT 9: ENTROPY AND FREE ENERGY

Contents

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 free energy

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

9.3 Entropy

In Units 5, 6 and 7, *we* studied the applications of the first law *of* thermodynamics,let us now study the entropy of a system.

Entropy refers to the randomness of a given system. It explains how a system is orderedor disordered.

Order and Disorder

We have an intuitive feeling of what we mean when we say a situation is ordered. By this we mean that it conforms to a predetermined set of rules. For example, suppose we have a large number of small squares arranged in a periodic array, like a checkerboard. If we have red and black checkers, we can ask in how many ways we could distribute them, one on each square, so that all the red checkers are on one side of the array and all the black checkers on the other. We can also ask in how many ways we could distribute them with no restriction on which color goes where. There are many more ways to arrange them in the latter case. The usual red and black checkerboard in which no similar colors are next to each other is the most ordered system. We can see this from the fact that the interchange of any two neighboring pieces destroys the order. Let us consider a system composed of red (R) and black (B) molecules. The system is said to be ordered if the R and B molecules stand in a regular periodic arrangement with respect to one another and to be disordered if the R and B molecules are randomly arranged as shown in Figure 9.1.

R	B	R	B
B	R	B	R
R	B	R	B
B	R	B	R

Ordered

R	R	B	B
B	R	B	R
B	R	B	R
R	B	R	B

Disordered

Figure 9.1 order and disorder arrangement

The ordered arrangement shown in Figure 9.1 is characteristic of certain crystals.
If one examines a small portion of this ordered system, one can predict the arrangementof molecules for the rest of the system even if the system is very large. Whether weconsider a situation ordered or not depends on the set of rules by which we judge thesituation, and on the attribute being considered. For example, we would consider a setof floor tiles arranged in a geometrical pattern as a situation exhibiting geometricalorder. If the tiles were each of a different color, however, we would probably not describe order to the array of tiles on the basis of color.But whatever we specify to be the ordered situation, the number of disorderedsituations is much larger than the number of ordered situations. Therefore, if selectionis done by chance, we are most likely to obtain a disordered arrangement. For example,suppose we wish to fill a square board with red and black checkers and we choose thecolor at each location by tossing a coin (i.e., we place a red checker if we toss heads,and a black checker for tails.) How many boards would you guess we would fill only tofind that we had a disordered configuration before we filled a board and found that theboard was perfectly ordered?

If the system is ordered, it is likely to become disordered. It isuseful to define a quantity **S** called **entropy**, which is a measure of the degree ofdisorder in a system. The entropy of a system increases as the disorder of the systemincreases.We now focus on the molecular motion of a system, which gives rise to theinternal energy of this system. Adding heat to this system increases the disorderbecause the heat increases the randomness of the molecular motion. So, the entropy ofthe system increases. The effect of adding heat to a system increases the molecularmotion, and this result in more disorder of the system. The effect of adding heat to acold system, one that has small molecular motion, produces more disorder than wouldhappen if one added the same amount of heat to the system if it were at a highertemperature. Why? It is because the hot system already has more molecular motionthan the cold system, so the percentage change in motion is not as great.
If the change in entropy only comes about because the internal energy of thesystem changes, the result is called a reversible process. In this case, the change inentropy $\Delta\mathbf{S}$ is given by equation 9.1.

$$\text{change in entropy} = \frac{\text{change in the heat of the system}}{\text{temperature}}$$

or

$$\Delta S = \frac{\Delta Q}{T} \qquad \text{……………………….9.1}$$

where

ΔS = change in entropy of a reversible process (joules/Kelvin or calories/Kelvin)
ΔQ = change in the heat of the system (joules or calories)
T = temperature (Kelvin)

A good example is found in an ice cube at 0^oC placed in a well-insulated chest at20 ^oC. The ice cube is the system and the chest is the environment. Heat flows fromthe chest to the ice cube because there is a difference in their temperatures. As heat isadded to the system (the ice cube), after some time the ice cube becomes a puddle ofwater at 0 ^oC. If we wait long enough, the puddle of water and the chest will reach thesame temperature, which will be less than 20 ^oC. Equation 9.1 must be applied carefully, because it is valid only if the temperatureof the substance remains approximately constant. However, we learnedthe amount of heat needed to change one gram of ice at 0 ^oC to one gram of water at0 ^oC. This is the latent heat, which is 80 calories/gram for ice. If the ice cube has amass of 100 grams (0.1 kg), we can find the heat added, which equals the increase in
thermal energy, using Equation below.

Q = **L$_{\text{heat}}$**x**M** **………………………………**9.2

= 80 cal/g x 100 g = 8,000 cal

These 8,000 calories are the difference between the initial and final thermal energy.During this phase change, the temperature remains at 0 ^oC. This means that we canfind the change in entropy by using Equation 9.1.

Example 9.1

What is the change in entropy when 100 grams of ice at 0 ^oC melt into 100grams of water at 0 ^oC?

solution

Using the 8,000 calories calculated above and converting the temperature of 0 ^oCinto 273 K, we find

$$\Delta S = \frac{\Delta Q}{T} = \frac{8{,}000\ \text{cal}}{273\ \text{K}} = 29.3\ \text{cal/K}$$

However, if heat is added after all of the ice has changed into liquid water, the temperature of the water will increase. Clearly the temperature is not constant. Generally, as heat is added to a substance, the temperature of the substance will rise. When this happens, you could use Equation 6.1 only by dividing the temperature changes up into small intervals, calculating ΔS for the initial temperature of each of these intervals, and adding the calculated values of ΔS for each of the intervals to find the total change in the entropy of the system. The smaller the temperature intervals you take for this calculation, the closer you will come to the exact value of the change of entropy of the system as heat is added to the system.

If you have studied calculus, you may realize that the procedure described above implies using calculus to find the change in entropy. Although we do not use calculus in this course, just for fun we will write down how we would use calculus to apply Equation 9.1 to calculate the change in entropy when a change in temperature occurs. A good example would be to find the change in the entropy of the liquid water at 0 ^{o}C as the liquid increases in temperature until the temperature of the liquid and the temperature of the chest are at the same temperature. Of course that temperature would be less than 20 ^{o}C. The liquid water and the chest are now at the same temperature, i.e. in thermal equilibrium with each other. In order to see what the change in heat would be in this situation, consider Equation 9.2, which tells you the heat required to change the temperature of an object.

$$\text{Heat} = (\text{Specific heat}) \times (\text{Mass}) \times (\text{Change in Temperature})$$

or

$$Q = s_{heat} \times M \times \Delta T$$

The change in entropy of the system is

$$\Delta S = S_{final} - S_{initial} = \int_{T_{initial}}^{T_{final}} \left(\frac{s_{heat}\ M\ \Delta T}{T} \right) = s_{heat}\ M \ln \left(\frac{T_{final}}{T_{initial}} \right)$$

You probably know that a diamond is very hard, with molecules tightly bound in an ordered crystal. Oxygen gas, on the other hand, has molecules that move independently of one another in a state of dynamic disorder. The molecular arrangement of the diamond molecules is more ordered than the molecular arrangement of the oxygen gas. Therefore, for an equal number of molecules of diamond and oxygen gas, the oxygen has much greater entropy. A calculation using Equation 9.1 shows that the entropy of the oxygen gas is nearly 100 times greater than the entropy of the diamond. We associate an increase in entropy with an increase in randomness in the system. In order to have zero entropy, a system would have to be perfectly ordered. The entropy of a diamond that is so ordered and that is held at absolute zero (0 Kelvin) is zero joules/Kelvin.

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 andmolten 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 crystallized out in a system;
b) There is freezing of a liquid.

Exercise9.2

Which of the following systems will have 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. 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 energy while unavailable energy is the one which is necessary to maintain the systematic specified temperature and is not available for conversion. These two parts of enthalpy can be represented as

$H=G+TS$,

where His enthalpy, G is free energy, T is temperature and Sis entropy, free energy G 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 H. Thus, for the two states ofthe system, we have:

For state 1: $H_1 \equiv G + T_1S_1$

For state 1: $H_2 \equiv G + T_2S_2$

$dH = (G_1 – G_2) + (T_2S_2 –T_1S_1)$

$dH = dG+TdS$

dH, G and dS are also 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 dG will make a reaction be spontaneous.

A spontaneous system 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.

$dH = dG+TdS$

$dG = dH– TdS$

Thus, from our last statement, dG will be negative, i.e. for any spontaneous reaction, dG will be negative. Whereas, if dHis 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 dG is positive. This implies that the reaction cannot occur spontaneously, or rather, the reverse reaction will occur. In a situation where dG 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 this 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 charge of two states of a system can be expressed as lli= aG + T65 (constant temperature), for an isothermal process.

9.7 References

Goldberg, David & Dillard, Cylide (1974), *College Chemistry,3rd Revised edition,* New York, Macmillan Publishing Co, Inc.

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

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UNIT 10: KINETICS

Contents

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. In this unit, we shall examine some basic concepts of kinetics. We shall also explain the dependence of heat of reaction on some factors.

10.2 Objectives

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

- Define rate of reaction;
- List the factors affecting rate of reaction and their effects;
- Calculate rates of reactions.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

10.3 Concept of kinetics

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

Rates of reactions process, 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 exceed. The rate of a chemical reaction can be simply understood as the amount of reaction which occurs in a given time. In fact, it is the amount (usually expressed in moles) of the reactant used up or product formed in a stated time interval, usually in seconds. We can also define the rate of reaction or the velocity of reaction qt a specified time as the decrease in the concentration of a reactant or the increase in the concentration of a product per unit temperature. The rate of reaction at specific time is known as instantaneous rate of reaction. It can be generally defined as the rate of change concentration of a specified species at a particular instant. While specifying the reaction rate, we use tension the component with respect to which it is stated. Let us consider a simple reaction;

$$A \rightarrow B$$

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:

d) 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

$$=\frac{\text{Decrease in the concentration of A}}{\text{Change in time}}$$

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

$d[A]$ means change in the concentration of A and ΔA 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).

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

$$\text{Rate of formation of B} = \frac{\text{Decrease in the concentration of B}}{\text{Change in time}}$$

$$=\frac{d[B]}{\Delta t}$$

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 N0.

