

NATIONAL OPEN UNIVERSITY OF NIGERIA

COURSE CODE: CHM 301

COURSE TITLE: PHYSICAL CHEMISTRY III



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CHM 301 – PHYSICAL CHEMISTRY III (3 Units)

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Introduction

The physical chemistry course (CHM 301) unlike the other aspect of

Chemistry deals with physical measurable constants of a reaction system. In this course we will look at the driving force upon which reactions proceed.

Many of the reactions you are familiar with are the same phase with the media, mostly liquid. Some reactions take place on different media, for example on solid surface. Their mode of actions and theories developed in explaining them will be discussed.

What You will Learn in this Course

This course CHM 301, physical chemistry III, is a core course for students of the Bachelor of Science degree in chemistry.

The course is made of four units. The course starts with the definition of terminologies that will be encountered in the course of this course and then goes on into the discussions on the laws of thermodynamics. A study of the chemical equilibrium of reactions, as it relates to properties such as fugacity, chemical potential and phase rule, are explained.

Course Aims

This course is aimed at providing the students with the knowledge of simple concepts and theories of thermodynamic, chemical potential and phase rule of degree of freedom of chemical system.

Course Objectives

After studying this course you will be able to

- define and explain all the laws of thermodynamics
- relates fugacity to chemical potentials of an equilibrium system
- understand the concept of colligative properties of solutes
- explain the degree of freedom for chemical components in a reaction system.

Working through this Course

In order to be able to successfully complete this course, you are required to carefully study each unit along with recommended textbooks and other materials that may be provided by the National Open University. You may also need to exploit other e-reading such as internet for further useful information on the course.

Each unit contains self assessment exercise and at certain points in the course you would be required to submit assignment for grading and recording purposes. You are also to participate in the final examination at the end of the course. It is recommended that you devote an abundant time for reading and comprehension. It is highly necessary that you avail yourselves the opportunity of attending the tutorial sessions where you will be able to compare your understanding of the course contents with your colleagues.

The Course Materials

The main components of this course are:

1. The Course Guide
2. Study Units
3. Self Assessment Exercise
4. Tutor Marked Assignments
5. Further Readings

Study Units

Module 1 Thermodynamics, Types of process, Heat change and Enthalpy of Reactions

Unit 1	Law of Thermodynamic
Unit 2	Types of processes
Unit 3	Heat Change
Unit 4	Enthalpies of Reactions

Module 2 Reversible and Irreversible Reactions, Entropy of Change

Unit 1	Reversible, Irreversible and Cyclic Process
Unit 2	Entropy of Change
Unit 3	Entropy of Mixing

Module 3 Spontaneous and Non-spontaneous Processes,

Unit 1	Changes in ΔA and ΔG
Unit 2	Maxwell, Gibbs-Helmholtz and Calusius-Clapeyron Equation
Unit 3	Criteria for Spontaneity

In Module 1 we define the various thermodynamics concepts and explain the Zeroth and first laws of thermodynamic, Module 2 deals with the second law of thermodynamic and the principle of Carnot engine. The third law of thermodynamic system was also discussed. Module 3 discusses the equilibrium system and fugacity as it relates to chemical potential of ideal system, Colligative properties of solute and degree of freedom of a chemical substance

Each of the unit is made up of one or two weeks' work consisting of introduction, objectives, reading materials, self assessment exercise, conclusion, summary and Tutor marked Assignment (TMA), suggestion for further reading and source materials. The unit directs you to work on exercises related to the required reading. Together with the TMAs, they are meant to test your basic understanding

and comprehension of the course materials, which is a prerequisite for the achieving the stated aims and objectives of the course.

Presentation Schedule

The course materials have important dates for the timely completion and submission of your TMAs and tutorial lessons. You are vividly reminded of the need to promptly submit answers to tutorials and assignments as at when due.

Assessment

The course assessment consists of three aspects namely the self assessment exercise, the tutor marked assignment and the written examination/end of course examination.

It is essential that you attempt all exercises and assignments and submit appropriately to the course facilitator for grading. Let your answers be concise and as accurate as possible. You are expected to consult other material course in addition to your course materials in order to be able to present accurate answers to the questions. Kindly note that the tutor marked assignment covers only 30% of the total marked for the course.

Tutor Marked Assignment (TMA)

The TMA is a continuous assessment component of your course. It accounts for 30% of the total score. You will be given a number of TMAs to answer. Nearly all of them must be answered before you are allowed to sit for the end of the course examination. The TMAs will be given to you by your facilitator and returned after you have done the assignment. Note that these assignments are already contained in the assignment file to be given to you. You may do yourself good by reading and researching well before you attempt to answer the questions.

You are warned to submit these assignments to the facilitator at the stipulated time as could be seen in the assignment file. However, if for any reason you are unable to meet the deadline, you are highly required to intimate the facilitator of your problem before the due date and seek for an extension which may be granted or not.

Final Examination and Grading

The end of the course examination for Physical Chemistry III will be for about 3 hours with maximum score value of 70% of the total course work. The examination will be made up of questions which normally reflect on what you have learnt in the course materials/further reading. In addition, they may be

prototype of the self assessment exercises and the TMAs. The end of the course examination is intended to cover information from all parts of the course.

Avail yourself the opportunity of the time-lag between the completion of the course content and the beginning of the examination to revise as much as possible the whole course materials, the exercise and assignments.

Course Marking Scheme

Assignment	Marks
Assignments	The best three marks of the submitted assignments count at 10% each i.e. 30% of the course marks
End of course Examination	70% of overall course marks
Total	100% of the course materials

Facilitators/Tutors and Tutorials

There are few hours of tutorials provided in support of this course. You will be informed appropriately of the name, telephone number and e-mail address of your facilitator. In addition, the time, dates and location of the tutorial lessons will be communicated beforehand. You are required to mail or submit your Tutor Marked Assignment to your facilitator, at least two working days, before the schedule date. Note that all the submitted assignments will be duly marked by the facilitator with further comments that can improve on your performances. The facilitator will from time to time takes track record of your comprehension, progress and difficulty in the course.

Be kind enough to attend tutorial lessons at the fixed appointment. It is probably the only avenue to meet face to face and discuss with you facilitator. There, you will be able to ask question or seek clarification on seemingly grey area in the course material. You may as well have prepared questions and comments for your facilitator before the due date. An active participation during the tutorial lessons will be an added advantage to boost confidence level.

In case any of the situations listed below arises, do not hesitate to intimate your facilitator using his or her telephone number or via e-mail address;

- . You do not understand any part of the study or the assigned readings
- . You are not skill enough to attempt the self assessment exercise
- . The questions in the TMAs are not clearly understood

Accept my best wishes in the course and I do hope that you benefit considerably from its application.

Module 1: Thermodynamics, Types of process, Heat change and Enthalpy of Reactions

Unit 1 Law of Thermodynamic

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Thermodynamic Terminology
- 4.0 State variables
- 5.0 The Zeroth Law of Thermodynamics
- 6.0 Extensive and Intensive Variables
- 7.0 Further Reading

1.0 INTRODUCTION

In this unit, we shall introduce you to some of the terms used in thermodynamics. The definitions of work, heat and heat capacity will be stated. The first law of thermodynamics will be explained with particular reference to isothermal and, adiabatic processes. The calculation of work, internal energy change and heat absorbed or evolved in reversible and irreversible processes will be outlined. The significance of enthalpy and enthalpy change of a system will be stated. Towards the end of this unit, you will study the importance of Joule - Thomson effect. In the next unit, we shall study the second law of thermodynamics.

2.0 Objectives

After studying this unit, you should be able to

- explain the terms - system, surroundings and thermodynamic variables,
- state the zeroth law of thermodynamics,
- differentiate between extensive and intensive variables,

3.0. THERMODYNAMIC 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.

System

Any part of the universe which is under study is called a system. It can be as simple as a gas contained in a closed vessel or as complicated as a rocket shooting towards moon. A system may be homogeneous or heterogeneous depending on its contents and conditions. A system is homogeneous 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 than two phases separated by mechanical boundaries.

Surroundings

The rest of the universe around the system is considered 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 moveable) 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 system

Isolated system is one which exchanges neither energy nor matter with its surroundings. There is no perfectly isolated system; but, a system which 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 thus approximates to an isolated system.

(ii) Closed system

Closed system allows 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) Open system

Open system allows exchange of both matter and energy with its surroundings. This is the most common type of system encountered in our daily life. All living things are examples of open system since these are capable of freely exchanging energy and matter with their

surroundings. Reaction vessels with permeable membranes are examples of open system.

4.0 State Variables

A thermodynamic system has to be macroscopic (i.e. of sufficiently large size); this facilitates measurement of its properties such as pressure, volume, temperature, composition and density. Such properties are therefore called macroscopic or bulk s. These are also called state or thermodynamic variables. These do not depend on the past history of the system. A state variable which depends on other variables is called a dependent variable; others, on which it is dependent, are called independent variables.

For example, an ideal gas equation is written as

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

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

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

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

State of a System

The state of a system is defined when the state variables have definite values. It is necessary to specify all the state variables since these are interdependent. For exam if the system is an ideal gas, then its pressure, volume, temperature, and the amount of the gas (number of moles) are related by the gas equation. Thus, if we specify three of these; the fourth variable is automatically fixed. Similarly many of its other properties like density, heat capacity etc. is also fixed although through more complicated relations.

Self Assessment Exercise 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.

5.0 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 these are in thermal contact, changes take place in the properties of both the systems, but, eventually a state is reached when there is no further change in any of the properties of the systems. This is the state of thermal equilibrium. Both the systems are at the same temperature. In order to find whether two systems are at the same temperature, the two can be brought into thermal contact; then the changes in the properties of either of these are to be observed. If no change occurs, they are at the same temperature.

The zeroth law of thermodynamics states that if a system A is in thermal equilibrium with system C and, system B is also in thermal equilibrium with C, then A and B are also in thermal equilibrium with each other. This is an experimental fact. This may be illustrated by assuming that systems A and B are two vessels containing different liquids, and C is an ordinary mercury thermometer. If A is in thermal equilibrium with C, then 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 temperature; the temperature scale will be discussed in unit 8.

The zeroth law of thermodynamics can be stated as follows:

Two objects that are in thermal equilibrium with a third object are in thermal equilibrium with each other.

6.0 EXTENSIVE AND INTENSIVE VARIABLES

We have defined homogeneous and heterogeneous systems in Sec 1.2. Let us now discuss the difference between the two with respect to the value of some variables. In this connection, we must first define extensive and intensive variables.

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

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

$$\begin{aligned} \text{Similarly, the volume 0.100 kg of water} &= \frac{\text{Mass of water}}{\text{Density of water}} \\ &= \frac{0.100 \text{ kg}}{1.00 \times 10^3 \text{ kgm}^{-3}} = 1.00 \times 10^{-4} \text{m}^3 \\ \text{Total volume} &= (1.09 + 1.00) 10^{-4} \text{m}^3 \\ &= 2.09 \times 10^{-4} \end{aligned}$$

An intensive property of a phase is independent of the amount of the phase. Thus refractive index, density and pressure are intensive properties. However if a system consists of several phase's, 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 273.15 K. For thermal equilibrium, the intensive property, temperature, has to be same throughout the system. Otherwise heat will flow from one point of the system to another. Similarly, for mechanical equilibrium, the intensive property, pressure, has to be the same throughout the system. An extensive property when divided by mass or molar mass of the system becomes an intensive property.

Self Assessment Exercise 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.

7.0. FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 1: Thermodynamics, Types of process, Heat change and Enthalpy of Reactions

Unit 2: Types of processes

1.0 Introduction

2.0 Objectives

3.0 Definition

4.0 Types of Processes

Work, Heat and Heat Capacity

5.0 The First Law of Thermodynamics

6.0 Isothermal Expansion

1.0. Introduction

When the state of a system changes, it is said to have undergone a process. Thus a process means change in at least one of the state variables of the system. The process may be accompanied by an exchange of matter and energy between the system and the surroundings. There are certain processes in which a particular state variable (thermodynamic property of the system) remain unchanged. Such processes are of the following types:

2.0. Objectives

At the end of the unit, students should be able to

- define isothermal, adiabatic and cyclic processes,
- explain the terms - work, heat and heat capacity,
- state the first law of thermodynamics,

3.0 Definition

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

In an **adiabatic process**, no heat is allowed to enter or leave the system. Systems in which such processes occur are thermally insulated from the surroundings. An

adiabatic; process may involve increase or decrease in the temperature of the system. We shall discuss these two processes in detail in Sees. 6.8 and 6.12.

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

In an **isochoric process**, volume of the system remains constant. Thus, a chemical of constant volume is an isochoric process.

A process is **cyclic** if the system (after any number of intermediate changes) returns to its original state. The initial and final value of each thermodynamic variable is identical after the completion of a cyclic process. Based on the value of the driving force applied we can classify the processes into two types, namely, reversible and irreversible.

A reversible process is one in which at any time, the driving force exceeds the opposing force only very slightly, and hence, the direction of the process can be reversed by merely a small change in a variable like temperature and pressure. The idea of a reversible process will become clear by considering the following example.

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

A tiny change in a property is called an infinitesimal change.

Note that "if" is common to all the three statements.

$$\text{If } \left\{ \begin{array}{lll} p_{ext} & = & p \quad \text{the system is static and piston does not move} \\ p_{ext} & = & p + dp \quad \text{the gas is compressed and the piston moves downwards infinitesimally slowly} \\ p_{ext} & = & p - dp \quad \text{the gas expands and the piston moves outwards infinitesimally slowly} \end{array} \right.$$

Hence, you can see that in a reversible process, the direction of a process is changed by changing the magnitude of the driving force by a small amount. You will in future studies learn about how reversible condition is used in constructing electrochemical cells.

Any process which is not reversible is termed as 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.

4.0 WORK, HEAT AND HEAT CAPACITY

Work, heat and energy have the same units, namely Joule (J). Energy is thermodynamic property of a system, whereas work and heat are not. The latter two are meaningful only when a process takes place. Let us first define heat.

Heat is a form of energy. Heat is not the property of a system but is exchanged between a system and the surroundings during a process, when there is a temperature difference between the two. Let us now explain the term, work, and its different kinds.

Work (W) is defined as the product of the force applied (F) and the distance (X) moved along the direction of the force.

$$W = F \cdot X \quad \dots(1.1)$$

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

- 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
- Electrical work: If an electric potential E is applied across a resistance R so that current i flows through it, then work done per second is Ei and in t seconds it is equal to Eit .
- Pressure-volume work: This is a type of mechanical work performed when a system changes its volume against an opposing pressure. This also is expansion or compression. We will study this in detail in later sections.

The energy gained or lost during heat exchange between the system and the surroundings can be stated in terms of heat capacity values. Let us now define the term, heat capacity.

Heat capacity is the heat required to raise the temperature of a body by 1K . If, during the process, the volume of the system remains constant, then it is called

heat capacity at constant volume (C_v); if the pressure remains unchanged, it is called heat capacity at constant pressure (C_p). For one mole of a pure substance, these are called molar heat capacity at constant pressure, \bar{C}_p and at constant volume, \bar{C}_v . Heat capacities per unit mass are called specific heats. The heat capacities change with temperature. This means that, the heat required to change the temperature by 1 K is different at different temperatures. However, over small ranges of temperature, these are usually taken as constant. The molar heat capacity and specific heat are intensive properties whereas heat capacity is an extensive property (guess the reason).

For 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), then we have

$$C_v = n\bar{C}_v = \frac{dq_v}{dT} \quad \dots(1.2)$$

$$C_p = n\bar{C}_p = \frac{dq_p}{dT} \quad \dots(1.3)$$

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,

$$q_v = \int_{T_1}^{T_2} C_v dT = \int_{T_1}^{T_2} n\bar{C}_v dT \quad \dots 1.4$$

$$q_p = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} n\bar{C}_p dT \quad \dots 1.5$$

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

Example 1

The equation for the molar heat capacity of butane is $C_p = (19.41 + 0.233 T) \text{ J mol}^{-1} \text{ K}^{-1}$.

$$\text{Molar heat capacity} = \text{Specific heat} \times \text{molar mass}$$

Calculate the heat necessary to raise the temperature of 3.00 mol of butane from 298 K to 573 at constant pressure. We have to calculate d_p as per Eq. 1.5.

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

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

$$T_2 = 573 \text{ K}$$

$$n = 3.00 \text{ mol}$$

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

See the box below for understanding the simplification of the terms I and II.

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

$$= \underbrace{3.00 \times 19.41 \int_{298}^{573} dT}_I + \underbrace{3.00 \times 0.233 \int_{298}^{573} T dT}_{II}$$

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

$$= 9.97 \times 10^4 \text{ J}$$

$$= 99.7 \text{ KJ}$$

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

We give below two general formulae for integration; (these two formulae will be useful throughout this course in working out numerical. Formula 1 is used in this unit in Example 1 and Formula 2 in Example 3.

Formula 1

If m is not requires to -1

$$\int_{x_1}^{x_2} ax^m dx = a \int_{x_1}^{x_2} x^m dx = \frac{a}{m+1} \left[x^{m+1} \right]_{x_1}^{x_2} = \frac{a}{(m+1)} (x_2^{m+1} - x_1^{m+1})$$

Where, a is a constant. This formula is used in the term marked II in. Example 1, where $a = 3.00 \times 0.233$, $x = T$, $m = 1$, $x_1 = 298$ and $x_2 = 573$.

Note that I term in Example 1 is also a special case of formula 1. If $m = 0$, then $x^m = 1$ and formula 1 becomes

$$\int$$

$$\int_{x_1}^{x_2} a dx = \frac{a}{(0+1)} (x_2 - x_1) = a(x_2 - x_1)$$

In I term of Example 1, $a = 300 \times 19.41$, $x = T$, $x_1 = 298$ and $x_2 = 573$

Formula 2

If m is equal to -1

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

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

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

$$\int_{x_1}^{x_2} a \frac{dx}{x} = 2.303 a \log \frac{x_2}{x_1}$$

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

We are now familiar with various terms used in the study of thermodynamics. In the next section, we shall discuss the first law of thermodynamics. Before proceeding to the next section, answer the following SAQ.

Self Assessment Exercise 1

The molar heat capacity of ethane at constant pressure is $52.6 \text{ J K}^{-1} \text{ mol}^{-1}$. Calculate the energy required to heat 3.00 mol of ethane from 305 K to 405 K at constant pressure.

Hints: i) Use Eq. 1.5

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

Logarithmic representation helps in denoting a very large or a small number which is of convenient magnitude.

Eg (i) Avogadro number = $N_A = 6.022 \times 10^{23}$ $\log N/A = 23.78$ (to four digits)
(ii) Dissociation constant of acetic acid K_a
 $-\log K_a = 4.74$ (to three digits)

'log' representation depicts a number in powers of 10. Similarly 'ln' representation depicts a number in power of 'e'

$$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \dots$$
$$= 2.718 \text{ (to four digits)}$$

For representing population of energy levels, radioactive decay etc., 'ln' is quite useful.

4.0 THE FIRST LAW OF THERMODYNAMICS

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

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

- The energy of an isolated system remains constant.
- Energy can neither be created nor destroyed although it can be changed from one form to another
- It is not possible to construct a perpetual motion machine which can work endlessly without the expenditure of energy. (Such a machine is known as 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 energy of a system will remain constant if it is left undisturbed. If, on the other hand, the system interacts with the surroundings, then its energy may change; but then, there will also be equal and opposite change in the energy of the surroundings. Since Work is a form of energy, it is not possible for a machine to keep on doing work indefinitely. As soon as its own energy is exhausted it will require a source of energy to continue doing work. The first law of thermodynamics; has no theoretical proof. It is a law based on observation. Since the law has never been contradicted, its truth is taken for granted.

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

$$E=mc^2 \quad \text{.....(1.6)}$$

This means that if mass m is destroyed, then energy E is produced; c is the velocity light. This is not a contradiction since mass can also be considered as a form of energy.

We shall shortly arrive at the mathematical forms of the first law of thermodynamics. Before that let us first introduce the term, internal energy.

Internal Energy

The internal energy U of a system is the entire energy of its constituent atoms or molecules including all forms of kinetic energy (due to translation, vibration and rotation) as well as energy due to all types of interactions between the molecules and subparticles. It is a state variable and an extensive property and its absolute value cannot be determined. However, in thermodynamics we are interested, in the changes in internal energy which accompany any process, but not in the absolute value of U .

These changes in internal energy can be brought about only by interaction of the system with its surroundings. The change in internal energy (ΔU) depends only on the initial and final states and is Independent of the path adopted.

The total energy of a system is the sum of the internal energy and some energy due to the motion or position of the system as a whole. For example, the total energy of water on the ground floor is different from its energy on the top of the building. The difference in total energy is mgh (m is the mass of water, h the height of the building and g the acceleration due gravity) whereas the internal energy is the same; in both cases. Similarly for a moving bullet, the total energy is the sum of the internal energy and its kinetic energy, $\frac{1}{2}mv^2$ (where m is the mass of the bullet and v its velocity).

The heat change, dq , and the work done, dw , contribute towards the change in the internal energy of the system] We adopt the convention that the change in the internal energy is equal to the sum of the heat absorbed by the system and the work done on it.

If dq is positive (heat absorbed by the system is positive), this leads to an increase in the internal energy of the system. A negative dq implies loss of heat from the system and $-$ denotes a decrease in internal energy.

If the work done on the system (dw) is positive, this increases the internal energy of the system.

A negative value of dw implies that work has been done by the system at the expense of its internal energy.

Let us now derive the mathematical forms of the first law of thermodynamics.

Mathematical Forms of the First Law of Thermodynamics

As mentioned earlier, work and heat bring about changes in the internal energy of the system. If the system absorbs a certain amount of heat, dq , then its internal energy increases by this amount; further if dw is work done on the system, then the internal energy again increases. Hence, the net change in the internal energy is given by

$$dU = dq + dw \quad \dots(1.7)$$

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

$$\Delta U = U_f - U_i = q + w \quad \dots(1.8)$$

where U_i and U_f are the initial and final internal energies of the system, and ΔU , the net change. It is obvious that ΔU can have either negative or positive value depending on q and w . But once the initial and final states of a system are fixed, ΔU is automatically fixed, no matter what path is adopted in carrying out the process. In other words, internal energy is a state function while heat and work are not. As an example consider a system being taken from the initial state where it has energy U_i to the final state having energy U_f along different paths I, II and III (Fig.1.1). Then in all these cases, ΔU is same. If this were not so, then it would have been possible to construct a perpetual motion machine by reaching the final state via a high energy change path (say, III) and coming back via a low-energy change path (IV) thereby releasing the energy difference for work. Eqs. 1.7 and 1.8 are mathematical expressions of the first law of thermodynamics.

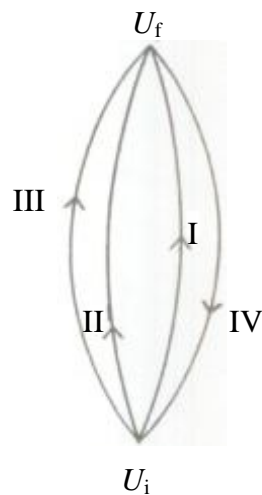


Fig. 1.1 Energy change through different onward paths. I, II and III and return path, IV.

Self Assessment Exercise 2

Suggest a statement for the first law of thermodynamics such that the law of conservation of mass is not violated.

5.0 ISOTHERMAL EXPANSION

6.0

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 air tight piston of area A . Assume that pressure of the gas is p and the external pressure is p_{ext} which is slightly less than the gas pressure. The gas will, hence, expand against an opposing force which is given by

$$F = P_{\text{ext}}A \quad \dots(1.9)$$

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

$$dw' = f dx = P_{\text{ext}} A dx \quad \dots(1.10)$$

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

$$dw' = P_{\text{ext}} dV \quad \dots(1.11)$$

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

$$dw = -P_{\text{ext}} dV \quad \dots(1.12)$$

Eq. 1.12 is a general expression useful in calculating pressure – volume work whether it is isothermal or adiabatic process. It can be seen that dw is negative when the gas expands and it is positive when the gas contracts, [$dV = +ve$ in expansion and $dV = -ve$ in compression].

Note that the value of the work (dw) done on the gas is obtained by reversing the sign of work (dw') done by the gas: or $dw = -dw'$

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 process.

This means that:

(i) the gas expands against a constant External pressure ($p_{ex} = \text{constant}$)

(ii) there is considerable difference between the gas pressure (inside the cylinder) and the external pressure (iii) that the temperature does not change during the process.

Let the initial and final volumes be V_1 , and V_2 , respectively. The total work, W , done on the system is obtained by integrating Eq. 1.12.

$$\left. \begin{aligned} W &= - \int_{V_1}^{V_2} p_{\text{ext}} dV = - p_{\text{ext}} \int_{V_1}^{V_2} dV \\ &= - p_{\text{ext}} (V_2 - V_1) = - p_{\text{ext}} \Delta V \end{aligned} \right\} \dots (1.13)$$

The symbol, ΔV , denotes the total change in volume during the process.

Let us work out an example to illustrate the use of Eq. 1.13

Example 2

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

We have to calculate work done under constant pressure using Eq. 1.13

$$\begin{aligned} \text{Hence, } W &= -p_{\text{ext}} (V_2 - V_1) = -1 \times 10^5 \text{ Pa} \times (12 \text{ m}^3 - 10 \text{ m}^3) \\ &= -2 \times 10^5 \text{ Pa m}^3 \left\{ \begin{array}{l} \text{because } 1 \text{ bar} = 1 \times 10^5 \text{ Pa} \\ \text{and } 1 \text{ Pa m}^3 = 1 \text{ J} \end{array} \right\} \\ &= -2 \times 10^5 \text{ J} \end{aligned}$$

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

It is also possible to calculate the work done under irreversible isothermal conditions, when the external pressure changes continuously. But then, the concerned equation is more complex than Eq. 1.13. Let us now calculate the work done under isothermal reversible process.

Isothermal Reversible Process

We have already mentioned that a reversible process can be carried out when external pressure (p_{ext}) is only infinitesimally different from the gas pressure inside a cylinder (p)

In such a case, $p_{ext} \approx p$ and hence, Eq. 1.12 can be written as,

$$dw = -pdV \quad \dots (1.14)$$

Note that the pressure of the gas inside the cylinder and the external pressure are very much different in an irreversible process.

The integration procedure used in Eq. 1.13 is similar to that of part I discussed in Example 1. Again, this is an application of formula 1 discussed in Sec. 1.6.

Note that dx and Δx refer to infinitesimal and finite (considerable or even large) changes in x , respectively. If dx or Δx is

- i) +ve, then x increases;
- ii) -ve, then x decreases and
- iii) zero, then x does not change or x remains a constant.

The total work done, W , as the gas expands isothermally and reversibly from V_1 to a volume V_2 is then given by integrating Eq. 1.14 within limits V_1 , and V_2 .

$$W = - \int_{V_1}^{V_2} p dV \quad \dots (1.15)$$

Let us assume that the gas behaves ideally. Hence,

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

Using this in Eq. 1.15

$$\begin{aligned} W &= - \int_{V_1}^{V_2} \frac{nRT}{V} dV \\ &= nRT - \int_{V_1}^{V_2} \frac{dV}{V} \end{aligned} \quad \dots (1.16)$$

$$= - nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{V_1}{V_2} \quad \dots (1.17)$$

$$\text{Hence, } W = - 2.303nRT \log \frac{V_2}{V_1} = 2.303 nRT \log \frac{V_1}{V_2} \quad \dots (1.18)$$

It can be seen that if V_2 is less than V_1 , then the gas has been compressed and, W is positive. Also, the value of W then happens to be the minimum work required for compressing the gas from (volume) V_1 to V_2 .

Similarly, if V_2 is greater than V_1 then the gas undergoes expansion and W is negative.

Note that the difference between Eqs. 1.13 and 1.15 is that p depends on volume in the latter; whereas, p_{ext} in Eq.1.13 is constant throughout. As a result of this, p_{ext} is taken out of integration sign in Eq. 1.13 whereas p in Eq. 1.15 is to be expressed as a function of volume.

Note that n , R and T are constants and are taken out of the integration sign in Eq. 1.16. Note that formula 2 of Sec. 1.6 is used here.

As compared to formula 2,

$$\begin{aligned} a &= nRT \\ x_1 &= V_1 \\ x_2 &= V_2 \\ x &= V \end{aligned}$$

Note that Eqs 1.18 and 1.21 are applicable only for an ideal gas undergoing isothermal reversible expansion or compression. If the gas does not have ideal behavior, suitable equation of state must be used.

Note that $-\log \frac{p_2}{p_1} = \log \frac{p_1}{p_2}$;

this follows from the mathematical principle that the numerator and denominator inside the "log" term can be interchanged by reversing the sign outside.

Step (i):

Note that this step contains logarithmic term,

$$\log \frac{6.00 \times 10^6 \text{ Pa}}{3.00 \times 10^5 \text{ Pa}}$$

When you come across a logarithmic term, first see whether the number inside the log term is greater than or less than one.

In the present case, $\frac{6.00 \times 10^6}{3.00 \times 10^5}$

is greater than one. Hence, do the following steps:

Step (ii):

From the logarithm of the numerator, subtract the logarithm of the denominator. In Example 3, this step gives (6.7782-5.4771).

Step (iii):

The answer to step (ii) is written (in Example 3, it is 1.3011); the multiplication is carried out in the usual way.

This means, work is done by the gas; $-W$ represents the maximum work available through expansion.

Eq. 1.18 can also be given in terms of initial and final pressures (p_1 and p_2) of the ideal gas.

For an ideal gas at constant temperature,

$$p_1 V_1 = p_2 V_2 \quad \dots(1.19)$$

$$\frac{V_2}{V_1} = \frac{p_1}{p_2} \quad \dots(1.20)$$

$$\begin{aligned} W &= -2.303 nRT \log \frac{p_1}{p_2} \\ &= 2.303 nRT \log \frac{p_2}{p_1} \quad \dots (1.21) \end{aligned}$$

Let us illustrate the use of Eq 1.21

Example 3

An ideal gas initially at 3.00×10^2 K and 3.00×10^5 Pa pressure occupies 0.831 m^3 space. What is the minimum amount of work required to compress the gas isothermally and reversibly so that the final pressure is 6.00×10^6 Pa?

$$p_1 = 3.00 \times 10^5 \text{ Pa}; p_2 = 6.00 \times 10^6 \text{ Pa}$$

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

We have to calculate the value of n (the amount of the gas) in order to use Eq 1.21; the value of n can be found out from the initial conditions using ideal gas equation.

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

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

Substituting the values in Eq. 1.21

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

Step (i)

$$= \frac{2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times (61.7782 - 5.4771)}{\text{Step (ii)}} \text{ J}$$

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

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

Using the principles studied above, answer the following SAQ.

Self Assessment Exercise 3

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

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 1: Thermodynamics, Types of process, Heat change and Enthalpy of Reactions

Unit 3: Heat Change

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Definitions
- 4.0 Heat Change under Constant Volume
- 5.0 Enthalpy and Enthalpy Changes
- 6.0 Relation between C_p and C_v of an Ideal Gas

2.0.

At the end of the unit, students are expected to

- explain the term, internal energy of a system,
- calculate the work done on an ideal gas in isothermal and adiabatic processes,
- state the significance of enthalpy and enthalpy change of a system,
- derive the relationship between \bar{C}_p and \bar{C}_v of an ideal gas, and

3.0. HEAT CHANGE UNDER CONSTANT VOLUME

The reactions are 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. In the next section, we shall discuss heat change under constant pressure conditions.

Let us examine Eq. 1.7. Let us assume that the work done on the system is only pressure-volume work, whereas electrical, magnetic or other types of work are not involved. Then from Eqs. 1.9 and 1.14

$$dU = dq - pdV \quad \dots(1.22)$$

$$\text{or } dq = dU + pdV \quad \dots(1.23)$$

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

$$dV - pdV = 0$$

$$\text{Hence, } dq_v = dU \quad \dots(1.24)$$

For finite changes in internal energy Eq.1.24 becomes,

$$q_v = \Delta U \quad \dots(1.25)$$

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

Let us try to correlate internal energy change with heat capacity at constant volume assuming that there is no phase change or chemical reaction. From Eqs 1.24 and 1.26

$$dU = C_v dT = n \bar{C}_v dT \quad \dots(1.26)$$

This holds good for n mol of an ideal gas.

can be rewritten as,

$$C_v = \left(\frac{\partial U}{\partial T} \right)_V \quad \dots (1.27)$$

i.e heat capacity at constant volume is equal to change in internal energy per 1 K rise in temperature at constant volume.

$\left(\frac{\partial U}{\partial T} \right)_V$ is called the partial differential of internal energy with respect to temperature at constant volume. It means the value U of a gas depends on V and T , but only the variation in U with respect to T is measured at constant volume. Interestingly for an ideal gas, U depends, only on T but not on V .
i.e

$$\left(\frac{\partial U}{\partial T} \right)_V = 0$$

In order to obtain ΔU when an ideal gas is heated from temperature T_1 to T_2 at constant volume, the integrated form of Eq. 1.26 is to be used.

$$\text{i.e } \Delta U = \int_{T_1}^{T_2} C_v dT = \int_{T_1}^{T_2} \bar{C}_v dT \quad \dots(1.28)$$

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

We have defined C_v through Eq. 1.27 What about C_p ? Is there some thermodynamic property to which C_p can be related in a similar way? For this purpose, we define the term, enthalpy, in the next section.

Self Assessment Exercise 1

Calculate the

- i) change in internal energy of an ideal gas undergoing isothermal reversible compression as discussed in Example 3.
- ii) What is the value of q for the same case?

5.0 ENTHALPY AND ENTHALPY CHANGES

Enthalpy of a system is defined by the relation,

$$H = U + pV \quad \dots(1.29)$$

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

$$\Delta H = H_2 - H_1 \quad \dots(1.30)$$

$$\begin{aligned} &= (U_2 + p_2 V_2) - (U_1 + p_1 V_1) \\ &= \Delta U + (p_2 V_2 - p_1 V_1) \end{aligned} \quad \dots(1.31)$$

In case of a constant pressure process ($p_1 = p_2 = p$), Eq. 1.31 can be written as,

$$\begin{aligned} \Delta H &= \Delta U + p(V_2 - V_1) \\ \Delta H &= \Delta U + p\Delta V \end{aligned} \quad \dots(1.32)$$

Rewriting Eq.1.23 for a finite change, we get

$$q_p = \Delta U + p\Delta V \quad \dots(1.33)$$

this means, the heat capacity at constant pressure is equal to the partial differential of H with respect to temperature at constant pressure. Interestingly for an ideal gas, H depends on T only and not on p ;

Using this equation in Eq 1.32, $q_p = \Delta H$ (1.34)

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

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

For a small change in enthalpy, we can write

$$dq_p = dH \quad \dots(1.35)$$

Using Eq. 1.3 and assuming that there is no phase change or chemical reaction we have.

$$dH = C_p dT = n\bar{C}_p dT \quad \dots(1.36)$$

In order to obtain ΔH value when an ideal gas is heated from temperature T_1 to T_2 , at constant pressure, the integrated form of Eq. 1.36 is to be used.

$$\Delta H = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} n\bar{C}_p dT \quad \dots(1.37)$$

Since many laboratory processes are carried out at constant pressure (atmospheric pressure), the enthalpy change of a system is of great significance. It may 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.

Using Eq. 1.36 C_p can be defined as $C_p = \left(\frac{\partial H}{\partial T} \right)_T$ this means, the heat capacity at constant pressure is equal to the partial differential of H with respect to temperature at constant pressure.

Interesting for an ideal gas, H depends on T only and not on P ;

i.e. $\left(\frac{\partial H}{\partial T} \right)_T = 0$ for an ideal gas.

Those processes in which heat is supplied to the system are called endothermic and, ΔH is given a positive sign; in exothermic processes (in which heat is evolved), ΔH is negative.

Enthalpy changes connected with certain typical processes are given special names. For example, enthalpy of vaporization or evaporation is the enthalpy change accompanying the conversion of one mole of a liquid to its vapour. Similarly, enthalpy of fusion and sublimation are the enthalpy changes 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 section, we shall study the relationship between \bar{C}_p and \bar{C}_v values of an ideal gas.

6.0 RELATION BETWEEN \bar{C}_p and \bar{C}_v OF AN IDEAL GAS

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

For one mole of an ideal gas,

$$H = U + pV = U + RT \quad \dots(1.38)$$

On differentiating we get,

$$dH = dU + RdT \quad [\text{because } R \text{ is a constant}]$$

Using Eqs 1.26 and 1.36 **one mole of an ideal gas**)

$$\bar{C}_p dT = \bar{C}_v dT + R dT \quad \dots(1.39)$$

$$\bar{C}_p = \bar{C}_v + R$$

and hence,

$$\bar{C}_p - \bar{C}_v = R \quad \dots(1.40)$$

Also, for n mol,

$$\bar{C}_p - \bar{C}_v = nR \quad \dots(1.41)$$

This means that \bar{C}_p is always greater than \bar{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 constant volume conditions). Hence, more heat will be required in raising the temperature- of the gas through 1 K under constant pressure conditions than under constant volume.

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 1 Thermodynamics, Types of process, Heat change and Enthalpy of Reactions

Unit 4 Enthalpy of Reactions

1.0 Introduction

2.0 Objectives

3.0 Definition

4.0 Adiabatic expansion

5.0 Joule-Thomson Effect

6.0 Kirchoff's equation

2.0. Objectives

- explain Joule-Thomson effect.
- derive kirchhoffs equation and state its significance
- derive Kirchhoffs equation and state its significance,
- define bond enthalpy, and
-
- calculate enthalpies of reactions from bond enthalpies.

3.0. Adiabatic Expansion

We have previously discussed the work done in an isothermal process. Let us now study how the work is calculated in an adiabatic process,

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

Hence, from Eq. 1.7 $dU = 0 + dw = dw$...(1.42)

But for one mole of an ideal gas, dU is given by Eq. 1-26 as,

$$dU = \bar{C}_v dT$$

During expansion, dw and hence, dU are negative. That is, as the system does expansion work, its internal energy decreases. This, again, according to Eq. 1.26 means that dT is negative; i.e., temperature decreases. In other words during adiabatic expansion, temperature of the system decreases. This principle is used in Claude's method of liquefaction of gases.

Let us now study the temperature-volume relation in a reversible adiabatic process. This could 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 Eq. 6.42, $dU = dw$

Substituting for dw and dU from Eqs. 1.14 and 1.26, we get for one mole of an ideal gas,

$$\bar{C}_v dT = -pdV$$

For one mole of an ideal gas,

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

Using this relationship in Eq. 1.43 we get

$$\bar{C}_v dT = \frac{-RTdV}{V} \quad \dots(1.44)$$

Rearranging we get,

$$\bar{C}_v \frac{dT}{T} = -R \frac{dV}{V} \quad \dots(1.45)$$

Integrating Eq. 1.43 between temperature limits T_1 and T_2 and volume limits V_1 and V_2 , we get

$$\bar{C}_v \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \quad \dots(1.46)$$

$$\bar{C}_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

$$= (\bar{C}_p - \bar{C}_v) \ln \frac{V_1}{V_2}$$

(Using Eq. 1.40)

$$\ln \frac{T_2}{T_1} = \left(\frac{\bar{C}_p}{\bar{C}_v} - 1 \right) \ln \frac{V_1}{V_2}$$

$$= (\gamma - 1) \ln \frac{V_1}{V_2}$$

The integrals on the left and right sides of Eq. 1.46 are solved using formula 2 given in Sec. 1.6. Note that \bar{C}_v is considered a constant in the temperature range, T_1 to T_2 . Of course, R is a constant.

The change of numerator and denominator inside the 'ln' term with a reversal of the sign outside it has already been explained in Sec.1.8.

Rearrangement of Eq. 1.47 is done using the general formula, $m \ln x = \ln x^m$ or $m \log x = \log x^m$. You can verify this formula using logarithmic tables in the following cases. You look for the logarithm of 10, 100, 2 and 8; see whether the following are true.

$$\begin{aligned} 2 \log 10 &= \log 10^2 = \log 10.0 \\ 3 \log 2 &= \log 2^3 = \log 8 \end{aligned}$$

Where γ is the ratio of the molar heat capacities, \bar{C}_p/\bar{C}_v .

Rearranging Eq. 1.47 we get,

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

Taking antilogarithms both the sides

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma - 1} \quad \dots(1.48)$$

$$\text{or } T_2 V_2^{\gamma - 1} = T_1 V_1^{\gamma - 1} \text{ or } TV^{\gamma - 1} = \text{Constant}$$

This equation gives the volume — temperature relationship in a reversible adiabatic process.

Also we can get pressure temperature relationship knowing that, for an ideal g

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

$$\frac{V_1}{V_2} = \frac{P_2 T_1}{P_1 T_2} \quad \dots(1.49)$$

substituting this in Eq. 1.48

$$\frac{T_2}{T_1} = \left(\frac{P_2 T_1}{P_1 T_2} \right)^{\gamma - 1}$$

$$T_2 (P_2 T_2)^{\gamma-1} = T_1 (P_1 T_1)^{\gamma-1}$$

i.e. $T_2^{\gamma} P_1^{\gamma-1} = T_1^{\gamma} P_2^{\gamma-1}$

or $\left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{P_2}{P_1}\right)^{\gamma-1} \quad \dots(1.50)$

For any reversible adiabatic expansion, T_2 can be determined using Eq. 1.48 or 1.50

For an ideal gas undergoing isothermal reversible expansion (or contraction), the pressure-volume relationship is, $p_1 V_1 = p_2 V_2$ whereas in an adiabatic reversible process, it is $p_1 V_1^{\gamma} = p_2 V_2^{\gamma}$. Here subscripts 1 and 2 stand for initial and final conditions.

Also it is possible to get pressure-volume relationship in a reversible adiabatic process using the rearranged form of Eq. 1.49,

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

In E.q 1.48 as follows:

$$\frac{P_2 V_2}{P_1 V_1} = \left(\frac{T_2}{T_1}\right)^{\frac{\gamma}{\gamma-1}}$$

Cross multiplying the terms,

$$\begin{aligned} P_2 V_2^{\gamma} &= P_1 V_1^{\gamma} \\ \text{or } P_1 V_1^{\gamma} &= P_2 V_2^{\gamma} \\ \text{or } P V^{\gamma} &= \text{Constant} \end{aligned} \quad \dots(1.51)$$

Eq. 1.51 describes pressure-volume relationship for an ideal gas undergoing reversible adiabatic expansion (or compression).

ΔU and W in a Reversible Adiabatic Process

The quantities dU and dw for an adiabatic process are related through Eq. 1.42 Using this equation and Eq. 1.26 get for 1 mol of an ideal gas,

$$dU = dw = \bar{C}_v dT$$

In case of n mol of an ideal gas,

$$dU = dw = nC_v dT \quad \dots(1.52)$$

The work done on the gas during an adiabatic expansion (W) as also the change in internal energy (ΔU) can be calculated by integrating Eq. 1.52 within temperature limit T_1 and T_2

$$\begin{aligned} \Delta U = W = n\bar{C}_v &= \int_{T_1}^{T_2} dT \\ &= n\bar{C}_v (T_2 - T_1) = n\bar{C}_v \Delta T \end{aligned} \quad \dots(1.53)$$

Note that C_v is assumed to be a constant in Eq 1.53 in the temperature range T_1 and T_2

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

Irreversible Adiabatic Expansion

If the work is done irreversibly and adiabatically, then the work done on the system is given by Eq. 1.48,

$$W = -p_{\text{ext}} \Delta V \quad \dots(1.54)$$

as in the case of irreversible isothermal process.

We can arrive at the temperature-volume relationship for an adiabatic irreversible process as follows:

Using Eq. 1.54 in Eq. 1.53 $-p_{\text{ext}} \Delta V = n\bar{C}_v \Delta T$

Hence,
$$\Delta V = (T_2 - T_1) = \frac{-P_{\text{ext}} \Delta V}{n\bar{C}_v} \quad \dots(1.55)$$

Eq. 1.55 is useful in calculating the final temperature of an ideal gas undergoing adiabatic irreversible expansion while Eq. 1.48 or 1.50 is of help in an adiabatic reversible process.