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

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:

Rate of consumption of NO_2 = Rate of formation of NO = Rate of formation of O_2

By convention, we can write this as:

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 02 are formed. In other words, the reaction rate is equal to half the rate of consumption of N02 or half the rate of formation of NO_2 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:

aA + bB + cC + dD

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

Rate of reaction = $\frac{1}{a}\frac{d[A]}{dt} = \frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$

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 $Ba(NO_3)_2$ and NCO_3 to form a precipitate of $BaC0_3$.

$Ba(NO_3)_2 + Na_2CO_3 \rightarrow BaCO_3(s) + 2NaNO_3$

As the concentration of $Ba(N0_3)_2$ increases, the rate of reaction also increases. the reactants involved in a chemical reaction have their concentrations increased in a

If 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 equivalent to its partial pressure. Thus, when the partial pressure of a gas is increased, the rate of 1 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 chemical laboratory, are enough proofs to show that whe1 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 reaction thereby energizing the molecules of some of the reactants involved. The reaction between C1 and r gas 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 sectors 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 ions 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:

a) What difference exists between positive and negative catalysts?

b) 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:

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

In Fig.10.1, a, band care 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.

Time/a	**[NO_2]/M**	**[NO]/M**	**[O_2]/M**
0	0.0100	0	0
50	0.0079	O.0021	0.0011
100	0.0065	*0.0135*	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)

$$\text{At } t = 200\text{s, slope of curve} = \frac{0.5}{3.2} \times \frac{0.001}{25}\ \text{Ms-}^{1}$$

$$= 6.25 \times 10\text{-}6\,\text{Ms-}^{1}$$

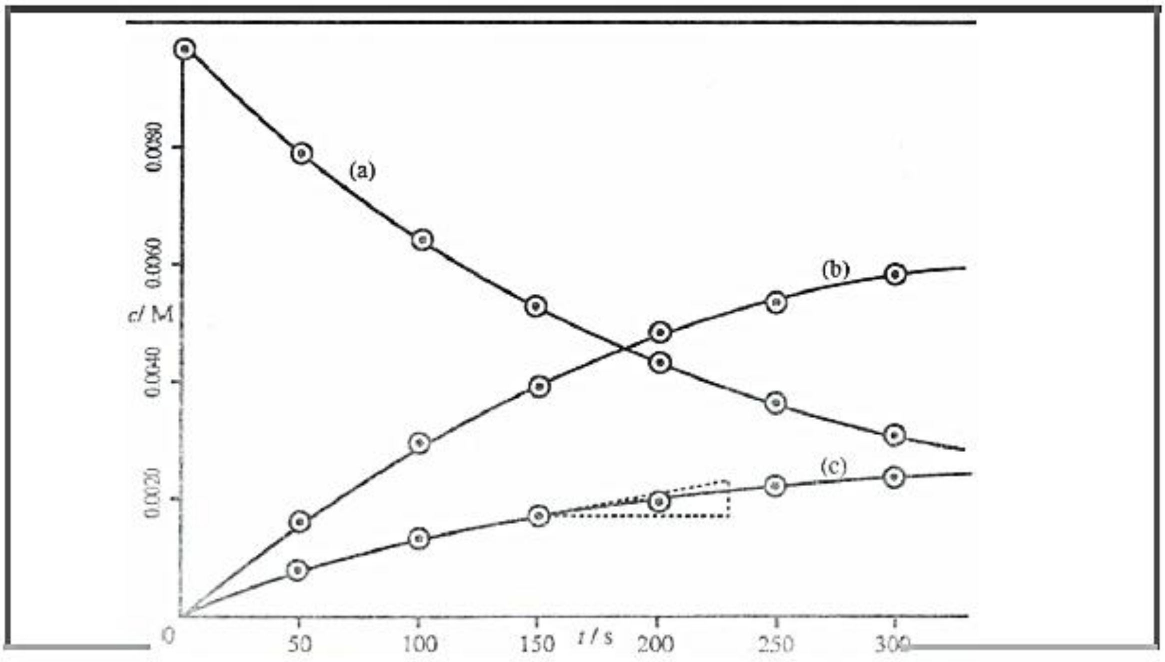

Fig. 10.. Con-en'Tation against time plot for N0$_2$

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,

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

the rate of consumption of hydrogen at a particular instant is 4.78 x 10-4 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

We shall start the unit by calculating the rates of 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:

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

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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

$2N_2O_5(g)$ --+ $4NO_2(g) + O_2(g)$

The instantaneous rates of this reaction calculated from the plot of [NO] against time are given in 25 Table 11.1.

Table 11.1 Rates for the decomposition of N_2O_5 at 323K

(N_2O_5)/M	**Rate Ms^{-l}**	**Rates/a (N_2O_5)**
0.300	$2.73 X 10^{-1}$	$9.1 X 10^{-1}$
0.150	$1.37 X 10^{-1}$	$9.1 X 10^{-1}$
0.100	$9.10 X 10^{-3}$	$9.1 X 10^{-4}$

From the first and second columns, you see that the rate of decomposition of N_2O_5 decrease with decrease in the concentration of $N_2O_{5.}$ The third column gives the ratio of the rate ofdecomposition of N_2O_5 to the concentration of N_2O_5. In all the three cases,it the constant shows that the rate is directly proportional to the concentration of N_2O_5,i.e

Rate α [N_2O_5]

Decomposition of hydrogen iodide

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

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

[H_2] M	**Rate Ms-1**	**Rate t [H_2]**	**Rate. Ms (HI)**
$3.00x10^{-1}$	$3.60 X 10^{-l}$	*1.2* X 10-1	$4.00x 10^{-2}$
$2.00 X 10^{-1}$	1.60 X 10-3	$5.0 x 10^{-4}$	$4.00x 10^{-2}$
$1.50 X 10^{-2}$	$9.01 X 10^{-6}$	$6.0 X 10^{-1}$	$4.00x 10^{-2}$

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_20_5. Furthermore, it is evident from the third column that rate [HI] is not a constant. The fourth column shows that rate/(HI) is a constant.

Hence, Rate = k (HI) Rate

Where k is a proportionality constant.

For many chemical reactions, the relationship ***R α C***the reaction rate and concentration can be expressed in a simple way such as we have seen for the decomposition of N_20_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

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 occier, 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_20_5 is a first order reaction and *n*=1.Thesignificance of this statement is that the reaction rate is proportional to the first power of concentration of N_2O_5, i.e.

rate =$k[N_20_5]$

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.

rate = k $[HI]^2$

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 amounts of reactants and products. Examples11.1 and 11.2 show the difference between stoichiometry and rate of reaction.

Example 11.1

The gas-phase decomposition of N_20_5yields N_2 and 0_2 at a particular temperature.

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

The experimentally observed rate law for the reaction rate = k $[N_2O_5]$.

Comment on the order and stoichiometry of the reaction.

Solution
It can be seen that the stoichiometric coefficient of N_20_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

$2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$.

The rate law is rate =.k[N_2O]
Comment on the order and stoichiometry of the reaction.

Solution
Again the stoichiometric coefficient of N 0 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

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

Rate = k [HI], 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:
a) 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, have we 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 Products if the rate law is experimentally found to be rate = k [A]m [B]n [C]p. Then, the overall order of the reaction = $m + n + p$.

The rate taws 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 11.l
In the decomposition of hydrogen iodide, what is the relationship between the rate of decomposition of HI and the rate of formation of?

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, 1.ht concentration of a reactant or product is followed at various time intervals, using any of the methods.1hese values are then used for calculating the rate constant.

Volume or pressure measurement

When at least, one •f 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.

Conductomery 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:

a) $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$

Hint Bromine absorbs strongly in the visible region, while hydrogen and hydrogen bromide do not.
b) CCHO(g) → CH(g) + CO(g) (at constant volume conditions)

11.4 Conclusion

In this unit, we examine 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

i) 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;

ii) Rate law is an equation expressing the relations.hip between the instantaneous reaction rate and the concentrations of the reactants in a reaction;

iii) Some of the physical and chemical methods for studying reaction rates include volume or pressure measurement, titrimetry, conductometry, polarimetry and spectrophotmetry.

11.6 Tutor - marked assignment

The rate constant for the decomposition of N_2O_5 at 340 K is $5.20 \times 10^{-3}s^{-1}$.
This reaction follows first order kinetics. If the initial rate of decomposition of N_20_5 is $2.60 \times 10^{-1}Ms^{-1}$, calculate the initial concentration of N_2O_5.

11.7 Reference

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

UNIT 12: INTRODUCTION TO CHEMICAL EQUILIBRIA

Contents

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:

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

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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 in1799 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:

$NaCO_3 + CaCl_2 \rightarrow CaCO_3 + 2NaCl$

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 realize 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) emphasizing the fact that it is a reversible reaction:

$NaCO_3 + Ca \rightarrow CaC0_3 + 2Na$

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, GuldbergandWagge showed experimentally that there exists an equilibrium between the reactants and products in a chemical reaction and that thus 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 expiration. Let *us* consider two reactions to clarify these points. Van t Hoff, in 1877, studied the hydrolysis of ethyl acetate:

Ester Water Acid Alcohol

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

$$k = \frac{C_2H_5OH \text{ x } CH_3COOH}{CH_3COOC_2H_5 \text{ x } cH20}$$

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 close 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, $H^+ + I = 2HI$. 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:

$A+B \rightarrow C + D$

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 $C +D \rightarrow A + B$, should also be less than the rate of the forward reaction $A + B \rightarrow C + D$. However, as the reaction processes, more of C and D are produced.

Since these are reactions are in opposite directions, there is no change in composition with time and it seems the reactions stopped. We then say that the reacting system is in the state of equilibrium. 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 stageno 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 earlier, for a system

$aA+bB\rightarrow cC+dD$

the equilibrium constant expression by Van't Hoff can be written as
K= [qC][D]d
[At[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
a) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
b) $2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

12.4 Summary

In this unit, you have learnt that:

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

12.5 Tutor-marked assignment

1 In a reaction A+ 2B 2C + 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.

2 In a 10.0 dm3 mixture of}, and HI at equilibrium at 698 K, there are 0.100 mol of}, 0.100 mol of and 0.740 mol of HI. If 0.500 mol of HI is now added to this system, what will be the concentrations of}, and HI, once equilibrium has been re-established?