Answer the following SAQ using Eq. 1.55

Self Assessment Exercise 1

Show that against zero external pressure, the expansion is simultaneously adiabatic and isothermal.

4.0 JOULE-THOMSON EFFECT

Our discussion so far centered around ideal gases. It was mentioned earlier that internal energy of an ideal gas is independent of pressure or volume. This, however, is not true for real gases 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 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. 1.2. 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 pressure p_1 and p_2 in the two compartments. Note that p_1 is greater than p_2 . The left hand side piston is then slowly pushed inwards so that, without changing the value of p_1 , a volume V_1 of gas is introduced through the plug into the other compartment. This results in the outward movement of the other piston and also in the 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:

$$W = -(p_2V_2 - p_1V_1) = p_1V_1 - p_2V_2$$

It should be remembered that p_2V_2 is the work done by the system and p_1V_1 the work on it. The conditions are adiabatic and so $q = 0$. For a finite process, Eqs. 1.12 and 1.56 can be combined and written as,

$$\Delta U = W = (p_1V_1 - p_2V_2)$$

Or $\Delta U + (p_2V_2 - p_1V_1) = 0$

Using Eq. 1.31, $\Delta U + (p_2V_2 - p_1V_1) = \Delta H$
From Eqs. 1.31 and 1.58 we note that

$$\Delta H = 0$$

Hence in the Joule-Thompson experiment, $\Delta H = 0$ or enthalpy is constant.

A detailed discussion of intermolecular forces and their effects on liquefaction, vaporization and fusion is available in Unit 3 of this course.

A porous plug has small holes which permit the flow of the gas from one side to another.

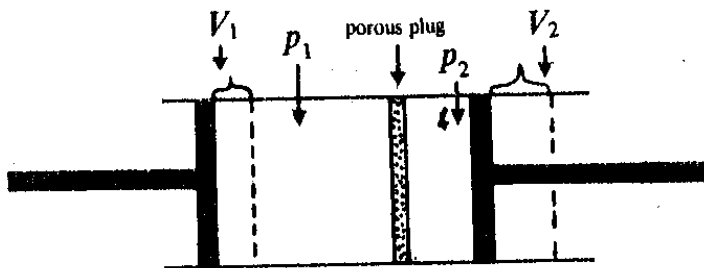


Fig. 1.2: Joule-Thomson Experiment

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

$$\mu_{JT} = \left(\frac{\partial T}{\partial P} \right)_H \quad \dots(1.60)$$

If μ_{JT} is positive, expansion causes cooling and if μ_{JT} is negative, expansion causes heating. But if μ_{JT} is equal to zero, there is neither cooling nor heating due to Joule-Thomson expansion. The temperature at which $\mu_{JT} = 0$ is called the inversion temperature (T_i) of the gas. If a gas is expanded above its inversion temperature, it is heated; if it is expanded below its inversion temperature, it is cooled. In order to decrease the temperature of a gas and then to liquefy by Joule-Thomson process, it is essential to bring its temperature below its inversion temperature.

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

5.0 KIRCHHOFF'S EQUATION

For A given reaction, $\Delta_r H$ and $\Delta_r U$ generally vary with temperature. It is of great importance to study these variations quantitatively so that these may be calculated for any temperature from the known values of $\Delta_r H$ and $\Delta_r U$ at any other temperature. The variation of $\Delta_r H$ and $\Delta_r U$ with temperature is described by Kirchhoff's equation. Let us derive this equation.

If C_p is the heat capacity of a substance, then for a temperature rise dT , the increase in enthalpy is given by Eq 1.36 as

$$dH = C_p dT \quad \dots(1.61)$$

In the case of enthalpy of a reaction ($\Delta_r H$), we can rewrite Eq. 1.61 as,

$$d(\Delta_r H) = \Delta C_p dT$$

Where $\Delta C_p = (\text{sum of } C_p \text{ values of products}) - (\text{sum of } C_p \text{ values of reactants})$

Also, $d(\Delta_r H)$ is the change in enthalpy of reaction due to change in temperature, dT .

Eq. 1.62 on integration gives,

$$\Delta_r H_2 - \Delta_r H_1 = \int_{T_1}^{T_2} \Delta C_p dT \quad \dots(1.63)$$

where $\Delta_r H_2$ and $\Delta_r H_1$ are the enthalpies of reaction at temperatures T_2 and T_1 , respectively. Eq.1.63 is called Kirchhoff's equation. Similarly we can also obtain the expression, 1.63.

$$\Delta_r U_2 - \Delta_r U_1 = \int_{T_1}^{T_2} \Delta C_v dT \quad \dots(1.64)$$

Where $\Delta_r U_1$ and $\Delta_r U_2$ are the changes in internal energy of the reaction at temperatures T_1 and T_2 , and ΔC_v is the difference in heat capacities between products and reactants at constant volume. Let us now consider three of the special cases of Eq. 1.63

i) If $\Delta C_p = 0$, then $\Delta_r H_2 - \Delta_r H_1$ implying thereby that the enthalpy of reaction does not change.

ii) If ΔC_p is constant i.e. it does not vary with temperature, then

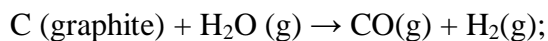
$$\Delta_r H_2 = \Delta_r H_1 + \Delta C_p (T_2 - T_1) \quad \dots(1.65)$$

i.e $\Delta_r H$ either decreases or increases regularly with temperature. For most reactions Eq. 1.65 is valid for small range of temperatures.

iii) If ΔC_p changes with temperature, then Eq. 1.63 has to be integrated by expressing C_p as a function of temperature. The variation in \bar{C}_p is usually expressed in the following way:
 $\bar{C}_p = a + bT + cT^2 + \dots$ the coefficients a,b,c,etc., are characteristic of a particular substance.

Let us work out an example to show the use of Eq. 1.65

Example 4: $\Delta_r H$ for the reaction,



at 298 K is 131.2 kJ. The C_p values are given below in the temperature range, 298 to 348 K.

Substance	$\bar{C}_p/\text{J mol}^{-1} \text{ K}^{-1}$
Graphite	15.93
$\text{H}_2\text{O (g)}$	30.04
CO (g)	26.51
$\text{H}_2 \text{ (g)}$	29.04

Calculate $\Delta_r H$ at 348 K.

The \bar{C}_p values given above are independent of temperature; hence, we can find $\Delta_r H$ at 348 K using Eq. 1.65

Let us first calculate ΔC_p

$$\Delta C_p = \left\{ \left[1 \times \bar{C}_p (\text{CO}) + 1 \times \bar{C}_p (\text{H}_2) \right] - \left[1 \times \bar{C}_p (\text{graphite}) + 1 \times \bar{C}_p (\text{H}_2\text{O}) \right] \right\} \text{ J K}^{-1}$$

(Since one mole of each component appears in the thermochemical equation)

$$= \left\{ (26.51 + 29.04) - (15.93 + 30.04) \text{ J K}^{-1} \right\}$$

$$= 9.58 \text{ J K}^{-1}$$

$$= 9.58 \times 10^{-3} \text{ kJ K}^{-1} \text{ (Remember } 1\text{J} = 10^{-3} \text{ kJ)}$$

ΔC_p is expressed in kJ K^{-1} , since $\Delta_r H$ at 298 K is given in kJ.

Using Eq. 1.65,

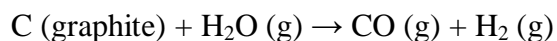
$$\begin{aligned} \Delta_r H \text{ at } 348 \text{ K} &= \Delta_r H \text{ at } 298 \text{ K} + \Delta C_p (348 - 298) \\ &= (131.2 + 9.58 \times 10^{-3} \times 50) \text{ kJ} \\ &= 131.7 \text{ kJ} \end{aligned}$$

\bar{C}_p is usually given in $\text{J mol}^{-1} \text{ K}^{-1}$ units. You should remember to convert it into $\text{kJ mol}^{-1} \text{ K}^{-1}$ (by division by 1000), if ΔH is in kJ mol^{-1} units.

Using the ideas developed above, work out the following SAQ.

Self Assessment Exercise 2

For the reaction,



Calculate ΔC , if the molar heat capacities at constant pressure for various species vary as per the equation, $\bar{C}_p = a + bT + cT^2$ where \bar{C}_p is in $\text{J mol}^{-1} \text{ K}^{-1}$. The a, b, and c, value of each of the substances are given below:

	a	$b \times 10^3$	$C \times 10^7$
Graphite	15.93	6.52	0.0
H ₂ O (g)	30.04	9.920	8.71
CO (g)	26.51	7.68	11.71
H ₂ (g)	29.04	-0.836	20.09

6.0. BOND ENTHALPIES AND ESTIMATION OF ENTHALPIES OF FORMATION

Bond enthalpy is a useful concept in thermochemistry. It finds application in the calculation of standard enthalpy of formation and standard enthalpy of reaction of many compounds.

In a molecule, atoms are linked through chemical bonds. When a molecule decomposes into atoms, the bonds are broken and the enthalpy increases. This is also defined as the enthalpy of atomization, ΔH_{atom} , and is always positive. For example, the enthalpy of the following reaction is the enthalpy of atomization of ethane gas:



Enthalpy of atomization is the enthalpy change accompanying a reaction in which a molecule is shattered into its component atoms.

Enthalpy of atomization of graphite is useful in the calculation of standard enthalpy of formation of organic compounds.

The significance of bond enthalpy in deciding the bond strength has been discussed in Unit 3 of Atoms and Molecules course.

On analysis of ΔH_{atom} for a large number of such reactions, it has been found that specific values of bond enthalpies may be assigned to different types of bonds (Table). These bond enthalpies correspond to the decomposition of a molecule in the gaseous state to atoms in the gaseous state. Certain substances in the solid state when sublimed are converted into gaseous atoms. Thus, graphite when heated is converted into gaseous atoms, and the heat required for one mole can be called the molar enthalpy of atomization of graphite which is equal to. 717 kJ

mol^{-1} . If graphite is considered the reference state for carbon, then the atomization can be written as follows:



Table 1.1 Bond Enthalpies

Bond	$\frac{\text{B}}{\text{KJ mol}^{-1}}$	Bond	$\frac{\text{B}}{\text{KJ mol}^{-1}}$	Bond	$\frac{\text{B}}{\text{KJ mol}^{-1}}$
H – H	436	C – F	484	C = C	813
O – H	463	C – Cl	338	N – N	163
C – H	412	C – Br	276	N = N	409
F – F	155	C – I	238	N = N	945
Cl – Cl	242	C – C	348	O – O	146
Br – Br	193	C = C ^a	612	O = O	497
I – I	151	C = C ^b	518	F – H	565
		C – O	358	Cl – H	431
		C = O	745	Br – H	366
				I – H	299

a – in alkenes

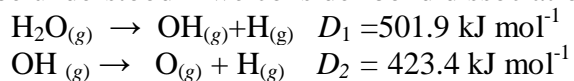
b – in aromatic compounds

The enthalpies of atomization of, some more elements which become atomized on sublimation are given: in Table 1.2

Table. 1.2: Standard enthalpies of Atomization at 298.15 K

Substance	$\frac{\Delta H_{\text{atom}}^{\circ}}{\text{KJ mol}^{-1}}$
C (graphite)	717
Na (s)	108
K (s)	90
Cu (s)	339

It should be made clear that bond enthalpy is not bond dissociation energy. This could be understood if we consider bond dissociation energy of water:



Bond enthalpy is the average amount of energy required to break one mole of similar bonds present in different gaseous compounds into gaseous atoms.

Note that in the place of bond enthalpy, the enthalpy of atomization is used for carbon (graphite) and other elements in the solid state.

The quantities D_1 , and D_2 are the first and second bond dissociation energies and are different from the bond enthalpy given for O — H in Table 1.1. Again, bond enthalpy is some kind of average of a large amount of experimental data. These are of immense value in estimating the standard enthalpy of formation of a large number of Compounds being synthesized and also for estimating the standard enthalpy of reactions involving these new molecules.

The following steps will help you in the calculation of standard enthalpy of formation from the bond enthalpies and enthalpies of atomization of elements:

- i) First write the stoichiometric equation; then write (the most acceptable) Lewis structure of each of the reactants and the product.
- ii) Use bond enthalpies from Table 1.1 and enthalpies of atomization from Table 1.2 to calculate the heat required to break all the bonds in the reactants and the heat released when the atoms form the product. The bond enthalpy of X-X bond can be denoted as $B(X-X)$ in arithmetic expressions.
- iii) The standard enthalpy of formation

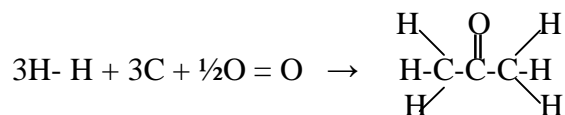
$$= (\text{Heat required to break all the bonds in the reactants}) - (\text{heat released when the atoms form the product}) \quad \dots(1.66)$$
- iv) Bond enthalpy value can be applied to compounds only if these are in gaseous state; if the compounds are in solid or liquid state, molar enthalpies of sublimation or vaporization also must be considered.

Example 4: Estimate the standard enthalpy of formation of acetone vapour and acetone liquid. (Enthalpy of vaporization of liquid acetone = 29 kJ mol^{-1})

Step (i) : The stoichiometric equation for the formation of acetone vapour is

$$3\text{H}_2(\text{g}) + 3\text{C}(\text{graphite}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{C}_2\text{H}_6\text{CO}(\text{g}) \quad \dots(1.67)$$

In terms of Lewis structures, the equation is given below:



Step (ii): The heat required to atomize the reactants
 $= 3B(\text{H}-\text{H}) + 3\Delta_{\text{atom}}H(\text{graphite}) + \frac{1}{2}B(\text{O}=\text{O})$
 $= [(3 \times 346) + (3 \times 717) + \frac{1}{2}(497)]\text{KJ}$
 $= 3708 \text{ KJ}$

The heat released when the atoms form the product
 $= 6B(\text{C}-\text{H}) + 2B(\text{C}-\text{C}) + B(\text{C}=\text{O})$
 $= [(6 \times 412) + (2 \times 348) + 745]\text{kJ}$
 $= 3913 \text{ kJ}$

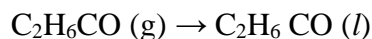
Step (iii): $\Delta_f H^\circ(\text{acetone(g)}) = (3708-3913) \text{ kJ mol}^{-1}$
 $= -205 \text{ kJ mol}^{-1}$

Hence; the standard enthalpy of formation of acetone vapour is -205 kJ mol^{-1} and, the actual value is -216 kJ mol^{-1} .

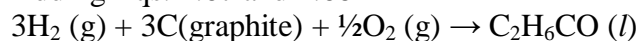
Step (v): Let us now calculate the standard enthalpy of formation of liquid acetone. The condensation of acetone (l), from acetone (g) can be represented by Eq. 7.29.

Note that for condensation of acetone (g), the enthalpy change

$$= -\Delta H^\circ_{\text{vap}}(\text{acetone}) = -29 \text{ kJ mol}^{-1} \quad \dots(1.68)$$



Adding Eqs. 1.67 and 1.68



Hence, $\Delta_f H^\circ(\text{acetone (l)}) = \Delta_f H^\circ(\text{acetone (g)}) - \Delta H^\circ_{\text{vap}}(\text{acetone})$. So, the standard enthalpy of formation of liquid acetone is -234 kJ mol^{-1} . Using the above principles, answer the following SAQ.

Self Assessment Exercise 2

Calculate the standard enthalpy of formation of hydrogen chloride gas. Use Table 1.1

SUMMARY

In this unit, you have been introduced to the first law of thermodynamics. The main aspects of these units are given below:

- The zeroth law of thermodynamics and the first law of thermodynamics have been stated.

- The extensive and intensive variables are explained with examples.
- The terms heat capacity, internal energy and enthalpy have been defined and discussed.
- The formulae for the calculation of work, heat exchange and internal energy change in isothermal and adiabatic processes are derived. Examples are also worked out to explain the use of these formulae.
- Joule-Thomson effect is explained and its importance in the liquefaction of gases is indicated.
- Kirchhoff's equation has been derived and used in the calculation of $\Delta_r H$ at a given temperature knowing its value at any other temperature.
- Bond enthalpy values have been used in the calculation of standard enthalpies of formation.

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 2 Reversible, Irreversible Reactions and Entropy of Change

UNIT 1 Reversible and Irreversible Reactions

- 1.0 Introduction
- 2.0 Objectives:
- 3.0 Reversible and Irreversible Reactions
- 4.0 The Carnot Cycle
- 5.0 Thermodynamic temperature scale

1.0 INTRODUCTION

As described in previous modules it is seen that the transfer of energy between a system and its surroundings takes place through heat and work. This is governed by the first law of thermodynamics which says that increase in the energy of a system must be accompanied by an equal decrease in the energy of the Surroundings and *vice versa*. However, it 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. For example, if a cup of hot tea is left on a table then 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 daily experience that the cup of tea will always cool till it acquires the temperature of the surroundings. Similarly, if a bottle of perfume is opened in a room, the perfume spreads throughout the room. The reverse process in which all the perfume vapours are collected in the bottle does not take place. These are examples of what are known as spontaneous processes which are irreversible and proceed only in one direction. Again, according to the first law, there is a direct relationship between heat and work. But it does not tell us whether heat can be completely transformed into work and if so, what is the effect on the system and the surroundings. These aspects are discussed in this Unit

We shall start this unit with the description of Carnot cycle and calculate the efficiency of Carnot engine. This discussion helps us in arriving at the concept of entropy and thermodynamic scale of temperature. We will also show how entropy changes can be used to distinguish between reversible and irreversible cyclic processes. Based on this discussion, the statements of the second law of thermodynamics will be given. The expressions useful in calculating the entropy changes under different conditions will then be derived. We shall finally discuss the physical meaning of entropy. Based on this unit, we can conclude that all spontaneous changes must be accompanied by entropy increase. In the next unit, we shall examine this aspect in a more detailed way.

2.0 Objectives

After studying this unit, you should be able to;

- differentiate between reversible and irreversible processes based on the value of q
- describe Carnot cycle and derive an expression useful in calculating the efficiency of a Carnot engine,

3.0 REVERSIBLE, IRREVERSIBLE AND CYCLIC PROCESSES

As already mentioned in Unit 1, all thermodynamic properties are state functions and, are independent of the path adopted by the system. Also, the internal energy change of a system is given by Eq. 6. 8 as $\Delta U = q + w$. Here ΔU is independent of the path chosen but q and w certainly depend upon it. Thus for the same ΔU , different values of q and w are possible by bringing about the process in different ways. It was also mentioned that 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 and an irreversible process in which ΔU is same. No matter how we carry out the process (reversible or irreversible), ΔU depends only upon the initial and final states of the system. Thus

$\Delta U = q_{\text{rev}} + w_{\text{rev}}$ for reversible process
 and $\Delta U = q_{\text{rev}} + w_{\text{irrev}}$ for irreversible process
 and so $q_{\text{rev}} + w_{\text{rev}} = q_{\text{rev}} + w_{\text{irrev}}$

We know that the work done **by** a system **under reversible conditions** ($-w_{\text{rev}}$) is larger than the work done by a system **under irreversible conditions** ($-w_{\text{irrev}}$).

$$\text{i.e.,} \quad -w_{\text{rev}} > -w_{\text{irrev}}$$

$$\text{Hence,} \quad w_{\text{rev}} < w_{\text{irrev}}$$

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 mentioned above are fairly different. Also, let us assume that the processes are not adiabatic so that q_{rev} or q_{irrev} is not equal to zero. Using Eqs. 2.3 and 2.5, we can write,

$$q_{\text{rev}} > q_{\text{irrev}}$$

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

conditions. This relationship will be used by us in Sec. 8.6 while calculating the entropy changes of isolated systems.

Now let us consider ΔU , q and w values of a system in a cyclic process. As defined in Unit 1, a cyclic process is one in which the system after under going any number of processes return to its initial state. This means that $\Delta U = 0$; hence, the work system during all these processes should be equal to the heat absorbed by the system.

$$\text{i.e., } q = q_1 + q_2 + \dots = -(w_1 + w_2 + \dots) = -w$$

Where q any w are the heat absorbed and work done on the system in the entire cyclic processes consisting of several processes; in the individual processes, q_1 , q_2 etc., are the heat absorbed by the system and, w_1 , w_2 etc., are the work done on the system.

Using Example 1 discussed below, you can understand the validity of Eqs. 2.5 and 2.6.

Example 1

1.00×10^2 mol of an ideal gas at 3.00×10^2 K temperature and 6.00×10^6 Pa pressure occupies $4.16 \times 10^{-2} \text{ m}^3$ 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 m^3 and 3.00×10^5 Pa: (a) Isothermal reversible conditions (b) isothermal irreversible conditions.

Solution

In an isothermal process, for an ideal gas, $\Delta U = 0$

Hence j using Eq. 1.8, $q = -w$

i.e., Heat absorbed by j the gas = - (work done on the gas)

This equation is applied for both the processes discussed below.