12.6 References

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IGNOU (1997), *Chemical Equilibrium and Electrochemistry: Physical Chemistry CHE-04,* NewDelhi.

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UNIT 13: LE CHATELIER'S PRINCIPLE AND CHEMICAL EQUILIBRIA

Contents

13.1 Introduction

In this unit, we shall consider the determination 0f 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:

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

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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 Gibb's 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 apply to any system under equilibrium, the system will tend to shift in such a way so as to neutral effect of that stress (jf 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 till at the effect of these changes is neutralised. Let us consider the effect of each one of these factors en equilibrium.

Effect of change of concentration

Let us consider the reaction $H_2(g) + I_2(g) \rightarrow 2HI(g)$ 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 • 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 HI 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 $H_2(g)+I_2(g) \rightarrow 2HI(g)$ again. Now, suppose that the pressure of the system is increase4, 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:

$N_2(g) + 3H_2(g) \rightarrow 2NH\ 3(g)$.

If the pressure of the system is increased at equilibrium, the effect of this increase can be eliminated by the formation of more ammonia. This is because 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 is 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 those 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 minimum cost. For instance, in the production of ammonia, we know from Le Chatelier's principle that high pressure and high concentration of N2 and f\ will favour the reaction. Similarly, U\i5 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 of a pressure of several mega pascals and temperature of between 650 and 710 K.

Exercise 13.1

1 Consider the reaction,

$PCI_5\ (g) \rightarrow PCI_3(g) + Cl_2(g)$.

How will the equilibrium be affected by:

a) the addition of Cl_2;

b) decrease in the volume of the container?

2 If $\Delta H^o = 41$ kJ $mol^{-1}$for the reaction

$H_2(g) + CO_2(g) \rightarrow H_2O(g) + CO(g)$.

what will be the effect of increase of temperature on the equilibrium?

13.5 Conclusion

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

13.6 Summary

In this unit, you have learnt that:

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

13.7 References

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IGNOU (1997)*, Chemical Equilibria and Electrochemistry: Physical Chemistry:CHE4,* New Delhi.

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UNIT 14: IONIC EQUILIBRIA(I)

Contents

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 i. 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:

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

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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; familiar 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 per chloride, nitric, hydrochloric, sulphuric, etc., fall in the category of strong electrolytes. Most of our discussions will be focused to equilibra involving weak acids and weak bases.
Presently, acids and bases are being defined in many different ways. The application of equilibrium experimentation 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, Browsted 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:
$HN0_3 \rightarrow H^+ + NO^-$;
$HI \rightarrow H^+ + I^-$

Bases:
$NaOH \rightarrow Na^+ + OH$
$KOH \rightarrow K^+ + OH$

Neutralisation:
$H^+ + CI^- + Na^+ + OH^- \rightarrow O + Na^+ + CI^-$
(Acid) (Base) (Water) (Salt)

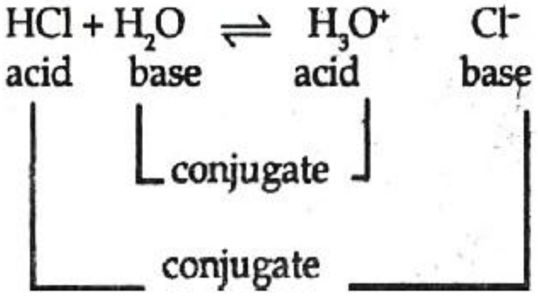
This is the most common and most frequently used concept. However, there are two main limitations to the concept. First, it does not take into account the role of the solvent in the process.

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, NH_3 behaves like a typical base in reacting with an acid but does not contain hydroxyl ions. Similarly, BF_3 molecule does not contain hydrogen ions but docs act as an acid toward a base like ammonia in the reaction:

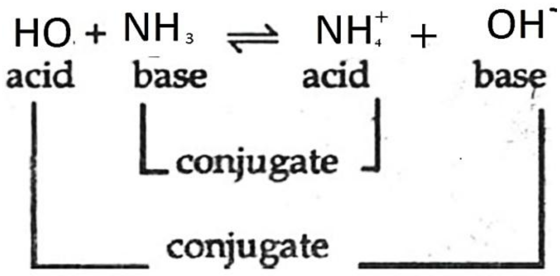
$BF_3 + NH_3 \rightarrow BF_3: NH_3$

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, HO is an acid which has a conjugate b l-ion. Every acid HA has a conjugate base A-formed by the loss of a proton and every base A^- has1 a conjugate acid formed when the base accepts a proton. Let us look at the reaction of HO with water:



Here, water molecule acts as a base (proton acceptor) towards the acid, HO (proton donor), producing conjugate add and base, respectively as H_2O^+ and Ct. It can be represented in another way as:



In this case, HO is acting as an acid and NH, 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 slighter base than chloride ion to produce a stronger acid (H_2O^+) and a weaker base, anion.

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 having no OH- acts *as* a base towards water. On the other hand, a compound containing a proton can behave like an add 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, and 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, HC10, HBr, HNO_3 etc. are all strong acids in water as shown in the following equations:

$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

$$HClO_4 + H_2O \rightarrow H_3O^+ + ClO_4^-$$

$$HBr + H_2O \rightarrow H_3O^+ + Br^-$$

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 the standards. 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 a solvent which is a weaker base than water, for instance, formic acid. The order of strength found in case is per chloric acid, nitric acid and hydrobromic acid. At first, the statement scunded 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 utilized 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 electron is a base. A few examples of Lewis acid-base reactions are:

$$\mathbf{Br_3 + NH_3 \rightarrow Br_3NH_3}$$
$$\mathbf{H^+ + NH_3}$$
$$\mathbf{H^+ + OH^- \rightarrow H2O}$$

Bronsted bases, like OH- or NH 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. 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 descriptions provided earlier on, what are the attributes of bases? They are bitter and feel slippery. You would recall that the use of some local soap 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?

i) The strength of an acid is determined by the concentration of the hydroxyl ions.
ii) The smaller the OH- ions the stronger the base.
iii) Ammonia is an example of a base.
iv) 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.1he 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,

i) it does not consider the role of the solvent in the process;
ii) there are many substances which do not contain hydro, en 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:

i) Strong acids and bases are supposed to dissociate almost completely in water whereas weak acids and bases are not.
ii) We can determine the dissociation constants of acids and bases under equilibrium conditions in terms of concentration.
iii) Water is a universal solvent and it is atmospheric in nature.
iv) The dissociation of water can be written as:

$H_2O \rightarrow H^+ + OH^-$ or $2H_2O \rightarrow H_3O^+ + OH^-$

14.7 References

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UNIT 15: IONIC EQUILIBRIAIN WEAK ACIDS AND BASES

Contents

15.1 Introduction

In the unit we shall concern ourselves with the ionization 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.QH). 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:

- write the equilibrium constant expressions for the dissociation of weak acids, weak bases and water.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

15.3 Ionic Equilibriain 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 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

$HA \rightarrow H^+ + A^-$........................(15.1)

And the corresponding dissociation constant expression as,

$$K_a = \frac{[H+][A-]}{[HA]} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (15.2)$$

If the initial concentration of the acid is C and a is the degree of dissociation, then the equilibrium concentrations would be:

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

Initial concentration C_o
Equilibrium concentration $(1-\alpha)\ C_o$
$\alpha\ C_o$
$\alpha\ C_o$

Substituting these values in Equation 15.2, we get:

$K= (\alpha\ C_o)\ (\alpha\ C_o) / (1-\alpha)\ C_o$

Or

$K= \alpha^2 C_o/1-\alpha$.............................. (15.3)

Application of Equation 15.3 can be seen from the following examples.

Example 15.1
At 98 K, a 0.100 M solution of acetic acid is 1.34% ionised. Calculate the ionisation constant of acetic acid.

Solution
Since a= 0.0134, $[H^+] = \alpha C_o = 0.0134 \times 0.100$ M

= 0.00134 M = [CH,COO];

also [COOH] = (1-0.0134} x 0.100 M = 0.09866 M

$\therefore$ K = $[H^+]$ $[CH_3COO]$ *I* $[CH_3COOH] = (0.00134)^2/0.09866$

or K. = 1.82×10^{-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 x 10).

Solution

As per Equation 15.1, we can write,

$$\mathrm{CH_2COOH} \rightarrow \quad \mathrm{H^+} \quad + \ \mathrm{CH_3COO^-}$$

$$Equilibrium\ concentration (1-\alpha)\mathrm{C_0}\alpha\mathrm{C_0}\alpha\mathrm{C_0}$$

Initial concentration of acetic acid, $C_o = 1.0$ M

$1.8 \times 10^{-3} = \frac{1 \times \alpha}{(1-\alpha)}$

Solving for a, we get a value of 4.2×10^{-3} the other value, being negative, has no physical significance.

Hence, $[H^+]$ in 1M acetic acid = αM

= 4.2×10^{-3}M

Equation 15.3 can be simplified further if the degree of dissociation is very small, i.e. if $\alpha = 1$, then $K = \alpha^2 C_o$

Multiplying both sides by $C_o$we get,

$KC_o = \alpha C_o$

Or $C_0\alpha = K\alpha C_0$

Or $[H^+] = KC_0$

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,

$BOH \rightarrow B^+ + OH^-$ .... (15.5)

And= $[B^+]\ [OH^-]/[BOH]$ .... (15.6)

If C0 is the initial concentration of the base and a is the degree of dissociation, then,

= $(\alpha C_0)\ (\alpha C_0) / (1-\alpha)C_0 = \ \alpha^2 C_0 / 1-\alpha$ ....(15.7)

Also, $[OH^-] = \alpha Co$ = vK., C if $\alpha = 1$.................. (15.8)

The value of a can be found by substituting Ka and C_o values in Equation 15.3;

Solving for a, we get a value of 4.2×10^{-3} the other value, being negative, has no physical significance.