The work done on the system is given the symbol, w . Since work done by the system is obtained by reversing the sign of the work done on the system, work done by the system

$$= -w$$

Work done by the system under reversible conditions

$$= -w_{\text{rev}}$$

Work done by the system under irreversible conditions

$$= -w_{\text{irrev}}$$

The transformation of Eq.2.4 to Eq. 2.5 becomes clear, once we understand the following relationship between numbers:

$$\begin{aligned} -3 &> -4 \text{ and} \\ 3 &< 4 \end{aligned}$$

- (a) Let us first calculate q_{rev} and w_{rev} using Eq. 1.18 for the isothermal reversible expansion.

$$\begin{aligned}
 q_{\text{rev}} = -w_{\text{rev}} &= -2.303 nRT \log \frac{V_1}{V_2} \\
 &= 2.303 nRT \log \frac{V_2}{V_1} \\
 &= 2.303 \times 1.00 \times 10^2 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.00 \times 10^2 \text{ K} \log \frac{0.832 \text{ m}^3}{4.16 \times 10^{-2} \text{ m}^3}
 \end{aligned}$$

$$\begin{aligned}
 &= 7.47 \times 10^5 \text{ J} \\
 \left. \begin{array}{l} \text{Hence, the heat absorbed by the gas} \\ \text{during isothermal reversible} \\ \text{expansion } (q_{\text{rev}}) \end{array} \right\} &= 7.47 \times 10^5 \text{ J}
 \end{aligned}$$

$$\text{and the work done on the gas } (w_{\text{rev}}) = -7.47 \times 10^5 \text{ J}$$

- (b) Let us calculate q_{irrev} and w_{irrev} for the isothermal irreversible process using Eq. 1.13; in this process, the final pressure of the gas is equal to the external pressure (p_{ext}).
Hence, using Eq. 1.13,

$$\begin{aligned}
 q_{\text{irrev}} = -w_{\text{irrev}} &= p_{\text{ext}} (V_2 - V_1) \\
 &= 3.00 \times 10^5 \text{ Pa} (0.832 \text{ m}^3 - 0.0416 \text{ m}^3) \\
 &= 3.00 \times 10^5 \times 0.7904 \text{ J} \\
 &= 2.37 \times 10^5 \text{ J}
 \end{aligned}$$

You can compare q and w values in the above two cases to verify the validity of Eqs. 2.5 and 2.6.

$$\begin{aligned}
 w_{\text{rev}} &= -7.47 \times 10^5 \text{ J}; w_{\text{irrev}} = -2.37 \times 10^5 \text{ J} \\
 \text{Hence, } w_{\text{rev}} &< w_{\text{irrev}} \text{ as per Eq. 8.5} \\
 q_{\text{rev}} &= 7.47 \times 10^5 \text{ J}; q_{\text{irrev}} = 2.37 \times 10^5 \text{ J} \\
 \text{Hence, } q_{\text{rev}} &> q_{\text{irrev}} \text{ as per Eq. 2.6}
 \end{aligned}$$

4.0 THE CARNOT CYCLE

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

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

Such an engine is known as Carnot engine. The temperature of the source (T_H) is higher than that of the sink (T_C). The source and the sink are assumed to be of infinite heat capacity; that is, the temperatures of the source and the sink are not affected by small amounts of heat exchange.

Carnot showed that the entire amount of the heat absorbed cannot be converted into work in a cyclic process, no matter how ideal the heat engine is. He deduced that only a fraction of the total heat absorbed is converted into work and this fraction is known as the efficiency of the Carnot engine. Let us now derive an equation useful in calculating its efficiency.

For the sake of simplicity, let us assume that the engine consists of a cylinder and a piston containing one mole of an ideal gas in between the two. The cylinder has perfectly insulated walls and a perfectly conducting base; the piston is frictionless. It is only for the sake of convenience that we have considered that the engine has ideal gas actually there can be any suitable fluid. We make use of the following expressions from Unit 1 (for one mole of the gas) in this section.

$$w_{\text{isothermal}} = RT \ln \frac{V_{\text{initial}}}{V_{\text{final}}} \quad \dots\dots(\text{Eq. 1.17})$$

$$w_{\text{adiabatic}} = \bar{C}_V (T_{\text{final}} - T_{\text{initial}}) \quad \dots\dots(\text{Eq. 1.53})$$

where w is the work done on the system and \bar{C}_V is the molar heat capacity of the gas.

The plot of the pressure-volume data is shown in Fig.2.1

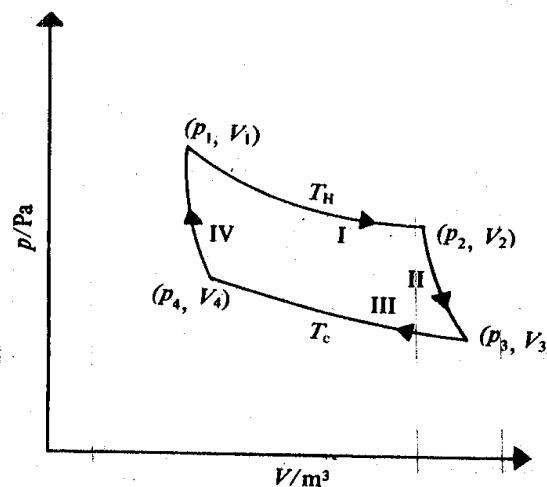


Fig: 2.1 Carnot cycle

The Carnot cycle operation can be described by the following four steps:
 (1) Isothermal Expansion (2) Adiabatic expansion (3) Isothermal compression and
 (4).Adiabatic compression. Let us discuss them one by one.

Step I: Isothermal Expansion

Initially the gas has pressure p_1 and volume V_1 . The cylinder is placed on a heat source maintained at the temperature T_H . The gas is isothermally and reversibly expanded to a volume V_2 and pressure p_2 . Let the work done on the gas be w_1 and the heat absorbed from the source be q_H . In an isothermal process, $\Delta U = 0$. Hence, using Eqs.1.8 and 1.17

$$w_1 = q_H = RT_H \ln \frac{V_1}{V_2} \quad \dots(2.8)$$

$$\text{or} \quad q_H = RT_H \ln \frac{V_2}{V_1} \quad \dots(2.9)$$

Step II: Adiabatic Expansion

The cylinder is now placed on a thermally insulated stand and the gas is adiabatically and reversibly expanded till it attains a pressure p_3 , volume V_3 and temperature T_c . During this period, no heat is absorbed by the system. The work done on the gas, w_2 , as the gas gets cooled from T_H to T_C is given by using Eq 1.53 as,

$$w_2 = \bar{C}_v (T_C - T_H) \quad \dots(2.10)$$

Step III: Isothermal Compression

The cylinder is now placed on a sink at temperature T_C and the gas is isothermally and reversibly compressed to a volume V_4 at pressure p_4 . During the process the work done on the gas is w_3 and the heat evolved to the sink is q_c (or q_c is the heat absorbed from the sink).

$$\text{Using Eqs. 1.8 and 1.17, } w_3 = -q_c = RT_C \ln V_3/V_4 \quad \dots(2.11)$$

$$\text{or } q_c = RTC \ln \frac{V_4}{V_3} \quad \dots(2.12)$$

Step IV: Adiabatic Compression

In the last step, the cylinder is again placed on an insulating stand and the gas is adiabatically and reversibly compressed until it reaches its initial state of volume

V_1 , and temperature T_H . Hence the work done on the gas, w_4 is given by Eq. 1.53 as,

$$w_4 = C_v (T_H - T_C) \quad \dots(2.13)$$

The net work done on the system

$$w = w_1 + w_2 + w_3 + w_4 \quad \dots(2.14)$$

$$\text{or } w = RT_H \ln V_1/V_2 + \bar{C}_v (T_C - T_H) + RT_C \ln V_3/V_4 + \bar{C}_v (T_H - T_C) \quad \dots(2.15)$$

$$\text{i.e. } w = RT_H \ln V_1/V_2 + RT_C \ln V_3/V_4 \quad \dots (2.16)$$

Eq. 1.48 of Unit 1 can be applied to relate the initial and final values of volume and temperature of the two adiabatic processes described in steps II and IV.

Applying Eq. 1.48 to Step II we get,

$$\frac{T_C}{T_H} = \left(\frac{V_2}{V_3} \right)^{\gamma-1}$$

Similarly applying Eq. 1.48 to Step IV, we get,

$$\frac{T_H}{T_C} = \left(\frac{V_4}{V_1} \right)^{\gamma-1} \text{ or } \frac{T_C}{T_H} = \left(\frac{V_1}{V_4} \right)^{\gamma-1}$$

$$\text{Hence } \left(\frac{V_2}{V_3} \right)^{\gamma-1} = \left(\frac{V_1}{V_4} \right)^{\gamma-1} \quad \dots(2.17)$$

$$\text{i.e. } \frac{V_2}{V_3} = \frac{V_1}{V_4}$$

$$\text{or } \frac{V_3}{V_4} = \frac{V_2}{V_1}$$

$$\text{Using this in Eq. 8.16, } w = RT_H \ln \frac{V_1}{V_2} + RT_C \ln \frac{V_2}{V_1}$$

$$\text{Hence, total work done on the system} = w = R (T_H - T_C) \ln V_1/V_2 \quad \dots(2.18)$$

$$\text{or total work done by the system, } = w' = -w = R (T_H - T_C) \ln V_2/V_1 \quad \dots(2.19)$$

since work done by the system = — (work done on the system)

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

The total heat absorbed by the system is,

$$q = q_H + q_C \quad \dots(2.20)$$

As expected, q turns out to be equal to $-w$ or w' since for the overall cyclic process, $\Delta U = 0$

$$\text{Hence, } q = q_H + q_C = w' = -w = R (T_H - T_C) \ln V_2/V_1 \quad \dots(2.21)$$

It may however be noted that out of the heat q_H , ($=RT_H \ln V_2/V_1$ as per Eq. absorbed from the source, only some of it is converted into useful work and the rest is lost to the sink. Let us now calculate w'/q_H , i.e., the ratio between the total work done by the system during one cycle and the heat absorbed in the first step. This quantity is called the efficiency ' η ' of a Carnot engine.

$$\text{Efficiency } (\eta) = \frac{\text{Total work done by the system}}{\text{(Heat Absorbed from the source at higher temperature)}} = \frac{w'}{q_H} \quad \dots(2.22)$$

Using Eqs 2.9 and 2.21

$$(\eta) = \frac{q_H + q_C}{q_H} = \frac{R (T_H - T_C) \ln V_2/V_1}{RT_H \ln V_2/V_1} \quad \dots(2.23)$$

$$(\eta) = \frac{q_H + q_C}{q_H} = \frac{(T_H - T_C)}{T_H} \quad \dots(2.24)$$

Since T_C and T_H are always positive and T_C/T_H is less than one, Eq. 2.24 can be rearranged as follows:

$$(\eta) = 1 - \frac{T_C}{T_H} = 1 + \frac{q_C}{q_H} < 1 \quad \dots(2.25)$$

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

This means that efficiency is always less than one, i.e., all the heat absorbed at a higher temperature is not converted into work. It is also clear that efficiency will be more if the ratio T_C/T_H is small. Thus, for efficient working of the engine, it should absorb heat at as high a temperature as possible and reject it at as low a temperature as possible. It should also be noted that efficiency is independent of the nature of the fluid. This is called Carnot theorem which can also be stated as:

In all cyclic engines working between the same temperatures of the source and the sink, the efficiency is same.

It must be pointed out that in the Carnot cycle, all processes have been carried out reversibly. Hence, maximum and minimum amount of work are involved in expansion and compression, respectively; this implies that there cannot be any engine more efficient than Carnot engine. In actual engines, there is irreversibility due to sudden expansion and compression and also due to the friction of the piston.

Let us work out an example to show the use of Eq. 2.24

Example 2

A Carnot engine works between 3.00×10^2 K and 4.00×10^2 K. Calculate its efficiency.

Solution

$$T_H = 4.00 \times 10^2 \text{ K} \quad T_C = 3.00 \times 10^2 \text{ K}$$

$$\text{Using Eq. 8.24 } \eta = \frac{T_H - T_C}{T_H} = \frac{(4.00 \times 10^2 - 3.00 \times 10^2) \text{ K}}{4.00 \times 10^2 \text{ K}}$$

$$= 0.250$$

Using the data given in this example, answer the following SAQ.

Self Assessment Exercise 1

If the Carnot engine mentioned in Example 2 absorbs 8.00×10^2 J heat from the source, calculate the work done by the engine and the heat rejected to the sink.

5.0 THERMODYNAMIC TEMPERATURE SCALE

For an engine of the type discussed above, both the efficiency and the ratio q_C/q_H can be easily calculated by measurement of the work and heat changes involved. The ratio, q_C/q_H , as shown above, depends only on the temperatures T_C and T_H and is completely independent of the properties of any particular substance. Thus, it is possible to establish a scale of temperature — the absolute or thermodynamic scale — which is not dependent on any particular substance.

We can see from Eq. 2.25, that if $T_C = 0$, $\eta = 1$. We can now define absolute zero as that temperature of the sink at which the efficiency of a Carnot engine will be unity. The size of the degree on this scale is the same as that on the centigrade scale. The Kelvin unit is named in honour of Lord Kelvin, who arrived at the thermodynamic scale of temperature based on the properties of reversible heat engines.

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 2 Reversible, Irreversible Reactions and Entropy of Change

Unit 2 Entropy of Change

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Entropy
- 4.0 Entropy changes in isolated system
- 5.0 Second law of Thermodynamics
- 6.0 Entropy changes during expansion and compression

2.0. Objectives

At the end of the lesson, students should be able to;
define the term entropy

- State the second law of thermodynamics,
- calculate the entropy changes for isothermal and non isothermal processes,

3.0 ENTROPY

The efficiency of an engine working on the principle of Carnot cycle is of immense use to engineers; but, its major use in physics and chemistry is in the discussion and understanding of the second law of thermodynamics. It leads to the

The following comparison may help you in understanding the transformation of Eq. 2.24 into Eq.

Eq. 2.24

Eq. 2.26

q_H

q_2

q_C

q_1

T_H

T_2

T_C

T_1

$$\left(\frac{q_H + q_C}{q_H} \right) = \left(\frac{T_H - T_C}{T_H} \right) \quad \left(\frac{q_2 + q_1}{q_2} \right) = \left(\frac{T_2 - T_1}{T_2} \right)$$

If in a Carnot engine, heat q_2 is absorbed at the higher temperature T_2 and q_1 is absorbed at the lower temperature T_1 (actually q_1 will be a negative quantity since heat is rejected) then, according to Eq. 8.24,

$$\frac{q_2 + q_1}{q_2} = \frac{T_2 - T_2}{T_2} \quad \dots(2.26)$$

$$\text{or } 1 + q_1/q_2 = T_1/T_2 \quad \dots(2.27)$$

$$\text{i.e., } q_1/T_1 =$$

Hence

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \quad \dots(2.28)$$

Thus, the sum of such quantities as obtained by dividing the heat absorbed reversibly by the temperature is zero over a complete Carnot Cycle.

Any reversible cyclic process can be broken into a large number of infinitesimal Carnot cycles (as in Fig. 2.7). If in each such small Carnot cycle, heat dq_1 is absorbed at temperature T_1' and dq_2 absorbed at T_2' , then for each small Carnot cycle,

$$dq_1/T_1' + dq_2/T_2' = 0 \quad \dots(2.30)$$

Summing these over all the cycles we can write in general, sum of $\frac{dq_i}{T_i}$ terms

over all the cycles = 0

$$\dots(2.31)$$

where 'i' stands for an individual process of expansion or contraction 'm', each cycle. Since the summation is continuous, we can replace the summation by integration and have,

$$\oint dq_{\text{rev}}/T = 0 \quad \dots(2.32)$$

where dq_{rev} is the heat absorbed reversibly at a temperature in an infinitesimal step in the cyclic process and \oint is the integral over a whole cycle.

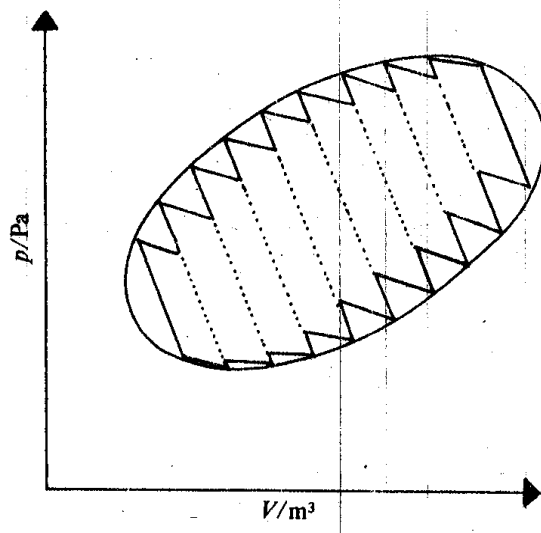


Fig. 2.2 Infinitesimal; Carnot cycles.

Now consider a system going in a reversible manner from an initial state A to an intermediate state B and then back to A via another path (Fig. 2.3) This cyclic

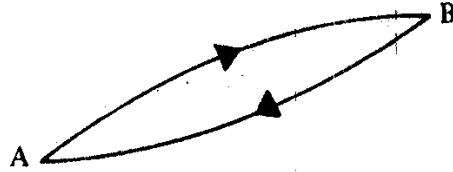


Fig. 2.3 The cyclic change ABA.

process can be broken up into a large number of Carnot cycles. Starting from A and following all these cycles we may reach A once again. The paths inside the figure cancel out each other and only a zigzag path is left) The larger the number of Carnot cycles, the closer will be the resemblance between this zigzag path and the overall path ABA.

Hence, in the entire cycle,

$$\text{sum of } dq_{rev}/T \text{ terms} = \sum dq_{rev}/T = 0 \quad \dots(2.33)$$

where once again dq_{rev} is the heat absorbed reversibly at temperature T in an infinitesimal process. We can break this up into two parts, i.e., one in which we go from A to B and the other in which we go from B to A. Thus,

$$\sum_{\text{Cycle}} dq_{rev}/T = \sum_{A \rightarrow B} dq_{rev}/T = \sum_{B \rightarrow A} dq_{rev}/T = 0 \quad \dots(2.34)$$

or in terms of integrals,

$$\int dq_{rev}/T = \int_A^B dq_{rev}/T + \int_B^A dq_{rev}/T = 0 \quad \dots(2.35)$$

and so

$$\int_A^B dq_{rev}/T = - \int_B^A dq_{rev}/T \quad \dots(2.36)$$

The symbol $\sum_{\text{Cycle}} \frac{dq_{rev}}{T}$ means

Summation of $\frac{dq_{rev}}{T}$ terms over the entire circle.

The term $\sum_{A \rightarrow B} dq_{rev}/T$ means

Summation of the dq_{rev} term for

The change from A to B.

Thus, the quantity $\int_A^B dq_{rev}/T$ is not dependent on the path chosen and is only

dependent on the initial and final states of the system. This means that it represents a change in some thermodynamic property. This property is called entropy (S), and we write,

$$dq_{rev}/T = dS \quad \dots(2.37)$$

$$\text{Thus, } \int dS = 0 \quad \dots(2.38)$$

Also if we represent the entropy of the initial state A as S_A and that of the final state B as S_B , then

$$\Delta S = S_B - S_A = \int_A^B dq_{rev}/T \quad \dots(2.39)$$

Let us relate the changes in internal energy and enthalpy to entropy change.

If we now put $dq = TdS$ (from Eq. 8.37), $dU = nC_v dT$ (from Eq. 6.26) and $dw = -pdV$ (from Eq. 6.12) in Eq. 6.17, we get Eq. 8.40. ...(1.7)

$$dU = dq + dw$$

Hence

$$dU = n\bar{C}_v dT = TdS - pdV \quad \dots(2.40)$$

AS per Eq. 1.29 of Unit 1

$$H = U + pV$$

Differentiation of this gives,

$$dH = dU + pdV + Vdp$$

$$\text{using Eq. 8.40, } dH = TdS - pdV + pdV + Vdp = TdS + VdP \quad \dots(2.41)$$

Eqs. 2.40 and 2.41 are the combined mathematical statements of the first and second laws of thermodynamics. The first law of thermodynamics is concerned with the conservation of energy and the second; law of thermodynamics introduces the concept of entropy.

It is worth mentioning that the entropy change in a system is given by,

$$dS = \frac{dq_{rev}}{T}$$

This means that the entropy change in a system is to be calculated assuming the process to be reversible, irrespective; of the fact that the process is reversible or not. This fact will be highlighted in the next section.

On the basis of the above ideas, answer the following SAQ.

Self Assessment 2

Calculate the change of entropy when 2.40×10^4 J of heat is transferred reversibly and isothermally to a system at 3.00×10^2 K.

4.0 ENTROPY CHANGES IN ISOLATED SYSTEMS

We are now interested in estimating the entropy change in an isolated system where cyclic processes of isothermal expansion and compression take place. Such cyclic processes can occur in two ways; one in which both expansion and compression are reversible and another, in which one is irreversible while the other is reversible. Let us consider an isolated system consisting of a cylinder which contains a gas between it and a smooth air tight piston and is placed in a heat reservoir.

Isothermal Reversible Expansion and Reversible Compression

Let the gas (system) undergo isothermal reversible expansion from volume V_1 to V_2 at a temperature T . In this reversible process, the gas absorbs heat, q_{rev} , from the reservoir; the entropy change of the system, ΔS_1 , is given by,

$$\Delta S_1 = \frac{q_{rev}}{T} \quad \dots(2.43)$$

Since the reservoir also loses heat q_{rev} in a reversible way, the entropy change, ΔS_2 , of the reservoir is given by,

$$\Delta S_2 = \frac{-q_{rev}}{T} \quad \dots(2.44)$$

The total entropy change of the isolated system, ΔS_a , in this reversible expansion process is, given by,

$$\Delta S_a = \Delta S_1 + \Delta S_2 = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0 \quad \dots(2.45)$$

Let the gas undergo isothermal reversible compression back to its original state. Assume that during this compression, heat lost from the system and the heat gained by the reservoir are both reversible. Then, the total entropy change (ΔS_b) of the isolated system mentioned above, during reversible compression, is also equal to zero.

$$\Delta S_b = 0 \quad \dots(2.46)$$

Hence, ΔS in this cyclic process = $\Delta S_a + \Delta S_b = 0$... (2.47)

The entropy change in a process is calculated by dividing the heat change under reversible condition by temperature, whether or not the process is reversible.

This means that the total entropy change in a Reversible cycle is zero. Let us now see how the entropy changes in a cyclic process involving an irreversible stage.