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:

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$................................ (15.9)

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$..............................(15.10)

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$ .... (15.11)

Each of these steps of dissociation is connected with an equilibrium constant which can be represented by,
= $[H^+]\ [H_2PO_4^-]\ /[H_3PO_4]$ .... (15.12)
= $[H^+]\ [H_2PO_4^-]/\ [H_2PO_4^-]$ .... (15.13)
and
= $[H^+]\ [PO_4^{3-}]/[HPO_4^{2-}]$ .... (15.14)

The actual values for the three equilibrium constants have been found to be= 7.5×10^{-3}, = 6.2×10^{-3} and = 1.0×10^{-3} which follows a decreasing order. This is to be expected since an undissociated molecule, PO, can lose its proton more easily than the negatively charged H_2P0_4 ion, which in turn, can give off its proton more easily than a double-negatively charged $HP0_4^-$ ion. Hence, in a solution of phosphoric acid, the predominant species will be H P0 , H^+ and $HP0_4^-$ with lesser amounts of HPO_4^- and still less of P04.
Another common example is 04 which dissociates as,

$H2SO4 \rightarrow H^+ + HSO4^-$

$$K_1 = [H^+][HSO_4^-]/[H_2SO_4] = 1.0 \times 10^3$$

$$HSO_4^- \rightarrow H^+ + SO_4^{2-};$$

$$K_2 = [H^+][SO_4^{2-}]/[HSO_4^-] = 1.3 \times 10^{-2}$$

As 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 1.0M NH_4OH at 298 K (= 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 different 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

IGNOU (1999).*Chemical Equilibria and Electrolysis-Physical Chemistry* 4*CHE - 04.*

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UNIT 16: IONIC PRODUCT OF WATER

Contents

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-10n effect en a system at equilibrium shall be studied and his application in the study of *buffer* solutions shall be discussed.

16.2 Objectives

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

- define ionic product of water;
- write the equilibrium constant expressions for the dissociation of water;
- define pH scale; and
- state the effect of the addition of a substance containing common ion on the dissociation of acids and bases.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

16.3 Ionic product of water

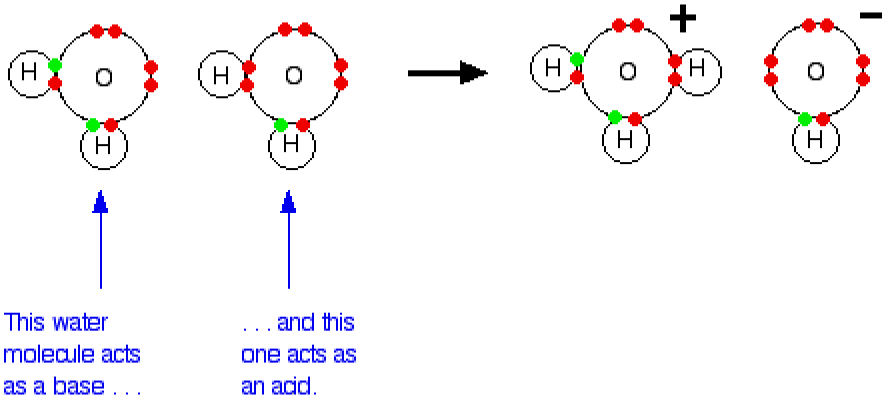
This page explains what is meant by the ionic product for water. It looks at how the ionic product varies with temperature, and how that determines the pH of pure water at different temperatures.

Kw and pKw

The important equilibrium in water

Water molecules can function as both acids and bases. One water molecule (acting as a base) can accept a hydrogen ion from a second one (acting as an acid). This will be happening anywhere there is even a trace of water - it doesn't have to be pure.

A hydroxonium ion and a hydroxide ion are formed.



However, the hydroxonium ion is a very strong acid, and the hydroxide ion is a very strong base. As fast as they are formed, they react to produce water again.

The net effect is that equilibrium is set up.

$$2H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$ ……………………….(16.1)

At any one time, there are incredibly small numbers of hydroxonium ions and hydroxide ions present. Further down this page, we shall calculate the concentration of hydroxonium ions present in pure water. It turns out to be 1.00x 10^{-7} $moldm^{-3}$ at room temperature.

You may well find this equilibrium written in a simplified form:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$$ ……………………..(16.2)

This is OK provided you remember that H^+(aq) actually refers to a hydroxonium ion.

Defining the ionic product for water, K_w

K_w is essentially just equilibrium constant for the reactions shown. You may meet it in two forms:

Based on the fully written equilibrium . . .

$$K_w = [H_3O^+]\,[OH^-]$$ ……………………………….. (16.3)

. . . or on the simplified equilibrium:

$$K_w = [H^+]\,[OH^-]$$ …………………………………….. (16.4)

You may find them written with or without the state symbols. Whatever version you come across, they all mean exactly the same thing.

You may wonder why the water isn't written on the bottom of these equilibrium constant expressions. So little of the water is ionised at any one time, that its concentration remains virtually unchanged - a constant. K w is defined to avoid making the expression unnecessarily complicated by including another constant in it.

The value of K_w

Like any other equilibrium constant, the value of K w varies with temperature. Its value is usually taken to be 1.00 x 10 -14 mol 2 dm -6 at room temperature. In fact, this is its value at a bit less than 25°C.

The units of K_w: K_w is found by multiplying two concentration terms together. Each of these has the units of mol dm^{-3}.

Multiplying $moldm^{-3}$ x $moldm^{-3}$ gives you the units above.

pK_w

The relationship between K w and pK_w is exactly the same as that between K a and pKa , or [H +] and pH.

The K_w value of 1.00 x 10-14 mol2 dm-6 at room temperature gives you a pK_w value of 14. Try it on your calculator! Notice that pK_w doesn't have any units.

The pH of pure water

Why does pure water have a pH of 7?

That question is actually misleading! In fact, pure water only has a pH of 7 at a particular temperature - the temperature at which the K w value is 1.00 x 10 -14 mol^2dm^{-6}. This is how it comes about.

To find the pH you need first to find the hydrogen ion concentration (or hydroxonium ion concentration - it's the same thing). Then you convert it to pH.

In pure water at room temperature the K_w value tells you that:

$[H +] [OH -] = 1.00 \times 10^{-14}$

But in pure water, the hydrogen ion (hydroxonium ion) concentration must be equal to the hydroxide ion concentration. For every hydrogen ion formed, there is a hydroxide ion formed as well.

That means that you can replace the [OH -] term in the K w expression by another $[H^+]$.

$[H +]^2 = 1.00 \times 10^{-14}$

Taking the square root of each side gives:

$[H +] = 1.00 \times 10^{-7}$ $moldm^{-3}$

Converting that into pH:

$pH = - \log 10 [H^+]$

pH = 7

That's where the familiar value of 7 comes from.

The variation of the pH of pure water with temperature

The formation of hydrogen ions (hydroxonium ions) and hydroxide ions from water is an endothermic process. Using the simpler version of the equilibrium:

$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$ ……………….(16.7)

The forward reaction absorbs heat.

According to Le Chatelier's Principle, if you make a change to the conditions of a reaction in dynamic equilibrium, the position of equilibrium moves to counter the change you have made.

Note: If you don't understand Le Chatelier's Principle, you should follow this link before you go on. Make sure that you understand the effect of temperature on position of equilibrium.

According to Le Chatelier, if you increase the temperature of the water, the equilibrium will move to lower the temperature again. It will do that by absorbing the extra heat.

That means that the forward reaction will be favoured, and more hydrogen ions and hydroxide ions will be formed. The effect of that is to increase the value of K w as temperature increases.

The table 16.1 below shows the effect of temperature on K_w. For each value of K_w, a new pH has been calculated using the same method as above. It might be useful if you were to check these pH values yourself.

Table 16.1: the effect of temperature on K_w

T (^oC)	**K w (mol^2dm^{-6})**	**pH**
0	0.114×10^{-14}	7.47
10	0.293×10^{-14}	7.27
20	0.681×10^{-14}	7.08
25	1.008×10^{-14}	7.00
30	1.471×10^{-14}	6.92
40	2.916×10^{-14}	6.77
50	5.476×10^{-14}	6.63
100	51.3×10^{-14}	6.14

You can see that the pH of pure water falls as the temperature increases.

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 acid or base in a solution. Thus, we can say the pH scale is a measure of the strength of acid (which is the hydrogen ion concentration introduction).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 Equation16.3,

$$K = [H^+] [OH^-] / [H_2O]$$

Suppose that we add a small quantity of add to water, thereby increasing the concentration of H^+ ion at equilibrium. The equf1lbrlum 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 16.1iJ 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 298K, whenever the concentration of hydrogen ion in water is greater than 1.0 x10"7 M, the solution it said to be acidic and whenever it is lets than 1.0×10^7 M, we refer to it as a basic solution.

Instead of expressing these small concentrations to negative powers of 10, we can state them more conveniently and u a small numbers by express them in terms of their negative logarithm.

Hence, instead of writing H• ion concentration as 1.0 x 10"7 M we write it as $-\log (10 \times 10^{-7})$ or simply *7* number it proceeded by a symbol pH (small letter p, followed by capital letter H).

Thus,

$pH = \log [H^+]$ ....(16.9)

or

$[H^+]$ 101-"...........................(16.10)

where H^+ ion concentration is expressed in $moldm^{-1}$. 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 insolution 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,

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

We get, $4.5 = -\log [H^+]$

or $\log [H^+] = -4.5$

i.e., $[H^+] = -4.5 \times 10^{-4}$

Pure water, where H^+ ion and OH^- ion concentrations are both equal to1.0×10^{-7} (at 298 K), will thus have a 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 happen to the self-ionisation equilibrium of water when we add a small quantity of a strong add i:o it. Consider a solution containing 0.010 mole of HCl in1dm^3 of water. The concentration of hydrogen ion due to HO will be 1.0 x 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 add (10-M/. Hence, the contribution due to water dissociation can be neglected in such a case and the pH of that solution will be 2.Theconcentration of OH-ion will then be given by;

$$[OH] = \frac{kw}{[H+]} = 1.0 \text{ X } 10^{-4}/1.0 \text{ X } 10^{-2}$$

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,

$= [H^+]\ [CH_3COO^-]\ I\ [CH_3COOH]$.-.....................6.12)
or
$H^+ = K.[CH,COOH]\ I\ [CH_3COO^-]$ ....(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 $CH3COO^-$ 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.
One basis of the abovediscussi9Il, answer the following exe.

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 $[H^+]$;
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.*
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UNIT 17: IONIC EQUILIBRIA(II)

Contents

17.1 Introduction

In Unit 16 we were concerned with ionic equilibria in acids and base. We also covered the pH scale and common-ion effect. In this unit, we s*hall* be discussing the buffer solution, hydrolysis and indicator & and their uses.

17.2 Objectives

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

- explain the meaning of buffer solution and their application; and
- state the meaning of hydrolysis and calculate hydrolysis constant.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self-assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

17.3 Buffer solutions

In this section, we shall examine buffer solution. What exactly do we refer to as 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 reveal that the hydrogen ion concentration (or the pH of the solution) shall have constant value equal to K, (or pK), to the concentrations of acetate ions and the undissodated acetic add become equal to each other. In other to find how this condition can be achieved and what are It & uses, let us consider a 1.0 M acetic acid solution for which K = 1.8×10^{-6}.We can write,

$$K = \frac{[H+][CH3COO-]}{[CH3COOH]}$$

or

$1.8 \text{ X } 10^{-5} = \frac{[\mathrm{H}][\mathrm{CH3COO-}]}{1.0M}$

Assuming that the amount of acetic acid concentrated is negligible in comparison to the Initial concentration of acetic acid (1.0 M), we can write the concentration of acid u, l.0M.

Therefore $[H^+]$ 1.13 x 10^{-5} x1.0 Ml

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, $[CH_3COOH]$, can be taken as1.0 M. Substituting these values in Equation 16.12 of Unit 16, we get,

pH= 4.74;

i.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 0.01M. *As* a result of this, 0.01M H^+ ions will react with 0.01Macetate ions to form 0.01Mundissociated acetic acid. Thus, the concentration of the undissociated acetic will increase from 1.0M to 1.01M. The concentration of acetate ion will correspondingly decrease by 0.01Mand its concentration at equilibrium will be (1.0M-0.01M) = 0.99 M. Substituting these values in Equation 16.13 of Unit 16, we get

$[H^+]$ =1.8 X 10^{-5} X 1.01/0.99

= 1.83 X 10^{-5}

Therefore, pH= 4.74; hence, we find that by the addition of 0.01M HO, 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:

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

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

Can therefore write,

$K = \frac{[H+][A-]}{a[HA]}$

or $[HA^+] = \frac{Ka\,[HA]}{[A]}$

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]

or $[H^+]= Ka\frac{[acid]}{[salt]}$ .... (17.1)

In the case of a buffer of a weak base and its salt, we can write that,

$[OH^-]$ =Kb [base] .... (17.2)
[salt]

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 1 and 10

Case (i) : $\frac{[acid]}{} = \frac{1}{}$
[salt] 10

Using Equation 17.1, [H] = Ka

Substituting, these values in Equation 17.1, we get
Taking logarithm, log $[H^+]$ =log K +log 1/10
= logK.-1
or -log $[H^+]$ = -log K.+ 1
i.e., pH = pK.+ 1

Case (ii) : $\frac{[acid]}{}$=10
[salt]

Again using Equation 17.1, $[H^+]$ = K.10
Following the steps shown in case (i) we get,
pH = pK.-1.............................. (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 contain CO/HC03 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 x 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

Hydrolysis is a reaction involving the breaking of a bond in a molecule using water. The reaction mainly occurs between an ion and water molecules and often changes the pH of a solution. In chemistry, there are three main types of hydrolysis: salt hydrolysis, acid hydrolysis, and base hydrolysis.

Salt Hydrolysis

In water, salts will dissociate to form ions (either completely or incompletely depending on the respective solubility constant, Ksp. For example:

$$NH_4Br_{(s)} \rightarrow NH_4{}^+{}_{(aq)} + Br^-{}_{(aq)} \text{ ......(1)}$$

The NH_4^+ is the hydrolysed as follows

$NH_4^+ + H_2O \rightarrow NH_3 + H_3O$

Because Br^- is a strong amin, it is not hydrolysed, and the resulting solution is acidic.

Here, the salt NH_4Br is put into water and dissociates into NH_4^+ and Br^- .

The following will determine if a salt will be hydrolysed in solution or not:

1. If the salt is formed from a strong base and strong acid, then the salt solution is neutral, indicating that the bonds in the salt solution will not break apart (indicating no hydrolysis occurred) and is basic.
2. If the salt is formed from a strong acid and weak base, the bonds in the salt solution will break apart and becomes acidic.
3. If the salt is formed from a strong base and weak acid, the salt solution is basic and hydrolyzes.
4. If the salt is formed from a weak base and weak acid, will hydrolyze, but the acidity or basicity depends on the equilibrium constants of K_a and K_b. If the K_a value is greater than the K_b value, the resulting solution will be acidic and vice versa.

Acid Hydrolysis

Water can act as an acid or a base based on the Brønsted-Lowry acid theory. If it acts as a Bronsted-Lowry acid, the water molecule would donate a proton (H^+), also written as a hydronium ion (H_3O^+). If it acts as a Bronsted-Lowry base, it would accept a proton (H^+). An acid hydrolysis reaction is very much the same as an acid dissociation reaction.

$CH_3COOH + H_2O \rightarrow H_3O^+ + CH_3COO^-$................................ (2)

In the above reaction, the proton H^+ from CH_3COOH (acetic acid) is donated to water, producing H_3O^+ and a CH_3COO^-. The bonds between H^+ and CH_3COO^- are broken by the addition of water molecules. A reaction with CH_3COOH, a weak acid, is similar to an acid-dissociation reaction, and water forms a conjugate base and a hydronium ion. When a weak acid is hydrolyzed, a hydronium ion is produced.

Basic Hydrolysis

A base hydrolysis reaction will resemble the reaction for base dissociation. A common weak base that dissociates in water is ammonia:

NH3 + H2O → $NH^+_4 + OH^-$………………………………………… (3)

In the hydrolysis of ammonia, the ammonia molecule accepts a proton from the water (i.e., water acts as a Bronsted-Lowry acid), producing a hydroxide anion (OH^-). Similar to a basic dissociation reaction, ammonia forms ammonium and a hydroxide from the addition a water molecule.

Use of Hydrolysis

In nature, living organisms are only able to live by processing fuel to make energy. The energy that is converted from food is stored into ATP molecules (Adenosine Triphosphate). Life requires many processes in order to sustain itself such as cellular respiration, respiration, muscle contraction, distribution of hormones, transmittance of neuro-transmitters in the brain, etc. All of these important processes require an input of energy. To distribute this energy, the energy from the ATP molecules must be released. To release the energy stored in the bonds of ATP molecules, hydrolysis must occur to break a phosphate group off of an ATP molecule, thus releasing energy from the bonds. ATP now becomes ADP (Adenosine Diphosphate) from losing a phosphate group through hydrolysis.

Examples 17.1

$H_2CO_3 + H_2O \rightarrow H_3O^+ + HCO_3^-$

1.a. Identify which of these is the conjugate base and which is the weak acid.
   b. Does the weak acid hydrolyze?
2. a. Write out the chemical equation for the hydrolysis HF.
   b. Is water acting as a Bronsted-Lowry acid or Bronsted-Lowry base?
3. a. Write out the equation for the dissociation of the salt NH_4Br.
   b. Write out the hydrolysis of the cation that is produced from the dissociation of the ammonium bromide.
   c. From what kinds of acids and bases is ammonium bromide (NH_4Br) made from? Strong acid/strong base?Strong acid/weak base?Strong base/weak acid?Weak base/weak acid?
   d. State whether salt hydrolyzes.
   e. State whether solution is acidic or basic.

Solutions

1) a. The conjugate base is the HCO_3^-. The weak acid is the H_2CO_3.
   b. Yes it hydrolyzes.

2) a. $HF + H_2O \quad H_3O^+ + F^-$
   b. Water is acting as a Bronsted-Lowry base because it is accepting a proton (H^+) from the HF.

3) a. $NH_4Br \rightarrow NH_4^+ + Br^-$
   b. Br^- does not hydrolyze; it is an ion.

$NH_4^+ + H_2O \quad H_3O^+ + NH_3^-$ <--- Hydrolysis of NH_4+

   c. HBr is a strong acid. Ammonia is a weak base. So NH_4Br is made of a strong acid and weak base.
   d. Yes it hydrolyzes.
   e. Acidic

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 in simply, the pH of the solution governs the colour of the dye. For example, phenolphthalein is an organic component and it shows a pink colour in basic medium but becomes colourless in acidic medium. Such substances are either weak adds or weak bases and when dissolved in water, their dissociated form acquires a colour different from that of the undiluted form. If the concentration of the undissociated form is more in solution we have one colour; on the other hand, if the concentration of the dissociated form is more, we see another colour. The concentration of dissociated or undissodated form depends greatly on the pH of the solution. The equilibrium of an indicator, which is a weak acid, can *be* represented by,

Hln → H^+ + In- .... (17.19}
Colour 1 Colour II

Where Hln 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 [Hln] to [In^-] in the solution. We can write the equilibrium constant expression for the reaction corresponding to eq17.19 as,

$$K=\frac{[H+][ln]}{[Hln]}$$

Or

$$\frac{[Hln]}{[ln]} = \frac{[H+]}{K} \text{.................................... (17.20)}$$

The human eye can detect the change in colour if the ratio of the two forms of indicator ranges between 0.l to10. Thus, in order to use the indicator effectively in this region, we should have a? solution *for* which H^+ ion concentration *is* very near to 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 given in Table17.1.

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	42-6.3
Bromothymol blue	Yellow	Blue	6.0 –7.6

The maximum use of indicators is found in the titration5 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 CH_3COO 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.
v) Indicators are weak acids or bases that exhibit different colours in dissociated andundissociated forms.
vi) Since different indicators change their colours in different pH regions, the use of a particular indicator for a titration, is influenced by the change of pH change near the equivalence point.

17.8 Tutor-marked assignment

1. Calculate the concentration of Cl_3CCOOH, Cl_3CCOO^-, and H^+ in a 0.25 M solution of trichloroacetic acid (K, for Cl_3CCOOH = 0.22).
Hint: Note that K is not much low.