Isothermal Irreversible Expansion and Reversible Compression

Let the gas undergo isothermal irreversible expansion from a volume V_1 , to V_2 at a temperature T . In this process, let us assume that the gas absorbs heat q irreversibly whereas the reservoir loses the same heat reversely. However, the entropy change of the system (ΔS_1) is still given by Eq. 2.43 per definition.

$$\Delta S_1 = \frac{q_{rev}}{T} \quad \dots (2.48)$$

But since the reservoir loses heat q reversibly, the entropy change of the reservoir, ΔS_2 , is given by,

$$\Delta S_2 = \frac{-q}{T} \quad \dots (2.49)$$

Hence the total entropy change of the isolated system, ΔS_a , in this irreversible expansion process is given by,

$$\Delta S_a = \Delta S_1 + \Delta S_2 = \frac{q_{rev}}{T} - \frac{q}{T} > 0 \quad \dots (2.50)$$

Since $q_{rev} > q$ as per Eq. 2.6

Let the gas now undergo isothermal reversible compression such that the heat loss by the system and the heat gain by the surroundings are both reversible. The total entropy change of the isolated system, ΔS_b , in this reversible compression process is given by,

$$\Delta S_b = 0 \quad \dots (2.51)$$

Hence, the total entropy change of the isolated system over the whole cycle

$$= \Delta S_a + \Delta S_b > 0 \quad \dots (2.52)$$

Hence for any reversible process or cycle $\Delta S_{total} = 0$... (2.53)

For any irreversible process or cycle $\Delta S_{total} > 0$... (2.54)

In other words, the second law of thermodynamics suggests that the entropy must increase in an irreversible or a spontaneous process. Since all natural processes are irreversible, the entropy of the Universe is continuously increasing. The first and the second laws of thermodynamics can be summed up as follows:

The first law : Energy of the universe is constant.

The second law : Entropy of the universe is tending to a maximum.

The fact that the entropy of an isolated system increases in an irreversible process can be illustrated using Example 3.

Example 3

Assume that an ideal gas undergoes isothermal irreversible expansion and is in contact with a heat reservoir inside an isolated system. Using the data given in Example 1, calculate the entropy change of (a) the gas, (b) the heat reservoir and (c) the isolated system as a whole.

Solution

It is true that the gas expands irreversibly and absorbs heat irreversibly from the heat reservoir. But the heat reservoir (or as a rule, the surroundings always) would lose (or gain) the heat reversibly

As per Example 1 (b), the heat Absorbed by the gas under isothermal irreversible conditions $= 2.37 \times 10^5 \text{ J}$.

That is, the gas absorbs $2.37 \times 10^5 \text{ J}$ **irreversibly** from the heat reservoir. But the heat reservoir loses $2.37 \times 10^5 \text{ J}$ **reversibly**.

It is to be remembered that the entropy is a state function and its value is given by dividing the heat change under reversible conditions by temperature.

- a) To calculate the entropy Change of the gas, we have to consider the heat absorbed if the gas were to expand reversibly. Hence, from Example 1, for q value of the gas, we should use $7.47 \times 10^5 \text{ J}$, which is the heat absorbed under reversible conditions but not $2.37 \times 10^5 \text{ J}$. The temperature of the gas is $3.00 \times 10^2 \text{ K}$

Using Eq. 2.43, the entropy change = $\frac{\text{Heat change under reversible conditions}}{\text{Temperature}}$

$$= \frac{7.47 \times 10^5 \text{ J}}{3.00 \times 10^2 \text{ K}} \\ = 2490 \text{ J K}^{-1}$$

- b) The heat reservoir loses $2.37 \times 10^5 \text{ J}$ heat reversibly,

$$\begin{aligned}\text{Using Eq. 2.37, the entropy change} &= \frac{-2.37 \times 10^5 \text{ J}}{3.00 \times 10^2 \text{ K}} \\ \text{of the heat reservoir } (\Delta S_{\text{reservoir}}) &= -790 \text{ J K}^{-1}\end{aligned}$$

The negative sign is due to loss of heat from the heat reservoir.

$$\begin{aligned}\text{c) The total entropy change of the} & \\ \text{isolated system} &= \Delta S_{\text{gas}} + \Delta S_{\text{reservoir}} \\ &= [(2490) + (-790)] \text{ J K}^{-1} \\ &= 1700 \text{ J K}^{-1}\end{aligned}$$

Hence the entropy of the isolated system increases by 1700 J K^{-1} in this irreversible expansion

To calculate the entropy change in the universe for a particular process, we should know the entropy change of the system and of the surroundings. We shall study in Sees. 2.8 to 2.11 the ways of calculating the entropy changes in the system. Let us now see how to calculate the entropy change of the surroundings in any particular process.

The surroundings of a system constitute a huge heat reservoir. Hence, the heat loss or gain from the surroundings (q^{surr}) is always (considered¹ reversible; this is true whether the system behaves reversibly or irreversibly. Let the temperature of the surroundings be T^{surr} .

$$\left. \begin{array}{l} \text{Hence, the entropy change of the} \\ \text{surroundings} \end{array} \right\} = \frac{q^{\text{surr}}}{T^{\text{surr}}}$$

This is true for all types of processes.

If a chemical reaction takes place at constant, pressure with an enthalpy change, ΔH , then $q^{\text{surr}} = -\Delta H$

$$\left. \begin{array}{l} \text{Hence, the entropy change of the} \\ \text{surroundings} \end{array} \right\} = \frac{q^{\text{surr}}}{T^{\text{surr}}} = \frac{-\Delta H}{T^{\text{surr}}}$$

Self Assessment Exercise 3

Calculate the entropy change in the surroundings in the formation of one mole of water from its elements in their standard state at 298.15 K. the standard enthalpy of formation of water is $-285.8 \text{ kJ mol}^{-1}$

(Caution: This entropy change in the surroundings is not related to the entropy of water or entropy of formation of water; see Example 7 in this unit.)

5.0 STATEMENTS OF THE SECOND LAW OF THERMODYNAMICS

What we have studied so far in this unit can be generalised to obtain the statements of the second law of thermodynamics. Three such statements are given below:

1. The entropy of an isolated system tends to increase and reaches a maximum. This implies that the most stable state of an isolated system is the state of maximum entropy. Since the universe may be considered as an isolated system, it follows that the entropy of the universe always increases.
2. It is impossible to transfer heat from a colder body to a hotter body without doing some work. This was postulated by Clausius.
3. According to Kelvin, it is not possible to take heat from a source (i.e., a hot reservoir) and convert all of it into work by a cyclic process without losing some of it to a colder reservoir.

6.0 ENTROPY CHANGES DURING EXPANSION AND COMPRESSION

In general, the entropy change of the system is defined by the entropy of the final state (B) minus the entropy of the initial state (A). This is equivalent to

$$\int_B^A dq_{rev}/T \text{ which at constant temperature can be written as } \frac{1}{T} \int_B^A dq_{rev} = q_{rev}/T,$$

where q_{rev} is the total amount of the heat absorbed reversibly in the process.

Entropy Change in the Isothermal Expansion of an Ideal Gas

If n mol of an ideal gas is isothermally and reversibly expanded from an initial state in which it has pressure p_1 and volume V_1 to the final state of volume V_2 and pressure p_2 , then as shown earlier,

$$q_{rev} = w = nRT \ln V_2/V_1 = nRT \ln p_1/p_2 \quad \dots(2.55)$$

$$\text{and hence, } \Delta S = \left. \begin{aligned} q_{rev}/T &= nR \ln V_2/V_1 = nR \ln p_1/p_2 \\ &= 2.303 nR \log V_2/V_1 = 2.303 nR \log p_1/p_2 \end{aligned} \right\} \quad \dots(2.56)$$

Hence, to calculate the entropy change of an ideal gas during isothermal expansion or compression, n , V_1 and V_2 or p_1 and p_2 must be known.

Example 4

1.00 mol of an ideal gas is compressed isothermally and reversibly from $1.00 \times 10^{-2} \text{ m}^3$ to $1.00 \times 10^{-3} \text{ m}^3$. Calculate the entropy change.

Solution

The numerator and denominator in Eq. 2.56 are interchanged along with a sign change, since $V_2 < V_1$,

$$\begin{aligned}\text{Using Eq. 8.56, } \Delta S &= -2.303 nR \log V_1/V_2 \\ &= -2.303 \times 1.00 \text{ mol} \times 8.314 \text{ J mol K}^{-1} \log \frac{1.00 \times 10^{-2} \text{ m}^3}{1.00 \times 10^{-3} \text{ m}^3} \\ &= -19.2 \text{ J K}^{-1}\end{aligned}$$

Entropy Change During Adiabatic Expansion

An adiabatic expansion involves no heat change which means $\Delta S = 0$ for the system.

Entropy Change of an Idea Gas when it is Expanded Under Conditions which are not Isothermal

Let n mol of an ideal gas be expanded from an initial state of V_1 and T_1 to a final state of V_2 and T_2 . Then according to the first law of thermodynamics (Eq.1.22),

$$\begin{aligned}dq_{rev} &= dU + pdV \\ \text{Using Eq. 1.26, } dU &= n\bar{C}_v dT\end{aligned} \quad \dots(2.57)$$

Where \bar{C}_v is the molar heat capacity of the gas under constant volume conditions.

According to ideal gas equation, $p = \frac{nRT}{V}$

Using the above two expressions in Eq. 2.57,

$$\begin{aligned}dq_{rev} &= n\bar{C}_v dT + nRT dV/V \\ \text{or } TdS &= n\bar{C}_v dT + nRT dV/V\end{aligned} \quad \dots(2.58)$$

$$\text{Hence, } dS = 1/T [n\bar{C}_v dT + nRT \frac{dV}{V}] \quad \dots(2.59)$$

$$= n\bar{C}_v dT/T + nR dV/V \quad \dots(2.60)$$

On integration between the limits $T_1 \rightarrow T_2$, $V_1 \rightarrow V_2$ and $S_1 \rightarrow S_2$

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} n\bar{C}_v dT/T + \int_{V_1}^{V_2} nR dV/V \quad \dots(2.61)$$

Assuming that \bar{C}_v is independent of temperature, we have

$$\begin{aligned}S_2 - S_1 = \Delta S &= n\bar{C}_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1} \\ &= 2.303 n \left(\bar{C}_v \log \frac{T_2}{T_1} + R \log \frac{V_2}{V_1} \right)\end{aligned} \quad \dots (2.62)$$

This is the case when we take T and V to be the variable quantities. Since for an ideal gas p , y and T are related by the ideal gas equation, only two of these are independent Variables.

Now suppose we consider T and p as the variables. Let them change from T_1 to T_2 and p_1 to p_2 during the process. Then these are related to the initial and final volumes V_1 and V_2 as

$$V_2/V_1 = T_2 P_1 / T_1 p_2 \quad \dots(2.63)$$

Hence, from Eq. 8.62, we have

$$\Delta S = n\bar{C}_v \ln T_2/T_1 + nR \ln T_2 P_1 / T_1 p_2 \quad \dots(2.64)$$

$$\Delta S = n\bar{C}_v \ln T_2/T_1 + nR \ln T_2/T_1 + nR \ln p_1/p_2 \quad \dots(2.65)$$

$$= (\bar{C}_v + R)n \ln T_2/T_1 + nR \ln p_1/p_2 \quad \dots(2.66)$$

$$\left. \begin{array}{l} \text{Since } \bar{C}_p - \bar{C}_v = R, \bar{C}_p = R + \bar{C}_v \\ \Delta S = n\bar{C}_p \ln T_2/T_1 + nR \ln p_1/p_2 \end{array} \right\} \quad \dots(2.67)$$

$$\left. \begin{array}{l} = 2.303 n(\bar{C}_p \log T_2/T_1 + R \log p_1/p_2) \end{array} \right\} \quad \dots(2.68)$$

Hence, using Eq. 2.62 or 2.68, we can calculate the entropy change of an ideal gas when its pressure or volume changes due to temperature change. Let us work out an example.

Example 5

1.00 mol of a monoatomic gas initially at 3.00×10^2 K and occupying 2.00×10^{-3} m³ is heated to 3.25×10^2 K and the final volume is 4.00×10^{-3} m³. Assuming ideal behaviour, calculate the entropy change for the process.

Solution

$$\begin{aligned} \text{For a monoatomic gas } C_v = 3/2 R &= 3/2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= 12.47 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$\text{Using Eq. 2.62, } \Delta S = 2.303 n(\bar{C}_v \log T_2/T_1 + R \log V_2/V_1)$$

$$\begin{aligned} &= 2.303 \times 1.00 (12.47 \log \frac{3.25 \times 10^2}{3.00 \times 10^2} + 8.314 \log \frac{4.00 \times 10^{-3}}{2.00 \times 10^{-3}}) \text{ J K}^{-1} \\ &= 6.76 \text{ J K}^{-1} \end{aligned}$$

Self Assessment Exercise 4

Show that under isothermal conditions, Eqs. 2.62 and 2.68 reduce to the form of Eq. 8.56

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 2 Reversible, Irreversible Reactions and Entropy of Change

Unit 3 Entropy of Mixing

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Entropy of Mixing
- 4.0 Entropy change in phase transitions
- 5.0 Entropy change in chemical reactions

2.0 Objectives

At the end of this unit, you should be able to;
derive an expression useful in calculating entropy of mixing,

- calculate the entropy changes in phase transitions and chemical reactions,

3.0 ENTROPY OF MIXING

Suppose that n_1 mol of an ideal gas initially present at pressure p and n_2 mol of another ideal gas also at the same initial pressure p are mixed at a constant temperature so that the total pressure is also p . This is possible by using a vessel of suitable volume. Let the partial pressure of the first gas in the mixture be p_1 and the partial pressure of the other gas be p_2 . Then the change in entropy for the first gas from Eq. 2.56 is

$$\Delta S_1 = n_1 R \ln p/p_1 \quad \dots(2.69)$$

Similarly for the other gas,

$$\Delta S_2 = n_2 R \ln p/p_2 \quad \dots(2.70)$$

The total entropy of mixing, ΔS_{mix} , is hence

$$\Delta S_{\text{mix}} = \Delta S_1 + \Delta S_2 = n_1 R \ln p/p_1 + n_2 R \ln p/p_2 \quad \dots(2.71)$$

If the mole fractions of the gases in the mixture are x_1 and x_2 respectively, then according to Dalton's law of partial pressures,

$$\Delta S_{\text{mix}} = n_1 R \ln p/x_1 p + n_2 R \ln p/x_2 p \quad \dots(2.72)$$

$$\Delta S_{\text{mix}} = n_1 R \ln 1/x_1 + n_2 R \ln 1/x_2 \quad \dots(2.73)$$

$$\begin{aligned}
 &= 2.303 n_1 R \log \frac{1}{x_1} + 2.303 n_2 R \log \frac{1}{x_2} \\
 \text{Hence, } \Delta S_{\text{mix}} &= 2.303 R (n_1 \log \frac{1}{x_1} + n_2 \log \frac{1}{x_2}) \quad \dots(2.74) \\
 &= -2.303 R (n_1 \log x_1 + n_2 \log x_2)
 \end{aligned}$$

If we know n_1 , and n_2 , ΔS_{mix} can be calculated. The mole fractions x_1 and x_2 are less than one, since $x_1 + x_2 = 1$; as a result of this, $\log 1/x_1$ and $\log 1/x_2$ are positive. Hence, ΔS_{mix} is positive.

Partial pressure of a gas = Total pressure \times mole fraction of the gas
Hence, $p_1 = p x_1$ and $p_2 = p x_2$

Example 6

Calculate the entropy of mixing of 1.00 mol of H_2 with 2.00 mol of O_2 assuming that no chemical reaction occurs.

Solution

$$n_{\text{H}_2} = 1.00 \text{ mol}; \quad n_{\text{O}_2} = 2.00 \text{ mol}$$

$$x_{\text{H}_2} = \frac{n_{\text{H}_2}}{n_{\text{H}_2} + n_{\text{O}_2}} = \frac{1.00 \text{ mol}}{3.00 \text{ mol}} = 0.333$$

Similarly,

$$x_{\text{O}_2} = \frac{2.00 \text{ mol}}{3.00 \text{ mol}} = 0.667$$

$$\text{Using Eq. 2.74 } \Delta S_{\text{mix}} = 2.303 R \left(n_{\text{H}_2} \log \frac{1}{x_{\text{H}_2}} + n_{\text{O}_2} \log \frac{1}{x_{\text{O}_2}} \right)$$

$$\begin{aligned}
 &= 2.303 \times 8.314 \left(1.00 \log \frac{1}{0.333} + 2.00 \log \frac{1}{0.667} \right) \text{ J K}^{-1} \\
 &= 15.88 \text{ J K}^{-1}
 \end{aligned}$$

On the basis of what you have studied in this section, answer the following SAQ.

Self Assessment Exercise 5

Does the entropy of mixing of ideal gases depend on temperature?

(Hint: Examine Eq. 2.74)

4.0 ENTROPY CHANGES IN PHASE TRANSITIONS

The change of matter from one phase (solid, liquid, gas, allotropic form) into another is called phase transition. Such changes take place at definite

temperatures called transition temperatures (melting points, boiling points etc.) at a given pressure. These transitions are accompanied by absorption or evolution of heat (called latent heat). Since absorption or evolution of heat at constant temperature leads to an entropy change, the entropy of transition is given as,

$$\Delta S_{\text{trans}} = q_{\text{rev}}/T = \Delta H_{\text{trans}}/T \quad \dots(2.75)$$

Eq. 2.75 is valid only when the transition takes place in a reversible manner, i.e., when the two phases are in equilibrium.

Thus, when one mole of a solid melts to the liquid phase, the entropy of fusion is given by

$$\Delta S_{\text{fus}} = \frac{\Delta H_{\text{fus}}}{T_f} \quad \dots(2.76)$$

where T_f is the melting point and ΔH_{fus} is the molar enthalpy of fusion. Similarly,

$$\Delta S_{\text{vap}} = \frac{\Delta H_{\text{vap}}}{T_B} \quad \dots(2.77)$$

where T_B is the boiling point and ΔH_{vap} is the molar enthalpy of vaporization.

It is obvious that the entropy of freezing and condensation (vapour into liquid) will be equal to $-\Delta S_{\text{fus}}$ and $-\Delta S_{\text{vap}}$, respectively. ,

In a similar manner, we can define the entropy change accompanying the transition of a substance from an allotropic form to another. If such a transition takes place at a temperature T_{trans} and, ΔH_{trans} is the molar enthalpy of transition, then the entropy change accompany the transition is,

$$\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} \quad \dots(2.78)$$

Thus, in phase transitions, ΔS values can be calculated from the corresponding ΔH values.

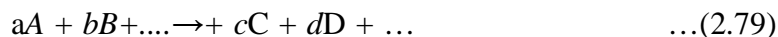
Using the material given above, answer the following SAQ.

Self Assessment Exercise 6

Calculate the entropy of fusion of benzene solid, if its melting point is 279 K and its enthalpy of fusion is 10.6: k J mol⁻¹

5.0 ENTROPY CHANGES IN CHEMICAL REACTIONS

Let us now calculate the entropy change accompanying a general chemical reaction of the type,



We define the entropy change for a reaction ($\Delta_r S$) as the difference between the total entropy of the products and the total entropy of the reactants. Thus, if S_A , S_B ...are the entropies of one mole of reactants, A, B, etc., and S_C , S_D ..., of the products, C, D, etc., then;

$$\Delta_r S = (cS_C + dS_D + \dots) - (aS_A + bS_B + \dots) \quad \dots(2.80)$$

where c , d , a , b ...etc., are the stoichiometric coefficients in Eq. 8.79. The variation of entropy change for a reaction with temperature can be readily deduced from Eq. 2.80 by differentiating with respect to temperature at constant pressure. Hence,

$$\begin{aligned} \left(\frac{\partial(\Delta_r S)}{\partial T} \right)_p &= \left[c \left(\frac{\partial S_C}{\partial T} \right)_p + d \left(\frac{\partial S_D}{\partial T} \right)_p + \dots \right] \\ &\quad - \left[a \left(\frac{\partial S_A}{\partial T} \right)_p + b \left(\frac{\partial S_B}{\partial T} \right)_p + \dots \right] \quad \dots(2.81) \end{aligned}$$

According to Eq. 2.41

$$dH = TdS + Vdp$$

or $C_p dT = TdS + Vdp$

At constant pressure ($dp = 0$),

$$C_p dT = TdS_p$$

or $\frac{dS_p}{dT} = \frac{\bar{C}_p}{T}$

or $\left(\frac{\partial S}{\partial T} \right) = \frac{\bar{C}_p}{T}$

\bar{C}_p is the molar heat capacity of a substance at; constant pressure.

Using the above result in Eq. 2.81,

$$\left(\frac{\partial(\Delta_r S)}{\partial T} \right)_p = \frac{[c\bar{C}_p(C) + d\bar{C}_p(D) + \dots] - [a\bar{C}_p(A) + b\bar{C}_p(B) \dots]}{T} \quad \dots(2.82)$$

$$\left(\frac{\partial(\Delta_r S)}{\partial T} \right) = \Delta C_p / T \quad \dots(2.83)$$

$$\overline{\frac{\partial T}{\partial T}}_p$$

where ΔC_p is the difference between the heat capacities of the products and reactants at constant pressure.

$$\text{or} \quad d(\Delta_r S) = \Delta C_p \frac{dT}{T} \quad \dots(2.84)$$

Assume that $\Delta_r S_1$, and $\Delta_r S_2$ are the entropy change at temperatures T_1 and T_2 and ΔC_p is independent of temperature. Then Eq. 2.84 on integration gives,

$$\int_{\Delta_r S_1}^{\Delta_r S_2} d(\Delta_r S) = \Delta C_p \int_{T_1}^{T_2} \frac{dT}{T} \quad \dots(2.85)$$

$$\text{or} \quad \Delta_r S_2 - \Delta_r S_1 = C_p \ln T_2/T_1 \quad \dots(2.86)$$

Eq. 2.86 is useful in determining $\Delta_r S$ value of a reaction at any particular temperature, if it is known at any other temperature along with C_p values.

Entropy values of substances can be determined using the third law of thermodynamics; we shall study this in the next unit. The entropy values of some of the substances in their standard states at 298.15 K are given in Table 8.1. These are known as standard entropy (S°) values. Similar to the Calculation of $\Delta_r S$ as per Eq. 2.8, we can calculate $\Delta_r S^\circ$ from the standard entropy values of the reactants and the products.

The standard states of the substances will be defined in the next unit.