2. Calculate the molarity of HCN solution that is 0.010% ionised at equilibrium. (**HCN = 6.0 X 10)**. Note that K is very much low.

17.9 References

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UNIT 18: SOLUBILITY AND SOLUBILITY PRODUCT

Contents

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:

- find the relationship between solubility and solubility product for different salts, and
- state its application in precipitation reactions.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

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, $CaF_2$and $BaCrO_4$ etc. We shall first derive a relationship between solubility on 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. But 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*BaCrO4* $x = 2$,y = 1
i) for $CaF_2 x = 1$, y = 2

In a saturated solution, there will be equilibrium between the sparingly soluble solid AB and its ions A and B in solution. For the sake of simplicity, we are omitting letters such as s, aq, g, in all such equilibria.

A,B → xA +yB ....(18.1)

For the present moment; we shall neglect continue charges on the cation A and *x*-charges on the anion B.

18.4 Solubility product

Solubility product constants are used to describe saturated solutions of ionic compounds of relatively low solubility. A saturated solution is in a state of dynamic equilibrium between the dissolved, dissociated, ionic compound and the undissolved solid.

M x A y (s) --> x M y+ (aq) + y A x- (aq)

The general equilibrium constant for such processes can be written as:

K c = [M y+] x [A x-]y

Since the equilibrium constant refers to the product of the concentration of the ions that are present in a saturated solution of an ionic compound, it is given the name solubility product constant, and given the symbol Ksp. Solubility product constants can be calculated, and used in a variety of applications.

Calculating Ksp's from Solubility Data

In order to calculate the K sp for an ionic compound you need the equation for the dissolving process so the equilibrium expression can be written. You also need the concentrations of each ion expressed in terms of molarity, or moles per liter, or the means to obtain these values.

Example: Calculate the solubility product constant for lead(II) chloride, if 50.0 mL of a saturated solution of lead(II) chloride was found to contain 0.2207 g of lead(II) chloride dissolved in it.

First, write the equation for the dissolving of lead(II) chloride and the equilibrium expression for the dissolving process.

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

Ksp = $[Pb^{2+}][Cl^-]2$

Second, convert the amount of dissolved lead(II) chloride into moles per liter.

(0.2207 g $PbCl_2$)(1/50.0 mL solution)(1000 mL/1 L)(1 mol $PbCl_2$/278.1 g $PbCl_2$) = 0.0159 M $PbCl_2$

Third, create a table.

	PbCl 2 (s)	**Pb 2+ (aq)**	**Cl - (aq)**
Initial Concentration	All solid	0	0
Change in Concentration	- 0.0159 M (dissolves)	+ 0.0159 M	+ 0.0318 M
Equilibrium Concentration	Less solid	0.0159 M	0.0318 M

Fourth, substitute the equilibrium concentrations into the equilibrium expression and solve for K sp.

K sp = [0.0159][0.0318] 2 = 1.61 x 10 -5

Calculating the Solubility of an Ionic Compound in Pure Water from its K sp

Example: Estimate the solubility of Ag 2CrO 4 in pure water if the solubility product constant for silver chromate is 1.1 x 10^{-12}.

Write the equation and the equilibrium expression.

Ag 2 CrO 4(s) --> 2 Ag + (aq) + CrO 42- (aq)

K sp = [Ag+]2 [CrO_4^{2-}]

Make a chart.Let "x" be the number of moles of silver chromate that dissolves in every liter of solution (its solubility).

	Ag_2CrO_4(s)	**Ag^+(aq)**	**CrO_4^{2-}(aq)**
Initial Concentration	All solid	0	0
Change in Concentration	- x dissolves	+2x	+ x
Equilibrium Concentration	Less solid	2x	x

Substitute the equilibrium amounts and the K sp into the equilibrium expression and solve for x.

1.1 x 10^{-12} = [2x] 2 [x]

x = 6.50 x 10^{-5} M

Calculating the Solubility of an Ionic Compound in a Solution that Contains a Common Ion

The solubility of an ionic compound decreases in the presence of a common ion. A common ion is any ion in the solution that is common to the ionic compound being dissolved. For example, the chloride ion in a sodium chloride solution is common to the chloride in lead (II) chloride. The presence of a common ion must be taken into account when determining the solubility of an ionic compound. To do this, simply use the concentration of the common ion as the initial concentration.

Example: Estimate the solubility of barium sulfate in a 0.020 M sodium sulfate solution. The solubility product constant for barium sulfate is 1.1 x 10^{-10}.

Write the equation and the equilibrium expression for the dissolving of barium sulfate.

$BaSO_4(s) \text{ --> } Ba^{2+} (aq) + SO_4^{2-}(aq)$

$Ksp = [Ba^{2+}][SO_4^{2-}]$

Make a chart.

Let "x" represent the barium sulfate that dissolves in the sodium sulfate solution expressed in moles per liter.

	$BaSO_4(s)$	**Ba^{2+} (aq)**	**SO_4^{2-} (aq)**
Initial Concentration	All solid	0	0.020 M (from Na_2SO_4)
Change in Concentration	- x dissolves	+x	+ x
Equilibrium Concentration	Less solid	x	0.020 M + x

Substitute into the equilibrium expression and solve for x. We will make the assumption that since x is going to be very small (the solubility is reduced in the presence of a common ion), the term "0.020 + x" is the same as "0.020." (You can leave x in the term and use the quadratic equation or the method of successive approximations to solve for x, but it will not improve the significance of your answer.)

$1.1 \times 10^{-10} = [x][0.020 + x] = [x][0.020]$

$x = 5.5 \times 10^{-9}$ M

Determining Whether a Precipitate will, or will not Form When Two Solutions are Combined

When two electrolytic solutions are combined, a precipitate may, or may not form. In order to determine whether or not a precipitate will form or not, one must examine two factors. First, determine the possible combinations of ions that could result when the two solutions are combined to see if any of them are deemed "insoluble" base on solubility tables (K sp tables will also do). Second, determine if the concentrations of the ions are great enough so that the reaction quotient Q exceeds the K sp value. One important factor to remember is there is a dilution of all species present and must be taken into account.

Example: 25.0 mL of 0.0020 M potassium chromate are mixed with 75.0 mL of 0.000125 M lead(II) nitrate. Will a precipitate of lead(II) chromate form. Ksp of lead(II) chromate is 1.8 x 10-14 .

First, determine the overall and the net-ionic equations for the reaction that occurs when the two soltutions are mixed.

$K_2CrO_4(aq) + Pb(NO_3)_2(aq) \text{-->} 2KNO_3(aq) + PbCrO_4\ (s)$

$Pb^{2+}\ (aq) + CrO_4^{2-}\ (aq) \text{-->} PbCrO_4\ (s)$

The latter reaction can be written in terms of K sp as:

$PbCrO_4(s) \text{-->} Pb^{2+}(aq) + CrO_4^{2-}\ (aq)$

$Ksp = [Pb^{2+}][CrO_4^{2-}]$

Using the dilution equation, $C_1V_1= C_2V_2$, determine the initial concentration of each species once mixed (before any reaction takes place).

$(0.0020\ M\ K_2CrO_4)(25.0\ mL) = (C_2)(100.0\ mL)$

C_2 for $K_2CrO_4 = 0.00050\ M$

Similar calculation for the lead(II) nitrate yields:

C_2 for $Pb(NO_3)_2 = 0.0000938\ M$

Using the initial concentrations, calculate the reaction quotient Q, and compare to the value of the equilibrium constant, Ksp .

$Q = (0.0000938\ M\ Pb^{2+})\ (0.00050\ M\ CrO_4^{2-}) = 4.69 \times 10^{-8}$

Q is greater than Ksp so a precipitate of lead(II) chromate will form.

*Exercise*18.1
At 298K, the solubility product of $Bi(OH)_3$ is 4.11 x10^3, calculate its solubility.

18.5 Common-ton effect and the solubiiity of a sparingly soluble salt

We have already seen the solubility of some salts in pure water, 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^+, CI^- and NO_3^- ions present. The CI^- 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

Ksp = C[Cl-]

$[Cl^-] = \frac{1.88 \times 10^{10}}{C}$ .... (18.11)

The chloride ion concentration must be equal to the number of moles of AgCl dissolved in $1dm^3$ of solution (or equal to its solubility).Hence,

$S = \frac{1.88 \times 10^{10}}{C}$ .... (18.11)

Example 18.2
Find the solubility of AgCl in 1 M AgNO, solution and compare with its solubility in water.

Solution
solubility of AgCl(s) in presence of 1M AgN03 is1.88 x 10^{-10} M. You can see that, as compared to the solubility of times less. AgCl in water (1.37 x 10"6 M), its solubility in presence of 1M $AgN0_3$ is l0S

Example 18.3
Find the solubility of CaF_2in .
i) water ii) 0.10 M NaF iii) 0.10 M $Ca(NO)_3$

Solution
(K = $4.0x10^{-11}$)
i) Let us assume that the solubility of CaF_2 in water is S. Since 1mole CaF_2can give 1mole of Ca^{2+} ion and two moles of F^- ion in solution, we can write the concentrations of Ca^{2+} and F^- ions as follows:
$[Ca^{2+}] = S$ and $[F^-] = 22$

Hence,
$Ksp = [Ca^{2+}][F^-]$

$4.0 X 10^{-11} = S (2S)^2 =3S^3$

$\therefore S = (1.0 x 10^{-11})^3= (10 x 10^{-22})^3 = 2.2 x 104M$ (approximated to two places)

Hence the solubility of CaF_2 in pure water is 2.2 x 10^{-4} M.

ii) In 0.10 M NaF
In the presence of NaF, the solubility of $[Ca^2]$ = Total [F-)= [F-) from CaF_2 +[F-) from NaF.