Table 2.1: Standard Entropy (S°) values at 298.15 K

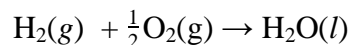
Substance	$S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$	Substance	$S^\circ/\text{J K}^{-1} \text{ mol}^{-1}$
C (graphite)	5.7	C ₆ H ₆ (l)	173.3
C (diamond)	2.4	He (g)	126.2
AgCl(s)	96.2	H ₂ (g)	130.7
AgBr(s)	107.1	Cl ₂ (g)	223.1
Ag(s)	42.6	CO ₂ (g)	213.7
Hg(l)	76.0	O ₂ (g)	205.1

Br ₂ (l)	152.2	CH ₄ (g)	186.3
H ₂ O(l)	69.9		

Example 7

Calculate the standard entropy of formation of H₂O(l) at 298.15 K using Table 2.18.

Solution



The standard entropy of formation of water ($\Delta_f S^\circ(\text{H}_2\text{O})$) can be calculated using Eq. 2.80. Note that the substances are in their standard states at 298.15 K; hence S° values are used instead of S .

$$\begin{aligned}\Delta_f S^\circ(\text{H}_2\text{O}) &= S^\circ(\text{H}_2\text{O}) - (S^\circ(\text{H}_2) + \frac{1}{2} S^\circ(\text{O}_2)) \\ &= [69.9 - (130.7 + (\frac{1}{2} \times 205.1))] \text{J K}^{-1}\end{aligned}$$

Since one mole of water is formed,

$$\Delta_f S^\circ(\text{H}_2\text{O}) = -163.4 \text{ J mol}^{-1} \text{ K}^{-1}$$

Self Assessment Exercise 7

- Calculate the entropy change of the system for the combustion of one mole of methane gas at 298.15 K; use Table 8.1.
- Calculate the entropy change; of the surroundings for the combustion of one mole of methane gas at 298.15 K, if the molar enthalpy; of combustion of methane is $-8.90 \times 10^5 \text{ J mol}^{-1}$.

2.12 SUMMARY

In this unit, we described the second law of thermodynamics and the concept of entropy. We started the unit indicating the main aspects of reversible, irreversible and cyclic processes. We then described Carnot cycle and derived an equation for calculating its efficiency. Using this equation, the concept of entropy was arrived at. The expressions were derived for calculating the {entropy changes in different physical processes. The {method of calculation of entropy changes in chemical reactions was indicated towards the end of the unit.

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 3 Spontaneous and Nonspontaneous Processes

UNIT 1 FREE ENERGY FUNCTIONS

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Spontaneous and Nonspontaneous Processes
- 4.0 Helmholtz Free Energy and Gibbs Free Energy
- 5.0 Changes in A and G

1.0 INTRODUCTION

In Units 1 and 2, we studied the application of the first law of thermodynamics in calculating the enthalpy and internal energy changes of the reactions. Such energy calculations do not tell us whether a given reaction is feasible or not. In Unit 2 the concept of entropy was introduced through the second law of thermodynamics; we studied that the total entropy value of the system and the surroundings can help us in deciding the spontaneity of a reaction. But the main difficulty is that it is not always possible to estimate the entropy change of: the Surroundings.

In this unit, we will introduce two more thermodynamic quantities known as Gibbs free energy (G) and Helmholtz free energy (A). We shall also discuss the importance of the Gibbs free energy change (ΔG) in predicting whether a given process (physical or chemical) will occur spontaneously or not. We shall derive Maxwell relations and state their applications. We shall then arrive at Gibbs-Helmholtz and Clausius-Clapeyron equation. We shall also explain the applications of these two equations. We shall then examine the criteria for spontaneity. We shall illustrate the utility of the Gibbs free energy of formation of substances in calculating the reaction free energies.

Finally we shall explain the third law of thermodynamics and discuss its application in calculating the entropies of the substances.

Objectives

After studying this unit, you should be able to:

- distinguish between spontaneous and nonspontaneous processes,
- define Helmholtz free energy (Δ) and Gibbs free energy (G),
- Calculate ΔA and ΔG for different processes,

3.0 SPONTANEOUS AND NONSPONTANEOUS PROCESSES

In this section, we will explain how spontaneous and nonspontaneous processes

differ. Let us try to understand what a spontaneous process is. We know that

- i) water flows down the hill spontaneously ;
- ii) a gas expands spontaneously into vacuum
- iii) heat is conducted spontaneously from the hot end of a metal bar to the colder end until the temperature of the bar is same throughout
- iv) a gas diffuses spontaneously into another gas.

But the reverse of the above changes does not occur spontaneously. All natural processes occur spontaneously. Thus we can define that a spontaneous or a natural process occurs in a system by itself. No external force is required to make the process continue. On the other hand a nonspontaneous process will not occur unless some external force is continuously applied. A chemist is always interested in knowing whether, under a given set of conditions, a reaction or a process is feasible or not. According to the second law of thermodynamics, $dS \geq \frac{dq}{T}$ in which the equality refers to a system undergoing a reversible process and the inequality refers to an irreversible process. For an isolated system for which $dq = 0$, the above equation is reduced to $dS \geq 0$. In an isolated system, an irreversible change is always spontaneous. This is because in such systems, no external force can interact with the system. Thus, the tendency of entropy of an isolated system to increase can be used as a criterion for a spontaneous change. Is this always true? Let us examine this question. Water freezes to crystalline ice spontaneously at 263 K. Ice is in a more ordered state than water and the entropy decreases in freezing. How do we explain the above process? The answer to this question lies in the fact that we must always consider the total entropy change, *i.e.*, the entropy change of the universe. This entropy change is equal to the sum of the entropy changes of the system and the surroundings.

$$\Delta S_{\text{Total}} = \Delta S_{\text{Universe}} = \Delta S_{\text{System}} + \Delta S_{\text{surroundings}} \quad \dots (3.1)$$

Eq. 9.1 is very difficult to apply for testing the spontaneity of a process. This is so since for evaluating the total entropy change, we have to evaluate ΔS for the surroundings also. In many cases, such calculations are extremely difficult and sometimes not even practical. Therefore, it will be advantageous if we can redevelop the criteria for spontaneity in such a manner that only changes in the properties of the system are considered. For this purpose, we define two energy functions called Helmholtz free energy and Gibbs free energy in the next section.

Any process which can take place without the application external force is a spontaneous process. All natural processes are spontaneous. Thermodynamic definition of a spontaneous process is given in Sec. 9.8

Self Assessment Exercise 1

Explain why the change in entropy in a system is not always a suitable criterion for spontaneous change?

4.0 HELMHOLTZ FREE ENERGY AND GIBBS FREE ENERGY

Helmholtz free energy (A) and Gibbs free energy (G) are defined by the expressions,

$$A = U - TS \quad \dots (3.2)$$

And $G = H - TS \quad \dots (3.3)$

since $H = U + pV$
 $G = U + pV - TS \quad \dots (3.4)$

A (denoting Helmholtz free energy) comes from the German word. Arbeit, which means work

Since U , H , p , S , V and T are state functions, A and G are also dependent only on the state of the system. In simpler words, a system in a given state has definite values of A and G . In the next section we shall derive equations useful in calculating changes in A and G at constant temperature.

Physical significance of A and G

Differentiating Eq. 3.2, we obtain ...(3.5)

$$dA = dU - TdS - SdT$$

At constant temperature ($dT = 0$), we have

$$dA = dU - TdS \quad \dots (3.6)$$

We know (from Unit 8, Eq. 8.37) that for a reversible process

$$TdS = dq_{rev}$$

Also Eq. 6.7 for a reversible process gives

$$dU = dq_{rev} + dw_{rev}$$

Substituting the values for TdS and dU in Eq. 3.6, we obtain,

$$dA = (dq_{rev} + dw_{rev}) - dq_{rev}$$

$$\text{or} \quad dA = dw_{\text{rev}} \quad \dots (3.7)$$

$$\text{or} \quad -dA = -dw_{\text{rev}} \quad \dots (3.8)$$

Since the process is carried out reversibly, $-dw_{\text{rev}}$ represents the maximum work done by the system. This is an important conclusion which states that the change in Helmholtz free energy is equal to the amount of reversible work done on the system; or decrease in Helmholtz free energy ($-dA$) is the maximum amount of work that can be obtained from the system ($-dw_{\text{rev}}$) during the given change. As a result, the function A is sometimes also referred to as the work function.

In a similar way, the differentiation of Eq. 3.4 yields,

$$dG = dU + pdV + Vdp - SdT - TdS \quad \dots (3.9)$$

At constant temperature ($dT = 0$) and pressure ($dp = 0$), Eq. 3.9 is reduced to

$$dG = dU + pdV - TdS \quad \dots (3.10)$$

Once again if the process is carried out reversibly, using Eq 1.7

($dU = dq_{\text{rev}} + dw_{\text{rev}}$) and $TdS = dq_{\text{rev}}$, we obtain from Eq. 3.10

$$dG = dq_{\text{rev}} + dw_{\text{rev}} + pdV - dq_{\text{rev}}$$

$$\text{or} \quad dG = dw_{\text{rev}} + pdV \quad \dots (3.11)$$

Now dw_{rev} consists of expansion work ($-pdV$) and some; other kind of work called the useful or the net work dw_{net} done on the system. Replacing dw_{rev} by $-pdV + dw_{\text{net}}$ in Eq. 3.11, we obtain,

$$dG = -pdV + dw_{\text{net}} + pdV$$

$$\text{or} \quad dG = dw_{\text{net}} \quad \dots (3.12)$$

$$\text{or} \quad -dG = -dw_{\text{net}}$$

Thus decrease in Gibbs free energy ($-dG$) is a measure of the maximum useful work that can be obtained from the system at constant temperature and pressure. Most experiments in the laboratory are carried out under such conditions. So the property G or the change associated with it (ΔG) is very important.

Self Assessment Exercise 2

What is the physical significance of decrease in Gibbs free energy?

4.0 CHANGES IN A AND G

When a system goes from state 1 to state 2 at constant temperature, the change in A can be obtained from Eq. 9.6 by integration between the limits $A_1 \rightarrow A_2$, $U_1 \rightarrow U_2$ and $S_1 \rightarrow S_2$.

$$\int_{A_1}^{A_2} dA = \int_{U_1}^{U_2} dU - T \int_{S_1}^{S_2} dS$$

or $A_2 - A_1 = U_2 - U_1 - T(S_2 - S_1)$

or $\Delta A = \Delta U - T\Delta S$ (3.14)

The change in G_2 when a system goes from a state 1 to state 2 can be obtained by integrating Eq. 3.10 at constant temperature and pressure between the limits $G_1 \rightarrow G_2$, $U_1 \rightarrow U_2$, $V_1 \rightarrow V_2$ and $S_1 \rightarrow S_2$.

$$\int_{G_1}^{G_2} dG = \int_{U_1}^{U_2} dU + P \int_{V_1}^{V_2} dV - T \int_{S_1}^{S_2} dS$$

or $G_2 - G_1 = U_2 - U_1 + p(V_2 - V_1) - T(S_2 - S_1)$

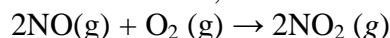
or $\Delta G = \Delta U + p\Delta V - T\Delta S$

We know that at constant pressure, $\Delta U + p\Delta V = \Delta H$ (Eq. 6.32)

Hence, $\Delta G = \Delta H - T\Delta S$ (3.15)

Example 1

For the reaction,



Calculate ΔG at 7.00×10^2 K. The entropy and enthalpy changes at 7.00×10^2 K are respectively, $-1.45 \times 10^2 \text{ J mol}^{-1} \text{ K}^{-1}$ and $-1.13 \times 10^2 \text{ kJ mol}^{-1}$

Solution

$$\Delta H = -1.13 \times 10^2 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta S &= -1.45 \times 10^2 \text{ J K}^{-1} \text{ mol}^{-1} = 1.45 \times 10^2 \times 10 \text{ kJ K}^{-1} \text{ mol}^{-1} \\ &= -1.45 \times 10^{-1} \text{ kJ K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$T = 7.00 \times 10^2 \text{ K}$$

$$\Delta G = \Delta H - T\Delta S$$

or $\begin{aligned} \Delta G &= (-1.13 \times 10^2 \text{ kJ mol}^{-1}) - 7.00 \times 10^2 \text{ K} (-1.45 \times 10^{-1} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= -1.13 \times 10^2 \text{ kJ mol}^{-1} + 1.015 \times 10^2 \text{ kJ mol}^{-1} \\ &= -0.115 \times 10^2 \text{ kJ mol}^{-1} = \\ &= -11.5 \text{ kJ mol}^{-1} \end{aligned}$

Variation of A and G with Temperature

From Eq. 3.5

$$dA = dU - TdS - SdT$$

Since $TdS = dq$

$$dA = dU - SdT - dq \quad \dots (3.16)$$

Substituting from the first law of thermodynamics,

$dU = dq - pdV$ in Eq 3.16, we have

$$dA = dq - pdV - SdT - dq$$

$$\text{or } dA = -pdV - SdT \quad \dots (3.17)$$

From Eq. 3.17 at constant volume ($dV = 0$), we have

$$(\partial A)_V = -S(\partial T)_V$$

$$\text{or } \left(\frac{\partial A}{\partial T} \right)_V = -S \quad \dots (3.18)$$

At constant temperature ($dT = 0$), Eq. 3.17 is reduced to

$$(\partial A)_T = -p(\partial V)_T$$

$$\text{or } \left(\frac{\partial A}{\partial V} \right)_T = -p \quad \dots (3.19)$$

Equations similar to Eqs. 3.18 and 3.19 can be obtained in the case of Gibbs free energy. From Eq. 3.9 we have

$$dG = dU + pdV + Vdp - SdT - TdS$$

Since $dq = TdS$ from Second law of thermodynamics and $dU = dq - pdV$ from first law of thermodynamics,

$$dG = dq - pdV + pdV + Vdp - SdT - dq$$

$$\text{or } dG = Vdp - SdT \quad \dots (3.20)$$

At constant pressure ($dp = 0$), Eq. 3.20 is reduced to

$$(\partial G)_p = -S(\partial T)_p$$

or
$$\left(\frac{\partial G}{\partial T} \right)_p = -S \quad \dots (3.21)$$

At constant temperature ($dT = 0$), we have from Eq. 3.20

$$(\partial G)_T = V(\partial p)_T \quad \dots (3.22)$$

or
$$\left(\frac{\partial G}{\partial P} \right)_T = V \quad \dots (3.23)$$

If G_1 , and G_2 are the free energies of the system in the initial and the final states, respectively, then at constant temperature, the free energy change (ΔG) is given by integrating Eq. 3.23.

$$\Delta G = \int_{G_1}^{G_2} dG = \int_{P_1}^{P_2} V dp$$

Where p_1 and p_2 are the initial and the final pressures, respectively.

For n mol of an ideal gas

$$pV = nRT \quad \text{or} \quad V = \frac{nRT}{p}$$

$$\begin{aligned} \therefore \Delta G &= \int_{G_1}^{G_2} nRT \frac{dp}{p} = nRT \int_{p_1}^{p_2} \frac{dp}{p} \\ &= nRT \ln \frac{p_2}{p_1} = 2.303 nRT \log \frac{p_2}{p_1} \end{aligned}$$

Since pressure is inversely proportional to volume for an ideal gas at constant temperature, we have,

$$\Delta G = 2.303 nRT \log \frac{p_2}{p_1} = 2.303 nRT \log \frac{V_1}{V_2} \quad \dots (3.25)$$

Example 2

Calculate the free energy change which occurs when 1.00 mol of an ideal gas expands reversibly and isothermally at 3.10×10^2 K from an initial volume of $5.00 \times 10^{-2} \text{ m}^3$ to 1.00 m^3 .

Solution

$$n = 1.00 \text{ mol}$$

$$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$V_1 = 5.00 \times 10^{-2} \text{ m}^3$$

$$\Delta G = 2.303 nRT \log \frac{V_1}{V_2}$$

$$= 2.303 \times 1.00 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.10 \times 10^2 \text{ K} \log \frac{5.00 \times 10^{-2} \text{ m}^3}{1.00 \text{ m}^3}$$

$$= (5.94 \times 10^3 \log \frac{1}{20}) \text{ J}$$

$$= (5.94 \times 10^3 \log 20) \text{ J}$$

$$= -7.72 \text{ KJ}$$

A state function depends only on the state of the system. It does not depend on that history of the system or how that state has been achieved.

$$dU = dq - pdV$$

For a reversible process.

$$dq = TdS$$

$$\text{Hence, } dU = TdS - pdV$$

Self Assessment Exercise 3

From the first and second laws of thermodynamics drive the following relations:

$$\text{i) } \left(\frac{\partial A}{\partial T} \right)_V = -S$$

$$\text{ii) } \left(\frac{\partial G}{\partial P} \right)_T = V$$

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 3 Spontaneous and Nonspontaneous Processes

Unit 2 Maxwell and Clausius-Clapeyron equation

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Maxwell relations,
- 4.0 Clausius-Clapeyron equation

2.0 Objectives

At the end of this unit, you should be able to;
derive Maxwell relations,

- derive Gibbs-Helmholtz equation,
- explain the significance of Clausius-Clapeyron equation,

3.0 THE MAXWELL RELATIONS

So far we have learnt about the five functions U , H , S , A and G which are state functions and extensive variables. The various expressions useful in estimating the changes in the above functions in a closed system in terms of temperature, pressure, volume and entropy may be written as:

$$dU = TdS - pdV \quad \dots(2.40)$$

$$dH = TdS + Vdp \quad \dots(2.41)$$

$$\begin{aligned} dA &= -SdT - pdV && \text{from Eq3.17} \\ dG &= -SdT + Vdp && \text{from Eq. 3.20} \end{aligned}$$

At constant volume ($dV = 0$), Eq. 2.40 becomes

$$\begin{aligned} (\partial U)_V &= T (\partial S)_V \\ \text{or} \quad \left[\frac{\partial U}{\partial S} \right]_V &= T \end{aligned}$$

and at constant entropy ($dS = 0$), Eq. 2.40 becomes

$$\begin{aligned} (\partial U)_S &= -P (\partial V)_S \\ \text{or} \quad \left[\frac{\partial U}{\partial V} \right]_S &= -P \quad \dots (3.27) \end{aligned}$$

Differentiating Eq. 3.26 with respect to volume at constant entropy and Eq. 3.27

with respect to entropy at constant volume, we get

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial T}{\partial V} \right)_S$$

or

$$\frac{\partial^2 U}{\partial S \partial V} = - \left(\frac{\partial P}{\partial S} \right)_V$$

Since U is a State function, it follows that

$$\frac{\partial^2 U}{\partial V \partial S} = \left(\frac{\partial^2 U}{\partial V} \right)_S$$

or

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V \quad \dots (3.28)$$

Following the same mathematical procedure as described above, the following expressions can be easily derived:

From Eq. 2.41,

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P \quad \dots (3.29)$$

From Eq. 3.17,

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V \quad \dots (3.30)$$

From Eq. 3.20,

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \dots (3.31)$$

Eqs. 3.28 to 3.31 are known as Maxwell relation. The Maxwell relations are important because they equate the rate of change of a particular quantity (which cannot be determined experimentally) with the rate of change of volume, pressure or temperature (which can be determined experimentally).

3.1 GIBBS-HELMHOLTZ EQUATION

The dependence of Gibbs free energy on temperature can be expressed in several ways. Starting from the definition (Eq. 2.3)

$$G = H - TS$$

or
$$-S = \frac{G - H}{T}$$

Substituting the expression for $-S$ in Eq. 3.21, we obtain,

$$\left(\frac{\partial G}{\partial T} \right)_P = \frac{G - H}{T} \quad \dots(3.32)$$

Sometimes it is important to know the variation of G/T on temperature. By differentiating G/T with temperature at constant pressure, we obtain

$$\left(\frac{\partial (G/T)}{\partial T} \right)_P = \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P - \frac{1}{T^2} G \quad \dots (3.33)$$

$$\begin{aligned} H &= U + pV \\ dH &= dU + pdV + Vdp \\ \text{But } dU + pdV &= dq = TdS \\ \text{Hence, } dH &= TdS + Vdp \end{aligned}$$

U is a thermodynamic function and dU is a total differential (see the Appendix for the explanation). The change in U with respect to both V and S is same whether we change U with respect to V first, keeping S , constant and then with respect to S , keeping V constant, or vice versa. Also see Eqs. 9.77 and 9.78 in sec. 9. 10.

Substituting the value of $\left(\frac{\partial G}{\partial T} \right)_P$ from Eq. 3.32 into Eq. 3.33, we get

$$\left(\frac{\partial (G/T)}{\partial T} \right)_P = \frac{G - H}{T^2} - \frac{1}{T^2} G$$

Hence,
$$\left(\frac{\partial (G/T)}{\partial T} \right)_P = \frac{G - H - G}{T^2}$$

or
$$\left(\frac{\partial (G/T)}{\partial T} \right)_P = \frac{H}{T^2} \quad \dots(3.34)$$

Eq. 3.34 is known as Gibbs-Helmholtz equation and it can be put in another form

by remembering that $d(1/T) = -\left(\frac{1}{T^2} \right) dT$; so on replacing ∂T in Eq 3.34 by

$$\frac{1}{T^2}$$

$-T^2 \partial(\quad)$, we have

$$\left(\frac{\partial (G/T)}{\partial (1/T)} \right)_P = - \frac{H}{T^2}$$

$$\text{or} \quad \left(\frac{\partial (G/T)}{\partial (1/T)} \right)_P = -H \quad \dots(3.35)$$

Similar equation for Helmholtz free energy can also be derived in the form

$$\left(\frac{\partial (A/T)}{\partial T} \right)_V = - \frac{U}{T^2} \quad \dots(3.36)$$

$$\left(\frac{\partial (A/T)}{\partial (1/T)} \right)_V = -U \quad \dots(3.37)$$

The dependence of Gibbs free energy on temperature can be expressed in another way also. Suppose the G_1 is the Gibbs free energy for a system in the initial state and at temperature T . Let the temperature change to $T + dT$ and the corresponding value of free energy to $G_1 + dG_1$.