Since [F$^-$] from NaF is much larger than [F-] supplied by CaF$_2$ the total fluoride ion concentration is equal to the NaF concentration which is 0.10 M. Substituting the proper values we get,

$$[Ca^{2}] = \frac{4.0 \text{ x } 10^{-11}}{(0.10)} = 4.0 \text{ X } 10^{-9} \text{ M}$$

Hence, solubility of CaF$_2$ in 0.10 MNaF is 4.0 x 10^{-9}M.
iii) In 0.10 M Ca(NO)$_2$
First we have to find [F$^-$]

[F$^-$] =.L or lFlz: -=:.L
J (Ca^{1+}] [Ca^{1+}]

Substituting the given values, we. get,

$$[F^-]= \frac{4.0 \text{ x } 10^{-11}}{0.10}$$
$$= 2.0 \text{ x } 10^{-5} \text{ M}$$

Since each mole of CaF$_2$ produces 2 moles of F$^-$ ion in solution, the solubility of CaF$_2$ will be equal to one half the concentration of the fluoride ion in solution or 1.0 x 10^{-5} M. When dealing with problems of this nature, two important points must be remembered. First, if the solubility of a salt like CaF$_2$*1* is given as S, then the concentration of Ca$^+$ ions would be S, but the concentration of fluoride ions would be 25. This is so because each mole of CaF2'.which goes in solution, gives 1mole of Ca 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 CaF2 can be expressed as,

[F-] = 2 [Ca^{2+}]

but not, [Ca^{2+}] = 2[F$^-$]

No doubt when 1mole 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 x (number of moles of Ca^{2+}) = [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 concentrations regarding the solubility of a sparingly soluble salt.
i) In a saturated solution Ka = 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

Ka> ionic product

ii) When the concentration of eiGeriun 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 precipitate. In other words, precipitation will occur when ionic product > KIP

Let us see the applications of these generalizations with the help of a few examples.

Example 18.4
Show that it is impossible to prepare a solution of chromium hydroxide, Cr(OH)y having 0.1 M concentration of Cr^{l+} ions at pH= 7; KIP for $Cr(OH)_3 = 6.3 \times 10^{-31}$

Solution
When the ionic product of Cr(OH)3 is equal to its solubility product, the solution will be saturated.
This will indicate the state of maximum concentration of Cr^{l+} ions in solution.
Thus in a saturated solution, Solubility product= ionic product= $[Cr^{l+}][OH^-]$
Substituting the given values we get,

$6.3 \times 10^{-31} = [Cr^{l+}]\ (1.0 \times 10^{-1})^3$

Therefore, $[Cr^{3+}] = \dfrac{6.3 \text{ X } 10^{-31}}{1.0 \text{ X } 10^{-21}}$ M

(since at neutral pH, $[OH^-] = 1.0 \times 10^{-7}$ M)
Hence, at pH= 7, the maximum concentration of Cr^{l+} ions in solution would be 6.3 x 10-31 M and itis impossible to prepare a solution having 0.1 M concentration of Cr^{l+} 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 Kop for CaF_2 is 4.0 x to-n and the solubility is 2.2 x 10-4M.The fluoride ions present in the solution through the dissolution of CaF_2 could further react with water, though to a small extent. 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_2will 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^{1+} 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 Ksp is very low. Thus, the addition of a calculate the mount of chloride ion will cause the ionic product of the sparingly soluble AgCl exceed its Ksp value; hence AgCl is precipitated. Under this condition, $NiC1_2$ and CuCl remain in solution since their K values are larger than their ionic product values. The precipitated AgCl can be separated 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? Can be represented as2HS → $2H^+ + 2S^-$
The equilibrium constant for this section is 1.3×10^{-21} and the concentration of H in a saturated solution is 0.1M. Substituting these values in the equilibrium constant expression, we get,

$1.3 \text{ X } 10\text{-}21 = \underline{2[H^{+}]\ 2[S^{-}]}$
0.1
or $[S^{-}] = \underline{1.3 \text{ X } 10^{-22}}$
[H]

Thus the sulphide ion concentration can be controlled by the adjustment of the pH of the solution.

The sulphides, which have low Ksp values, can be precipitated with rather small concentrations of sulphide ions in solution. This is achieved if the solution is acidic. The metallic sulphide, which have higher Ksp values, need higher concentration of sulphide ions for their precipitation and a higher pH (pH *>7) of t*he solution is to be maintained.

As an example, let us consider a solution of pH= 3, which contain 0.010M la!ch of Mn^{2+}andCu^{2+} ions at pH= 3. Let us pass H25 through the solution such that. [H25] = 0.1 M. At this pH, the concentration of sulphide ion would be, ·

$[S^{-}] = \underline{1.3 \text{ x } 10^{-22}}$
$1.0\ \underline{\text{x}}\ 10^{6}$f
$=13 \text{ x } 10^{-16}$ (since $[H^{+}] = 1.3 \text{ x } 10^{-6}$ at Dli. =3)

And therefore
$[Cu^{2+}][S^{2-}] = \underline{(1\ 0 \text{ x JC}^{-2})(1.3 \text{ x } 10^{-16})}$
$1.3 \text{ X } 10^{15}$
The KIP for CuS = $6.3 \text{ x I}0^{-36}$ since, we find that the ionic product (LP.) > K, Cu; will precipitate from the solution.

Exercise 18.2
5cm^{3} of a saturated solution of sodium chloride at 30^{o}C gave on careful evaporation 1.95g of solid salt. What is solubility of sodium chloride at 30^{o}C.

18.6 Conclusion

In this unit, we have examined the concepts of solubility, solubility products, common-ion effect 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:
i) 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

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UNIT 19: FARADAY'S LAWS OF ELECTROLYSIS

Contents

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:

- describe the nature of ions in solution;
- list the possible interactions among the ions; and
- state Faraday's laws of electrolysis.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

19.3 Interactions in solutions

Now, there is no doubt that water is the most commonly used solvent. Thus 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

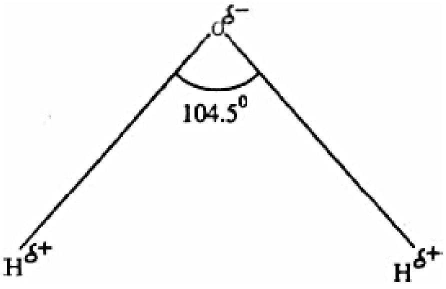

Fig.19.1 Structure of a water mofecule

It is a bent molecule with H-0-H bond angle being approximately 104.5°. It shows polar character due to a large difference in the electro negativities of oxygen and hydrogen atoms. It also 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 interaction, there is a net force of attraction between the molecules. In addition, there will be hydrogen bonds present between oxy en 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 m 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 dipo1es lie along the field direction in order to minimize the energy of the system. The negative 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 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 particular ion. 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 *sovolysis*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. 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 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 salvation number of an ion is defined as the mean number of solvent molecules in the primary salvation 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 are 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.

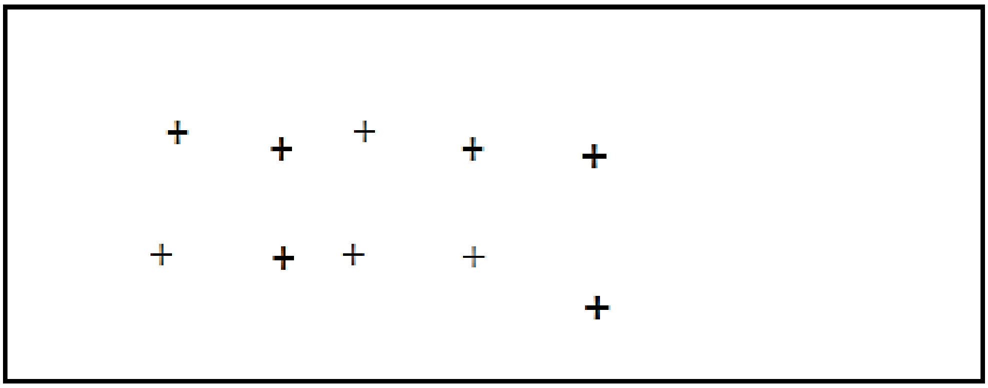

Fig.19.2 Atmosphere of oppositely charged ions around each cation and anion

The measure of an electrostatic interaction is given by a tern 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,

where mi is the molar concentration of ion's in solution and Zi is the charge associated with the same ion. In the case of a dilute solution (of density, d), its molarity (Ci) is related to its molality, Mi as in Equation 19.2.

Ci= Mid…………………….. ....19.2

Substituting the value of Equation 19.2 into Equation 19.1we get.

$$I \approx \frac{1}{2} d \sum_i c_i Z_i^2 \qquad \text{........19.3}$$

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 anion. The radii of ion-atmosphere around sodium ion in 1.0 x 10"2 M, 1.0 x 10"4 M and 1.0 x 1Q-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 anode are known ca*tions*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 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:

At the anode: $Cu \rightarrow Cu^{2+} + 2e^-$ (oxidation)
At the cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ (.reduction)

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 fat-time t, then the ·quantity of electric current (Q) passed through is given by the product of current and time.

$Q = It$ .... (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 *voltmeter* (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.

$Ag^+ + e^- \rightarrow Ag$ ·····………………………..·····(19.5)

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 weight (w) of a product formed at an electrode is directly proportional to the quantity of electricity (q)* used *i.e.* .

W α q ……………………………………… (19.6)

2. *The masses of different products (SIJY* W,*-and W for two substances l 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 is 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 $1.602 \ x \ 10^{-19}$C. Hence, the charge on one mode of electrons would be $1.602X \ 10^{-19}X \ \ 6.022X10^{23}$ C or 96,489 C
It is usual to approximate one faraday as being 96500C.
Consider an electrode reaction;
The quantity of electricity required for the deposition of 1mole 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 1mole atoms of an element X. Therefore, for the deposition of M kg (or 1mole) 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 Mkg (or 1 mole) of an element.
Hence, q coulomb of Electricity deposits $\frac{Mq}{n.96500}$ kg of the element

$$= \frac{Mq}{n.96500}\textbf{kg} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \textbf{(19.7)}$$

Substitution the value of q from Equation 19.4 into Equation 19.7 we get.
M.I.t

$$w= \frac{MIT}{n.96500} \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots .... (19.8)$$

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 $5.0 \ x \ 10^{-3}$ 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 kg mol^{-1}

Solution

$Ag^+ + e \rightarrow Ag$

Substituting the values in Equation 19.8 we get

$$= \frac{0.1079 \text{ kg mol-l X } 5.0 \text{ X } 10\text{-}3 \text{ A X } (100 \text{ X } 60) \text{ S}}{1 \text{ x } 96500 \text{ C mol-1}}$$

(n =1, since 1 mole of Ag^+ ions needs 1mole of electrons)

$= 0.4 \text{ X } 10^{-5}g$

Tutor marked Assignment

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: $Mg^{2+} + 2e^- \rightarrow Mg$

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 interactions 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 summarized 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 salvation shell;
iv) faraday is the quantity of electricity carried by 1 mole electrons.