Similar for the final state of the system, let the Gibbs free energies be G_1 and $G_2 + dG_2$ at temperature T and $T + dT$, respectively. At constant pressure, Eq. 3.20 to reduces to

$$(\partial G)_P = -S(\partial T)_P \quad \dots (3.38)$$

$$\text{and so } (\partial G_1)_P = -S_1(\partial T)_P \quad \dots (3.39)$$

$$(\partial G_2)_P = -S_2(\partial T)_P \quad \dots (3.40)$$

Where S_1 and S_2 are the entropies of the system in the initial and the final states, respectively. Subtraction of Eq. 3.40 gives

$$(\partial G_2 - \partial G_1)_P = -S_2(\partial T)_P - (-S_1(\partial T)_P)$$

$$\text{or} \quad [\partial(G_2 - G_1)]_P = -(S_2 - S_1)(\partial T)_P$$

$$\text{or} \quad [\partial \Delta G]_P = -\Delta S(\partial T)_P \quad \dots (3.41)$$

$$\text{i.e.,} \quad \left(\frac{\partial (\Delta G)}{\partial T} \right)_P = -\Delta S \quad \dots(3.42)$$

As per Eq. 3.15

$$\Delta G = \Delta H - T\Delta S = \Delta H + T(-\Delta S) \quad \dots(3.43)$$

Substituting Eq. 3.42 in Eq. 3.15 we have

$$\left(\frac{\partial (\Delta G)}{\partial T} \right)_P$$

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

The term $\left(\frac{\partial(\Delta G)}{\partial T}\right)_p$ and $\left(\frac{\partial(\Delta A)}{\partial T}\right)_p$ are the temperature coefficients of ΔG and ΔA at constant pressure and volume, respectively. The temperature coefficient of a particular parameter tells us how that parameter varies with respect to temperature.

If $\left(\frac{\partial(\Delta G)}{\partial T}\right)_p$ for example is

(i) Positive, it means ΔG increase with increasing temperature: and

(ii) negative, it means ΔG decrease with increasing temperature

Also, $\left(\frac{\partial(\Delta G)}{\partial T}\right)_p$

$$= \left(\frac{\Delta G_2 - \Delta G_1}{T_2 - T_1} \right)$$

where ΔG_2 and ΔG_1 are the free energy changes at temperatures, T_2 and T_1 .

$$\Delta A = \Delta U + T \left(\frac{\partial(\Delta A)}{\partial T} \right)_v \quad \dots(3.44)$$

The Gibbs-Helmholtz equation permits the calculation of ΔU or ΔH provided ΔA or ΔG and their respective temperature coefficients,

$$\left(\frac{\partial(\Delta A)}{\partial T} \right)_v \text{ or } \left(\frac{\partial(\Delta G)}{\partial T} \right)_p \text{ are known}$$

Example 3

The free energy change ΔG for a particular process is $-121.00 \text{ kJ mol}^{-1}$ at 298 K and $-117.00 \text{ kJ mol}^{-1}$ at 308 K . Calculate the enthalpy change for the process at 303 K .

Solution

$$\Delta G \text{ at } 298 \text{ K} = -121.00 \text{ kJ mol}^{-1}$$

$$\Delta G \text{ at } 308 \text{ K} = -117.00 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \left(\frac{\partial(\Delta G)}{\partial T} \right)_p &= \frac{(\Delta G_{308} - \Delta G_{298})}{(303 - 298) \text{ K}} = \frac{[(1-117.00 \text{ KJ mol}^{-1}) - (-121.00 \text{ KJ mol}^{-1})]}{(308 - 298) \text{ K}} \\ &= \frac{4.00 \times 10^{-1} \text{ KJ mol}^{-1}}{10 \text{ k}} = 4.00 \times 10^{-1} \text{ KJ mol}^{-1} \text{ K}^{-1} \end{aligned}$$

At 303 K, the value of ΔG may be taken as the average of at 298 K and 308 K.

$$\text{Hence, } \Delta G \text{ at 303 K} = \frac{-117.00 \text{ KJ mol}^{-1} - 121.00 \text{ mol}^{-1}}{2}$$

$$= -119.00 \text{ kJ mol}^{-1}$$

Substituting the values in the Gibbs-Helmholtz equation

$$\Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_p$$

$$-119.00 \text{ kJ mol}^{-1} = \Delta H + 303 \text{ K} \times 4.00 \times 10^{-1} \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$= \Delta H + 121.20 \text{ kJ mol}^{-1}$$

$$\Delta H = -121.20 \text{ KJ mol}^{-1} - 119.00 \text{ kJ mol}^{-1} = -240.20 \text{ kJ mol}^{-1}$$

When applied to chemical reactions, the Gibbs-Helmholtz equation will take the following form:

Initial state (Reactants) \rightarrow Final state (Products)

Free energy G_i G_f

Eq. 3.34 applies to both the initial and final states, i.e.

$$\left(\frac{\partial (G_i/T)}{\partial T} \right)_p = -\frac{H_i}{T^2} \quad \text{and} \quad \left(\frac{\partial G}{\partial T} \right)_p = -\frac{H_f}{T^2}$$

Subtracting we get,

$$\left(\frac{\partial}{\partial T} \left(\frac{G_f}{T} - \frac{G_i}{T} \right) \right)_p = - \left(\frac{H_f}{T^2} - \frac{H_i}{T^2} \right)$$

$$\text{or} \quad \left(\frac{\partial (\Delta G/T)}{\partial T} \right)_p = -\frac{\Delta H}{T^2} \quad \dots(3.45)$$

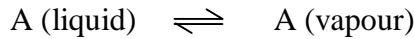
The above equation is important because from the knowledge of enthalpy of reactions we can predict whether increase in temperature will favour the reaction in one direction or other.

4.0 CLAUSIUS-CLAPEYRON EQUATION

From Eq. 3.30 we have

$$\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

The above equation can be applied to any closed system consisting of two phases of the same substance in equilibrium with each other. Let us consider a closed system in which a: pure liquid and its vapour are in equilibrium with each other.



The vapour pressure of the liquid (A) depends upon the temperature but is independent of the volume of the liquid and the vapour.

Hence,

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{dp}{dT} \quad \dots(3.46)$$

When one mole of the liquid is vaporized isothermally and reversibly in such a way that during the process, the liquid and the vapour remain in equilibrium, the increase in enthalpy is equal to the molar enthalpy of vaporization (ΔH_{vap}). Since the process is reversible, it follows from Eq. 2.77,

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T} \quad \dots(3.47)$$

where T is temperature.

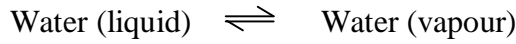
Let the increase in volume and entropy during the vaporization of one mole of liquid be ΔV and ΔS , respectively. Then we have at constant temperature (using Eq. 3.47).

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{\text{vap}}}{T\Delta V} \quad \dots(3.46)$$

Comparing Eqs. 3.30, 3.46 and 3.48, we have

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{T\Delta V} \quad \dots(3.47)$$

Eq. 3.49 was first deduced by Clapeyron (1834) and is known as Clapeyron equation. It was later extended by Clausius (1850). Eq. 3.49 was derived for a system consisting of liquid and vapour in equilibrium. The same equation can, however, be derived for equilibrium between any two phases such as, solid and liquid, solid and vapour, two crystalline forms of the same Substance etc. For a system consisting of water in the two phases, liquid and vapour, in equilibrium with each other,



Eq. 3.49 can be written as,

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{T(V_g - V_l)}$$

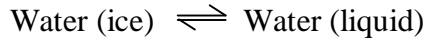
Where

ΔH_{fus} = Molar enthalpy of vaporization of water

V_g = Molar volume of water vapour at temperature T

V_l = Molar volume of liquid water at temperature T

For a system consisting of ice at its melting point, the two phases in equilibrium are ice and liquid water.



Eq. 3.49 may be written as

$$\frac{dp}{dT} = \frac{\Delta H_{\text{fus}}}{T(V_l - V_s)} \quad \dots(3.50)$$

Where

ΔH_{fus} = Molar enthalpy of fusion of ice

V_s = Molar volume of water in the solid (ice) state

V_l = Molar volume of water in the liquid state

In the liquid \rightleftharpoons vapour equilibrium, Clausius assumed that the molar volume of a liquid is much less than the molar volume of its vapour; hence $V_g - V_l$ can be taken approximately as V_g . Eq. 3.50 may be written as,

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{TV_g} \quad \dots(3.52)$$

Assuming that the vapour behaves ideally,

$$V_g = \frac{RT}{p} \quad \dots(3.53)$$

Substituting for the volume V_g in Eq. 3.52, we have

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{T} \times \frac{p}{RT} = \frac{\Delta H_{\text{vap}} p}{RT^2} \quad \dots(3.54)$$

Eq. 3.54 is known as Clausius-Clapeyron equation and can be rewritten as,

$$\frac{dp}{dT} = \frac{\Delta H_{\text{vap}}}{R} \times \frac{dT}{T^2} \quad \dots(3.55)$$

Eq 3.55 can be integrated between limits $p_1 \rightarrow p_2$ and $T_1 \rightarrow T_2$ assuming that ΔH_{vap} remains constant over a small range of temperature.

$$\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta H_{\text{vap}}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \quad \dots(3.56)$$

$$\text{or} \quad \ln \frac{p_2}{p_1} = \frac{-\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots(3.57)$$

$$\text{or} \quad 2.303 \log \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots(3.58)$$

$$\text{or} \quad \log \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad \dots(3.59)$$

This is integrated form of Clausius-clapeyron equation

The left hand side of Eq. 9.56 is integrated using formula 2 of Sec. 1.6 of Unit1. The right hand side of Eq. 3.5 is integrated using formula 1 of Sec. 1.6. Substitute $x_1 = T_1$, $x_2 = T_2$, $x = T$, $m = -2$ and

$a = \frac{\Delta H_{\text{vap}}}{R}$ in that formula

$$\frac{\Delta H_{\text{vap}}}{R} \int_{T_2}^{T_1} \frac{dT}{T} = \frac{\Delta H_{\text{vap}}}{R} \int_{T_2}^{T_1} T^{-2} dT$$

$$= \frac{\Delta H_{\text{vap}}}{R} \left[-T^{-1} \right]_{T_2}^{T_1}$$

$$= -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$= -\frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

The applications of Clausius-Clapeyron equation are given below:

1. If the vapour pressure of a liquid at a different temperatures are known then its molar enthalpy of vaporization can be calculated using Eq. 3.59
2. If the vapour pressure of a liquid at any one temperature is known then that at another temperature can be calculated using Eq. 3.59.
3. Eq. 3.59 can also be used for calculating the effect of pressure on the boiling point of a liquid.

Example 4

$$\ln \left(\frac{p_2}{p_1} \right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Calculating the vapour pressure of water at 298 K. Molar enthalpy of vaporization of water is its normal boiling point is $4.10 \times 10^4 \text{ J mol}^{-1}$

Solution

The standard pressure is $1.00 \times 10^5 \text{ Pa}$ and the boiling point of water at this pressure (known as its normal boiling point) is 373 K

$$\begin{array}{ll} P_1 & = ? \\ T_1 & = 298 \text{ K} \\ R & = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \\ \Delta H_{\text{vap}} & = 4.10 \times 10^4 \text{ J mol}^{-1} \end{array} \quad \begin{array}{ll} P_2 & = 1.00 \times 10^5 \text{ Pa} \\ T_2 & = 373 \text{ K} \end{array}$$

Substituting these values in Clausius-Clapeyron equation (eq. 3.59).

$$\begin{aligned} \ln \frac{p_2}{p_1} &= \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ \ln \frac{1.00 \times 10^5 \text{ Pa}}{p_1} &= \frac{4.10 \times 10^4 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{298 \text{ K}} - \frac{1}{373 \text{ K}} \right) \\ &= 1.445 \end{aligned}$$

$$\text{or } \ln 1.00 \times 10^5 - \ln p_1 = 1.445$$

$$\begin{aligned}\text{or } 5.00 - \log p_1 &= 1.445 \\ \text{or } \log p_1 &= 5.00 - 1.455 = 3.555 \\ \text{or } p_1 &= \text{Antilog of } 3.555 = 3.59 \times 10^3 \text{ Pa}\end{aligned}$$

Self Assessment Exercise 4

Either boils at 306 K at 1.00×10^5 Pa pressure. At what temperature will it boil at a pressure of 9.85×10^3 Pa? Given that the molar enthalpy of vaporization of either is 2.74×10^4 J mol⁻¹

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 3 Spontaneous and Nonspontaneous Processes

Unit 3 CRITERIA FOR SPONTANEITY

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Criteria if or spontaneity
- 4.0 Gibbs Free Energy
- 5.0 Third law of thermodynamics
- 6.0 Summary

2.0 Objectives

At the end of this unit, you should be able to;
explain the criteria if or spontaneity,
state and explain the third law of thermodynamics.

3.0 Criteria for Spontaneity

We have seen that entropy can be used as a criterion for determining the spontaneity of a process. We can also express the criteria for spontaneity in terms of other thermodynamic properties, namely U , H , A and G .

Internal Energy Change as a Criterion for Spontaneity

From the first law of thermodynamics, we know

$$dq = dU - dw \text{ (true for irreversible or reversible process) and since } dq_{rev} = TdS \text{ (as per Eq. 2.37)}$$

$$TdS = dU - dw \text{ (for a reversible process)}$$

$$\text{For an irreversible process, } dq_{irrev} < dq_{rev}$$

$$\text{Hence, } dq_{irrev} < TdS.$$

$$\text{So, for an irreversible process, } dU - dw < TdS$$

$$\text{or } TdS > dU - dw$$

Thus for any process:

$$TdS \geq dU - dw$$

$$\text{or } TdS \geq dU + (-dw)$$

If we consider only the pressure-volume work ($dw = pdV$), then

$$TdS \geq dU + pdV$$

Subtracting TdS from both sides, $0 \geq dU + pdV - TdS$

$$\text{or } dU + pdV - TdS \leq 0 \quad \dots(3.60)$$

...i.e., for a process to be, feasible, the condition given in Eq. 3.60 must hold good. At constant volume ($dV=0$) and entropy ($dS=0$), Eq. 3.60 thus reduces to

$$(\partial U)_{V,S} \leq 0 \quad \dots(3.61)$$

According to Eq. 3.61 when the volume and entropy remain constant, the internal energy of a system remains constant in a reversible process $[(\partial U)_{V,S} = 0]$ whereas in an irreversible process the internal energy decreases $[(\partial U)_{V,S} < 0]$.

Enthalpy Change as a Criterion for Spontaneity

We know that $H = U + pV$

Differentiating the above expression, we get

$$dH = dU + pdV + Vdp$$

Since from first law, $dU = dq + dw$

$$dH = dq + dw + pdV + Vdp$$

Considering only pressure-volume work done on the system, we can write as per Eq. 1.14 $dw = -pdV$; we then have

$$dH = dq - pdV + pdV + Vdp$$

$$\text{or } dH = dq + Vdp$$

or $dH - Vdp = dq$ (true for both reversible and irreversible processes). For a reversible process $dq_{rev} = TdS$ and, for an irreversible process $dq_{irrev} < TdS$.

Thus we have for any process

$$dH - Vdp \leq TdS \quad \dots(3.62)$$

At constant pressure ($dp = 0$) and constant entropy ($dS = 0$)

Eq. 3.62 reduces to

$$(\partial H)_{p,S} \leq 0 \quad \dots(3.63)$$

According to Eq. 3.63, when the pressure and entropy remain constant, the entropy of a system remains constant in a reversible process $[(\partial H)_{p,S} = 0]$, whereas in an irreversible process the enthalpy decreases $[(\partial H)_{p,S} < 0]$.

Helmholtz Free Energy change as a Criterion for Spontaneity

From $A = U - TS$ we have

$$dA = dU - TdS - SdT$$

Since $dU = dq + dw$

$$dA = dq + dw - TdS - SdT$$

$$dA - dw + TdS + SdT = dq \text{ (true for both reversible and irreversible processes)}$$

Since $dq_{\text{rev}} = TdS$ and $dq_{\text{irrev}} < TdS$

$$dA - dw + TdS + SdT \leq TdS$$

or $dA - dw + SdT \leq 0$ (cancelling TdS from both the sides)

Considering only pressure-volume work done on the system,
($dw = -pdV$), we have

or $dA + pdV + SdT \leq 0$

At constant volume ($dV = 0$) and constant temperature ($dT = 0$), the above form reduces to,

$$(\partial A)_{T,v} \leq 0 \quad \dots(3.64)$$

According to Eq. 9.64, when the temperature and volume remain constant, the Helmholtz free energy of a system remains constant in a reversible process [$(\partial A)_{T,v} = 0$], whereas in an irreversible process the Helmholtz free energy decreases [$(\partial A)_{T,v} < 0$]

Gibbs Free Energy change as a Criterion for Spontaneity

$$G = H - TS = U + pV - TS$$

or $dG = dU + pdV + Vdp - TdS - SdT$

Since $dU = dq + dw$

$$dG = dq + dw + pdV + Vdp - TdS - SdT$$

or $dG - dw - pdV - Vdp + TdS + SdT = dq$ (true for reversible and irreversible processes)

Since, $dq_{\text{rev}} = TdS$ and $dq_{\text{irrev}} < TdS$

$$dG - dw - pdV - Vdp + TdS + SdT \leq TdS$$

or $dG - dw - pdV - Vdp + SdT \leq 0$ (cancelling TdS terms both sides)

If only pressure-volume work is done ($dw = -pdV$), we have

$$dG + pdV - pdV - Vdp + SdT \leq 0$$

or $dG - Vdp + SdT \leq 0$

At constant temperature ($dT = 0$) and constant pressure ($dp = 0$), the above equation reduces to

$$(\partial G)_{T, p} \leq 0 \quad \dots(3.65)$$

According to Eq. 9.65, when the pressure and temperature remain constant, the Gibbs free energy of a system remains constant in a reversible process $[(\partial G)_{p, T} = 0]$, whereas in an irreversible process, Gibbs free energy decreases $[(\partial G)_{p, T} < 0]$.

Thus the criterion for spontaneity in terms of Gibbs free energy is that the process would be feasible if ΔG is negative.

By combining Eqs. 9.15 and 9.65, we can draw some useful conclusions. From Eq. 9.15 we have

$$\Delta G = \Delta H - T\Delta S$$

It can be seen from Eqs. 9.15 and 9.65 that

1. If ΔH is negative and ΔS is positive, ΔG will be negative at all temperatures; hence, the process would be spontaneous at all temperatures.
2. If ΔH is positive and ΔS is negative, ΔG will be positive at all temperatures; hence, the process would not be feasible at any temperature.
3. If ΔH and ΔS are both positive or negative, ΔG will be positive or negative depending upon the temperature.

There are four possibilities for ΔG based on the signs of ΔH and ΔS . These are outlined in Table 9.1.

Table 9.1: Criterion for Spontaneous Change

Case	ΔH	ΔS	ΔG	Result
1	-	+	-	spontaneous at all temperatures

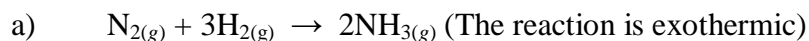
$$2 \quad - \quad - \quad \begin{cases} - & \text{spontaneous at low temperatures} \\ + & \text{nonspontaneous at high temperatures} \end{cases}$$

3 + + $\left[\begin{array}{l} + \\ - \end{array} \right.$ nonspontaneous at low temperatures
spontaneous at high temperatures

4 + - + nonspontaneous at all temperatures

Self Assessment 5

Under what conditions, would you expect the following reactions to occur spontaneously



4.0 THE GIBBS FREE ENERGY OF FORMATION

It is obvious from the definition of Gibbs free energy (Eqs. 9.3 and 9.4) that the absolute value of G is not determinable since the absolute values of U and H are unknown. However, in most cases, this is not a handicap as we require only changes in Gibbs free energy for a given process. In this section, we are interested in showing the method of calculation of standard Gibbs free energy of a reaction. Before that, let us define the standard states of the substances

The term fugacity comes from the Latin word for “fleetness” (meaning to move rapidly) The fugacity is a measure of the molar Gibbs energy of a real gas. The fugacity has the same units as pressure and approaches the pressure (value) as pressure approaches zero

The standard states of solids and liquids correspond to their most stable form at 1 bar pressure and the specified temperature. For a gas, the standard state is pure gas at unit fugacity. For ideal gas, fugacity is unity when pressure is 1 bar at a specified temperature. In all these cases, the most stable form has the lowest free energy. The standard state convention may be summarized as given below:

Ideal solution will be defines in Unit 10 of this course.

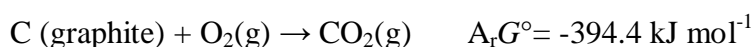
For a solid : The pure substance at 1 bar external pressure and at a specified temperature.

For a liquid : The pure substance at 1 bar external pressure and at a specified temperature.

For a gas : An ideal gas at 1 bar partial pressure and at a specified temperature.

For a solute : An ideal solution at one molar concentration and at a specified temperature.

The standard Gibbs free energy of formation, $\Delta_f G^\circ$, of a substance is defined as the change in the Gibbs free energy that accompanies the formation of one mole of the substance in its standard state from the elements in their standard states. Just like $\Delta_f H^\circ$, the standard Gibbs free energy of formation of all elements by definition is zero. Thus $\Delta_f H^\circ$ (CO₂) is the Gibbs free energy for the reaction,



It may be mentioned that $\Delta_f G^\circ$ can be defined at any temperature but generally these values are tabulated at 298.15 K. The values of $\Delta_f G^\circ$ for some selected substances at 298.15 K are given in Table 3.2.