19.7 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 NT210.

UNIT 20: ELECTROLYTIC CONDUCTANCE

Contents

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 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:

- define electrolytic conductance;
- define specific and molar conductance of a solution; and
- describe the dependence of conductance on concentration.

How to Study this Unit

1. You are expected to read carefully through this unit at least twice before attempting to answer the self assessment questions or the tutor marked assignments
2. Do not look at the solution given at the end of the unit until you are satisfied that you have done your best to get all the answers
3. Share your challenges with your mates, facilitators and by consulting other relevant materials, particularly, the internet.
4. Note that if you follow these instructions you will feel self-fulfilled that you have achieved the aim of studying this unit. This should stimulate you to do better.

20.3 Electrolytic conductance

The Ohm s law can he 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;

$$R\ \alpha\ \frac{L}{A}$$

$$R = P\frac{L}{A}$$

………… ……. ‥…….(20.1)

The proportionality constant, p, is known as its *electrical resistivity*. The unit of resistance is ohm (W) while the unit of resistivity is ohm meter (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 = 1/k. 1/A

∴ k= 1/AR .... (20.2)

Since the resistance is expressed in ohm, the reciprocal of ohm (1/ ,)was earlier used as the unit for conductance. However, in51system, the unit for conductance is Siemens and it's given the symbol S. Hence, the unit for conductivity will be S m-1 (1S =1n^{-1}).

For the measurement of electrical resistance (R) of a sample, we use a set-up known as Wheatstone bridge. It consists of two wires R, of known resistance values, and a third resistance, R,, the value of which can be adjusted. These-are all connected to a battery source, E, as shown in Fig. 20.1. R, is adjusted until points *a* and*b are* exactly at the same potential. there will be no deflection in the ammeter.

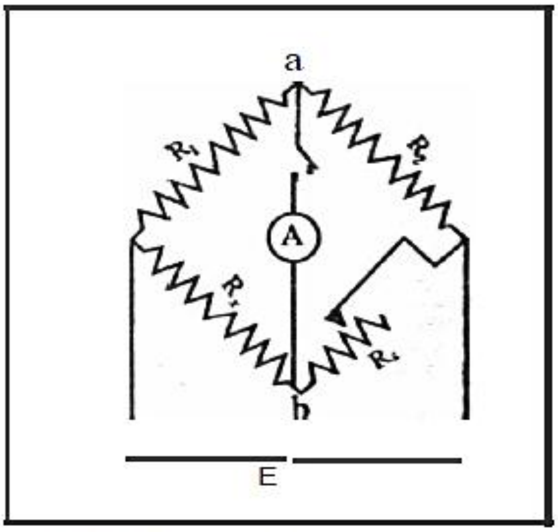

Fig. 20.1 Wheatstone bridge

Under these conditions, the following relation will hold good:

Rt = 1/F
Rt

Finding the resistance of a solution (Rt, we makes light 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, Ri=R...........(20.4)
The relationship between specific conductance and resistance is given as

k=1/*p*=C/R

i.e. k= keen 1/R

where keen is the cell constant representing the ratio 1/A; it is a constant as far as the same cell is used for measurements. Since the conductiveness of certain standard solution have been carefully measured, we could use such a solution in, 1 cell and measure its resistance. Thus knowing K and 1t 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 concentrations.** Use 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 W at 298 K. When filled with a 0.050MAgN03 solution, it has a resistance of 94.2 W. The specific conductance of 0.020 MKVl is 0.2768S m^{-1}. What is the specific conductance of 0.050 AgN0 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, 1M which is the conductivity per unit molar concentration and is given by the expression:

Am = K/C .... (20.6)

where C is in $molm^{-3}$ units. The molar conductivity is usually expressed in Sm^2mol^{-1} or Scm^2mol^{-1}. It may be remembered that, Sm^2mol^{-1}= 10000 Scm^2mol^{-1}.
It might be thought that L, should be a quantity independent of concentration. However, it is an experimental fact that lm for NaCl, KBr, etc. in aqueous solution does vary with concentration.

This is due to the ionic interactions, which change with concentration. This, m tum, affects the conductivity, k. 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 inter ionic 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 $2.00x10^{-2}$M KCl is 195.96 W and that of $2.50x10^{-3}$ M SO_4 is 775.19 W. The specific conductance (k) of 2.00 x 10^{-2} M KCl at 2bK is 0.2768 Sm^{-1}. Calculate the molar conductivity of SO_4 solution.

Solution
First, we have to find out the cell constant. Using the equation K..,11=k x R.
Substituting the given values for 2.0 x 10-2 MKCI, we get,
K_{cell}= 0.2768 Sm^{-1}X 195.96 W
= 54.24 m-1
Next, we have to calculate the k of K_2SO_4 solution.

k = $\frac{K_{cell}}{R}$ = 54.24 m^{-1}/775.19 n

= 0.06997S m-1

The concentration of 504 is given in morality. Hence, its concentration in $molm^{-3}$ units may be obtained by

C = 1000 x 2.50 x 10^{-3}mol m^{-3}
= 2.50 mol m^{-3}

We can calculate Λm.... using

Λm = K/C = (0.06997/2.50) m^2mol^{-1}

= 0.0285m^2mol^{-1}

20.5 Molar conductance at infinite dilution, Λm

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 20.1Molar conductance at 298 K

	Concentration		Λm/Sm^2mol^{-1}	
M	HClKCl	CHCOOH	$AgNO_3$	
1.000	0.3328	0.11119	-	-
0.100	0.03913	0.01289	0.00052	0.01110
0.010	0.04120	0.04120	0.00162	0.01210
0.001	0.04214	0.01469	0.04860	0.01305
0.0005	0.04227	0.01478	0.01350	0.01314

Moreover, as a consequence of inter ionic interactions; every ion in solution has a diffused ionic atmosphere of opposite charges. The inter ionic focuses 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 non conductance extrapolated to zero concentration should be independent of inter ionic interactions. This is called *limiting molar conductivity* or *molar conductance at infinite* *dilution* and given the symbols Λm. Kohlrausch gave an empirical formula on the basis of his experimental results, which connects the molar conductivities with concentration, for strong electrolytes:

$$\Lambda m = \Lambda m^o \ \ K\sqrt{c}$$

Where Λm 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 KCI, NaOH, NaCl, etc. have the same value of A whereas BaCl, CuSO, 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

$$\Lambda_m^o = v_+\lambda_+ + v_-\lambda_-$$

Where v+ and v- are numbers of cations and anions per formula unit, respectively and Λm^o 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 Λm^o values. These values can be explained if we assume that Λm^o 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 CI- and NO_3^-.

Table 20.2: Λm values of some electrolytes

Electrolytes	$\Lambda m/Sm^2mol^{-1}$	Electrolytes	$\Lambda m/Sm^2mol^{-1}$	Electrolytes	$\Lambda m/Sm^2mol^{-1}$
KO	**0.01498**	KOH	0.02715	KNO_3	0.01450
NaO0.01264		NaOH0.02481		NaNO0.01216 3	
Difference	**0.00234**		0.00234		0.00234
KCI	**0.01498**	KNO_3	0.01450	KCI04	0.01400
LiO0.01150		$LiNO_3$	0.01101	LiCIO0.01051	
Difference	**0.00348**		0.00349		0.00349
LiCl0.01150		KCl	0.01498	NaCl0.00349	
$LiNO_3$*0.01101*		$KNO_3$0.01450		NaNO0.01216	
Difference	**0.00049**		0.00048		0.00048

Ostwald's dilution law

Wilhelm Ostwald's **dilution law** is a relationship between the dissociation constant K_d and the degree of dissociation α of a weak electrolyte. The law takes the form

$$K_d = \frac{[A^+][B^-]}{[AB]} = \frac{\alpha^2}{1-\alpha} \cdot c_0$$

Where the square brackets denote concentration, and c_0 is the total concentration of electrolyte.

Concerning conductivity, this results in the following relation:

$$K_c = \frac{\Lambda_c^2}{(\Lambda_0 - \Lambda_c)\Lambda_0} \cdot c$$

Derivation

Consider a binary electrolyte AB which dissociates reversibly into A^+ and B^- ions. Ostwald noted that the law of mass action can be applied to such systems as dissociating electrolytes. The equilibrium state is represented by the equation:

$$AB \rightleftharpoons A^+ + B^-$$

If α is the fraction of dissociated electrolyte, then αc_0 is the concentration of each ionic species. $(1 - \alpha)$ must, therefore be the fraction of *undissociated* electrolyte, and $(1 - \alpha)c_0$ the concentration of same. The dissociation constant may therefore be given as

$$K_d = \frac{[A^+][B^-]}{[AB]} = \frac{(\alpha c_0)(\alpha c_0)}{(1-\alpha)c_0} = \frac{\alpha^2}{1-\alpha} \cdot c_0$$

For very weak electrolytes $\alpha \ll 1$, implying that $(1 - \alpha) \approx 1$.

$$K_d = \frac{\alpha^2}{1-\alpha} \cdot c_0 \approx \alpha^2 c_0$$

This gives the following results;

$$\alpha = \sqrt{\frac{K_d}{c_0}}$$

Thus, degree of dissociation of a weak electrolyte is proportional to the inverse square root of the concentration, or the square root of the dilution. The concentration of any one ionic species is given by the root of the product of the dissociation constant and the concentration of the electrolyte.

$$[A^+] = [B^-] = \alpha c_0 = \sqrt{K_d c_0}$$

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; and
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 ask/C.

20.9 References

IGNOU (1997) *Chemical Equilibria and Electrolysis-Physical Chemistry 4CHE -04.*

Sharma, K. L. and K. Sharma, (1997), *A Textbook of Physical Chemistry, 3rd Revised Edition,* New Delhi, Vikas Publishing House.