Table 3.2: Standard Gibbs Free Energies of Formation at 298.15 K of some Selected Substances

Substance	$\Delta_f G^\circ / (\text{kJ mol}^{-1})$	Substance	$\Delta_f G^\circ / (\text{kJ mol}^{-1})$
H(g)	203.3	NH ₃ (g)	-16.5
O(g)	230.1	CH ₄ (g)	-50.8
Cl(g)	105.4	C ₂ H ₆ (g)	-32.9
Br(g)	82.4	C ₂ H ₄ (g)	68.1
Br ₂ (g)	3.1	C ₂ H ₂ (g)	209.2
I(g)	70.3	Benzene (l)	124.3
I ₂ (g)	19.3	Methanol (l)	-166.4
H ₂ O(g)	-228.6	Ethanol (l)	-174.1
H ₂ O(g)	-237.2		
HF(g)	-273.2		
HCl(g)	-95.3		

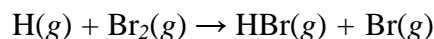
HBr (g)	- 53.4
HI (g)	1.7
CO (g)	- 137.2
CO ₂ (g)	- 394.4

The table of standard Gibbs free energies of formation can be very useful for calculating the standard Gibbs free energy of a reaction. This is defined as the change in Gibbs free energy that accompanies the conversion of reactants in their standard states to products in their standard states. In other words,

$$\left\{ \begin{array}{l} \text{Standard Gibbs free} \\ \text{energy for a reaction} \end{array} \right\} = \Delta_r G^\circ = \left\{ \begin{array}{l} \text{(sum of } \Delta_r G^\circ \text{ values of products)} - \\ \text{(sum of } \Delta_r G^\circ \text{ values of reactants)} \end{array} \right\} \dots (3.66)$$

Example 5

Using the data in Table 3.2 calculate the standard Gibbs free energy for the reaction.



Solution

$$\begin{aligned} \Delta_r G^\circ &= [\Delta_r G^\circ(\text{HBr}) + \Delta_r G^\circ(\text{Br})] - [\Delta_r G^\circ(\text{H}) + \Delta_r G^\circ(\text{Br}_2)] \\ &= \{[-53.4 + 82.4] - [203.3 + 3.1]\} \text{ kJ mol}^{-1} \\ &= -177.4 \text{ kJ mol}^{-1} \end{aligned}$$

Hence, hydrogen atom can spontaneously react with bromine gas to give hydrogen bromide.

Self Assessment Exercise 6

Why are the values of $\Delta_r G^\circ$ of some of the elements given in Table 3.2 different from zero?

In the next section, we study the third law of thermodynamics and its application in calculating the entropy of substances.

5.0 THE THIRD LAW OF THERMODYNAMICS

The second law of thermodynamics has been used to calculate entropy changes in various chemical and physical processes. However, the absolute values of entropy

have so far remained uncalculable. We now try to devise a scale of standard entropies so that we can associate definite entropies with different states of a given system.

The Nernst Heat Theorem

We start with Gibbs-Helmholtz equation (Eq. 3.43)

$$\Delta G = \Delta H + T \left(\frac{\partial(\Delta G)}{\partial T} \right)_p \quad \dots(3.43)$$

In Sec. 3.6 we mentioned that it is possible to calculate ΔH by knowing ΔG at two different temperatures. A question which remained unanswered was whether we can calculate ΔG from ΔH data. One thing which is clear from Eq. 9.43 is that as we approach the absolute zero of temperature, ΔG and ΔH must be equal unless

$\left(\frac{\partial(\Delta G)}{\partial T} \right)_p$ assumes an infinite value. Richards, however, found, during his studies on the electromotive force values of cells, that the quantity $\left(\frac{\partial(\Delta G)}{\partial T} \right)_p$

actually decreases as temperature is lowered. This observation prompted Nernst to

conclude that $\left(\frac{\partial(\Delta G)}{\partial T} \right)_p$ decreases in such a way that it reaches zero value

gradually at absolute zero. This implies that ΔG and ΔH not only approach each other near absolute zero, but do so asymptotically (i.e. in such a manner that their curves overlap at this point as in Fig. 3.1

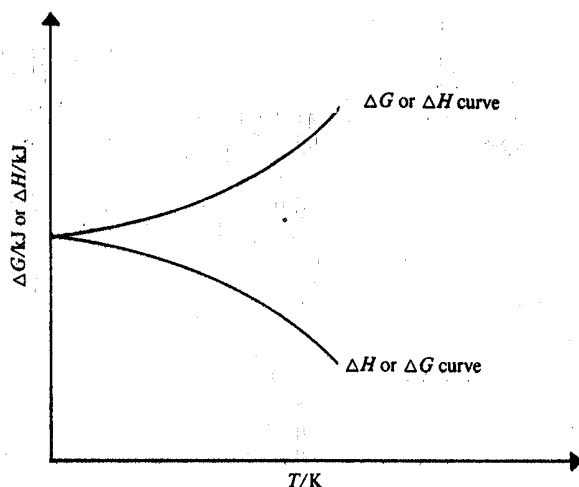


Fig. 3.1 ΔG and ΔH variation with temperature.

Mathematically this statement is equivalent to

$$\lim_{T \rightarrow 0} \frac{d(\Delta G)}{dT} = \lim_{T \rightarrow 0} \frac{d(\Delta H)}{dT} = 0 \quad \dots(3.86)$$

This is known as Nernst Heat Theorem and it is strictly applicable only to pure solids and not to liquids and gases which are not capable of existence at absolute zero.

As per Eq. 1.62 of Unit 1

$$\left(\frac{\partial(\Delta G)}{\partial T} \right)_p = \Delta C_p$$

and again, according to Eq. 3.42

$$\left(\frac{\partial(\Delta G)}{\partial T} \right)_p = -\Delta S$$

Here ΔS represents the change in entropy accompanying a reaction and ΔC_p is the difference between the total heat capacities of the products and those of the reactants at constant pressure. We can put Eq.3.86 in the form,

$$\lim_{T \rightarrow 0} \Delta S = \lim_{T \rightarrow 0} \Delta C_p = 0 \quad \dots(3.87)$$

In other words, at absolute zero, there is no difference between the heat capacities of the reactants and the products at constant pressure; this implies that the C_p values of all substances at 0 K are same. Later studies have shown that at the absolute zero of temperature, the heat capacity of a solid should be zero.

$$\text{i.e., at 0 K, } C_p = 0 \quad \dots (3.88)$$

A similar argument for the entropy change accompanying a reaction leads to the conclusion that all solids have the same entropy at absolute zero and, according to Max Planck, this value of entropy is zero.

The results so far discussed can be stated as the Third Law of Thermodynamics: "The entropy of a pure, perfectly crystalline solid approaches zero, as temperature approaches absolute zero.

The zero entropy of such solids can be readily understood since a perfectly crystalline solid implies a perfectly ordered arrangement of atoms, molecules and ions; or at absolute zero of temperature, number of microscopic states (Ω) of Eq. 2.87 (of Unit 2) is equal to unity and the entropy of the substance is zero.

$$S = k \ln \Omega = k \ln 1 = 0 \quad \dots(3.87)$$

In Eq. 2.87, Ω stands for the number of microscopic states on modes of arrangement of the species. At absolute zero, for a perfectly crystalline substance, there is only one mode of arrangement.

In case, the solid is not perfectly crystalline in nature, then its absolute entropy at 0 K is not zero, This has been discussed in Sec. 2.12 of Unit 2.

Applications of The Third Law of Thermodynamics

A lower limit on entropy enables us to determine the absolute value of the entropy of a system, if we can deduce an expression for the variation of entropy with temperature. Let us begin with the familiar relations, $TdS = dq$ (Eq. 2.37 of Unit 2) and $dq_p = C_p dT$ (Eq. 1.3 of Unit 1)

Hence at constant pressure, $TdS = C_p dT$

$$\text{i.e.,} \quad dS = C_p \frac{dT}{T} \quad \dots(3.89)$$

If we integrate Eq. 3.89 between the temperature limits 0 and T and entropy limits 0 and S , we have,

$$\int_0^S dS = \int_0^T C_p \frac{dT}{T} \quad \dots(3.90)$$

Where S is the entropy at temperature T and by the third law, entropy at 0 K (S_0) is zero.

$$\text{Hence, } S_T - S_0 = S_T = \int_0^T C_p \frac{dT}{T} = \int_0^T C_p d \ln T \quad \dots(3.91)$$

To calculate the value of S_T , the heat capacity of the substance should be known from 0 K to the temperature at which the entropy is to be calculated. The heat capacities of solids are known up to about 10 K to 15 K. Below this temperature, the heat capacities of solids are determined using the Debye equation,

$$C_p \approx C_v = aT^3 \quad \dots (3.92)$$

where a is constant; the value of a is determined from the value of C_p at some low temperature. This temperature is denoted as T_{\min} ; it is the lowest temperature at which C_p of the solid can be measured conveniently. Eq. 3.92 is valid for crystalline solids at low temperatures near 0 K. Eq. 3.91 may be written as,

$$S_T = \int_0^{T_{\min}} C_p \frac{dT}{T} + \int_{T_{\min}}^T C_p \frac{dT}{T} = \int_0^{T_{\min}} aT^3 \frac{dT}{T} + \int_{T_{\min}}^T C_p d\ln T \quad \dots(3.93)$$

The first integral is evaluated using the Debye equation (Eq. 3.92). The second integral is evaluated by plotting C_p vs $\ln T$ (Fig. 3.2); the shaded area under the curve is equal to the value of the second integral.

Eq. 3.93 can be simplified as follows:

$$S_T = \int_0^{T_{\min}} aT^3 \frac{dT}{T} + \int_{T_{\min}}^T C_p d\ln T$$

$$S_T = a \int_0^{T_{\min}} T^2 dT + \int_{T_{\min}}^T C_p d\ln T \quad (\text{Since } a \text{ is constant})$$

$$a \left[\frac{T^3}{3} \right]_0^{T_{\min}} + \int_{T_{\min}}^T C_p d\ln T$$

$$\text{Hence, } S_T = \frac{a}{3} T_{\min}^3 + \int_{T_{\min}}^T C_p d\ln T$$

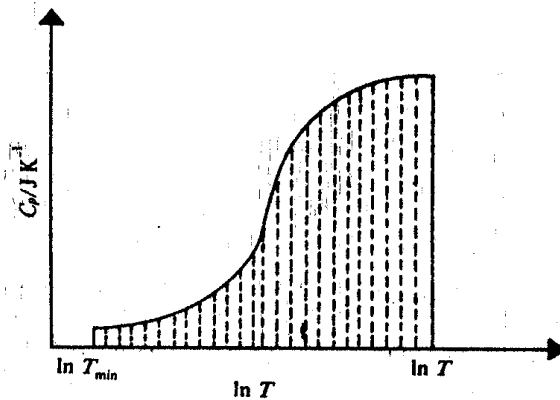


Fig. 3.2: C_p vs $\ln T$ plot

While using this method, it must be remembered that any phase change taking place between the temperatures zero kelvin (0 K) and TK , also contributes

towards the absolute entropy. The entropy of phase change. ΔS_{trans} is given by Eq. 2.75 of Unit 2

$$\Delta S_{\text{trans}} = \frac{\Delta H_{\text{trans}}}{T} \quad (\dots 3.75)$$

where ΔH_{trans} and T are the enthalpy and transition temperature, respectively for the phase transition. The phase transition includes changes such as solid to liquid, liquid to vapour and one allotropic form to another.

Let us now calculate the absolute molar entropy of a substance in the vapour phase at T K. This absolute molar entropy will be given by the sum of the entropy changes involved in various stages as given below:

$$\begin{aligned}
S = & \frac{a}{3} T_{\min}^3 && \left. \begin{array}{l} \text{(entropy change for bringing} \\ \text{the temperature of the solid from 0 K to } T_{\min}) \end{array} \right\} \\
& + \int_{T_{\min}}^{T_f} \bar{C}_p(s) d\ln T && \left. \begin{array}{l} \text{(entropy change for heating the solid from} \\ T_{\min} \text{ to its melting point)} \end{array} \right\} \\
& + \frac{\Delta H_{\text{fus}}}{T_f} && \left. \begin{array}{l} \text{(entropy change for the fusion of the solid} \\ \text{into liquid)} \end{array} \right\} \\
& + \int_{T_f}^{T_B} \bar{C}_p(l) d\ln T && \left. \begin{array}{l} \text{(entropy change for heating the substance} \\ \text{(in the liquid state) from its melting point to} \\ \text{the boiling point)} \end{array} \right\} \\
& + \frac{\Delta H_{\text{fus}}}{T_B} && \left. \begin{array}{l} \text{(entropy change for the vaporization of the liquid)} \end{array} \right\} \\
& + \int_{T_B}^T \bar{C}_p(g) d\ln T && \left. \begin{array}{l} \text{(entropy change for heating the vapour from} \\ \text{the boiling point to the temperature } T) \end{array} \right\}
\end{aligned}$$

where $\bar{C}_p(s)$, $\bar{C}_p(l)$ and $\bar{C}_p(g)$ are the molar heat capacities of the solid, liquid and gaseous phases, respectively; T_f and T_B are the melting and boiling points and ΔH_{fus} and ΔH_{vap} are the molar enthalpies of fusion and vaporization, respectively. Hence, by substituting in Eq. 3.95 the values of the molar heat capacities, the molar enthalpies and the temperatures, the absolute molar entropy of a substance can be calculated.

If a substance exists in different allotropic modifications, then ΔS_{trans} of the allotropic transition as given by Eq. 2.75 also must be added while calculating the absolute molar entropy of a substance.

6.0 SUMMARY

For a spontaneous change, the total entropy of the system and the surroundings must increase. If entropy is used as a criterion for spontaneity, it is necessary to determine the entropy change for both the system and the surroundings. This is inconvenient as one has to consider the changes taking place both in the system and the surroundings. Therefore, a criterion for spontaneity is developed in such a manner that only changes in the properties of the system are considered. For this purpose, two more state functions called, Helmholtz free energy (A) and Gibbs free energy (G) are defined. Decrease in Helmholtz free energy is equal to the maximum amount of work that can be obtained from the system during a given change. The decrease in Gibbs free energy is a measure of maximum useful work that can be obtained from the system at constant temperature and pressure. The Gibbs free energy change (given by the relation $\Delta G = \Delta H - T\Delta S$) of a physical or

a chemical process is a criterion for spontaneity of a process. ΔG has a negative value for a spontaneous process.

Maxwell relations equate the rate of change of a quantity (which cannot be determined experimentally) with the rate of change of volume, pressure or temperature. Gibbs-Helmholtz equation permits the calculation of ΔU or ΔH provided ΔA or ΔG at two temperatures are known. Clausius-Clapeyron equation is useful for calculating the molar enthalpy of vaporization of liquids if the values of vapour pressure at two different temperatures are known. The standard free energy change, $\Delta_r G^\circ$, is based on the conversion of reactants in their standard states to products in their standard states.

According to Nernst heat theorem, ΔG and ΔH not only become equal to each other at absolute zero but also approach each other gradually at temperatures near absolute zero. At the absolute zero of temperature, the entropy of every substance may become zero and it does become zero in the case of a perfectly crystalline substance.

APPENDIX

Total Differentials

Let us consider a dependent variable, x , such that its value depends on the variables y and z only,

$$\text{i.e., } x = f(y, z) \quad \dots(\text{A.1})$$

For any change in y and z , there will be a change in x also; also if the change in x (i.e., dx) so produced is irrespective of the path followed, then dx is called total differential. The value of dx in terms of changes in y and z can be expressed as follows:

$$dx = \left[\frac{\partial x}{\partial y} \right]_z dy + \left[\frac{\partial x}{\partial z} \right]_y dz \quad \dots (\text{A.2})$$

The meaning of this equation is given below:

$$\left\{ \left[\begin{array}{l} \text{change in } x \text{ due to} \\ \text{change in } y \text{ by one} \\ \text{unit when } z \text{ remains} \end{array} \right] \times \begin{array}{l} \text{actual} \\ \text{infinitesimal} \\ \text{change in } y \end{array} \right\} + \left\{ \dots \right\}$$

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$$\text{Total change} = \left[\begin{array}{l} \text{constant} \\ \text{In } x \\ \text{change in } x \text{ due to} \\ \text{change in } z \text{ by one} \\ \text{unit when } y \text{ remains} \\ \text{constant} \end{array} \times \begin{array}{l} \text{actual} \\ \text{infinitesimal} \\ \text{change in } z \end{array} \right]$$

By comparison you can recognise that Eqs. A.1 and 3.67 as well as Eqs. A.2 and 3.68 are similar. The only difference is that x depends on two variables y and z only, whereas G depends on four variables T , P , n and n_2 . Consequently Eq. 3.68 contains four terms in the right hand side, each term depicting a change in G due to a given change in a particular variable:

One of the characteristics of a total differential is that the second order differentials of a variable such as x given above are the same.

$$\text{i.e.,} \quad \frac{\partial^2 x}{\partial y \partial z} = \frac{\partial^2 x}{\partial z \partial y} \quad \dots(\text{A.3})$$

This means that the change in x is same, whether it is varied with respect to z first and y next or *vice versa*

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 4 Colligative Properties

UNIT 1 SYSTEM OF VARIOUS COMPARISON

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Partial molar quantities
- 4.0 Gibbs- Duhem Equation
- 5.0 Chemical potential of a perfect gas
- 6.0 Fugacity
- 7.0 Chemical potential of components of ideal gas

1.0 INTRODUCTION

In this unit we shall be discoursing on the principles of fugacity and how it relates to chemical potential of an ideal system. The colligative properties of solution and phase rule of component system will be treated. Also a brief introduction on statistical thermodynamic will be undertaken.

2.0 Objectives

- At the end of the unit, students should be able to;
- . define the partial molar quantities
- Define fugacity
- Identify the components of an ideal gas

3.0 PARTIAL MOLAR QUANTITIES AND Chemical POTENTIAL

The enthalpy change involved in the dissolution of a solute in a Solvent is very much dependent on the amounts of the solute and solvent present. Similarly other thermodynamic properties like volume, internal energy, Helmholtz free energy and Gibbs free energy also depend on the composition of the system. Until now however, we have considered only the closed system in which the amounts of the reactants and the products are fixed. We shall now Consider open system in which the amounts of the components may vary.

Molar volume of water

Molar mass of water

Density of water

$$\frac{1.8 \times 10^{-2} \text{ kg}}{1.0 \times 10^3 \text{ kg m}^{-3}}$$

$$= 1.8 \times 10^{-5} \text{ m}^3$$

$$= 18 \text{ cm}^3 \text{ (since } 1 \text{ cm}^3 = 10^{-6} \text{ m}^3 \text{)}$$

Eq. 4.1 is to be read as follows:

G is a function of T, P, n_1 and n_2 .

This means that the free energy of a two component system depends on the pressure, temperature and the amounts of the components 1 and 2.

Eq. is written from Eq. since dG is a perfect or total differential. The value of a total differential (such as dG) depends only on the values of the variables (such p, T, n_1 and n_2) and not on the type of the process which the system may adopt. For a better understanding of the total differential, see the Appendix at the end of unit 3.

If we consider a single homogeneous phase consisting of only one component, then the value of an extensive property divided by the amount of the substance becomes the molar property. These molar properties are indicated by putting a bar above the symbols.

Thus, $\bar{V} = \frac{V}{n}$ and $\bar{H} = \frac{H}{n}$, where n is the amount (the number of

the single component. V and H are the volume and the enthalpy of n mol of a substance. \bar{V} and \bar{H} are the molar volume and the molar enthalpy of the substance. However, if the system is a phase consisting of several components, then the addition of one mole of any pure substance in the mixture does not necessarily mean that it increases the value of the extensive property by the molar quantity. Thus, in a mixture of water and alcohol, if one mole of water is added, then the increase in volume is not equal to 18 cm^3 but depends on the composition of the mixture. Thus we introduce the concept of partial molar quantities. These are of particular use in the case of solutions of two or more components. The partial molar quantity of a component is defined as the change in the extensive property of a mixture when one mole of the pure component is added in such a way that there is no change in temperature ($dT = 0$), pressure ($dp = 0$) and composition ($dn = 0$). This is possible if we consider the system to be very large.

When the composition of the system varies, then for a small change of temperature, pressure and the amounts of the constituents, the change in Gibbs free energy for a two component system is given by.

$$G = f(T, p, n_1, n_2)$$

...(4.1)

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p,N} dT + \left(\frac{\partial G}{\partial p} \right)_{T,N} dp + \left(\frac{\partial G}{\partial n_1} \right)_{T,p,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{T,p,n_1} dn_2 \quad \dots(4.2)$$

Where n_1 and n_2 are the number of moles of components 1 and 2 and $N=n_1+n_2$ =total number of moles of components.

The subscripts p and N in the first term of the right hand side denote the fact that the pressure and composition are kept constant while noting the change in G with respect to temperature. Similarly the Subscripts T, N or T, p, n_2 or T, p, n_1 signify the parameters kept Constant while G is varied with respect to a parameter not mentioned as a subscript outside the bracket.

The partial derivative $\left(\frac{\partial G}{\partial n_1} \right)_{T,p,n_2}$ represents the rate of change in free energy per mole of component 1 added to the system, when temperature, pressure and the amount of component 2 are constant. It is also called the partial molar free energy (G_1) or simply chemical potential (μ_1) of the component 1. The chemical potentials of the two components are defined as,

$$\left(\frac{\partial G}{\partial n_1} \right)_{T,p,n_2} = \mu_1 \text{ and } \left(\frac{\partial G}{\partial n_2} \right)_{T,p,n_1} = \mu_2 \quad \dots(4.3)$$

At constant temperature ($dT = 0$) and constant pressure, ($dp = 0$), Eq. 3.68 may be written as,

$$dG_{T,p} = \mu_1 dn_1 + \mu_2 dn_2 \quad \dots(4.4)$$

It is possible to define chemical potential in terms of other thermodynamic functions also; but we consider it in terms of Gibbs free energy only.

If a system has definite composition having n_1 and n_2 moles of the respective components, then on integrating Eq. 3.70, we have

$$G_{T,p} = \mu_1 n_1 + \mu_2 n_2 \quad \dots(4.5)$$

Eq. 3.71 describes the free energy of a system of two components in terms of the partial molar free energies of the components. Similar expressions can be written for other thermodynamic quantities of the system also in terms of the partial molar quantities.

The importance of partial molar quantities can be understood from the following example. When one mole of Water is added to a sufficiently large volume of

ethanol, it is found that the increase in volume is not equal to the molar volume of water (18 cm^3) but only 14 cm^3 . The quantity, $14 \text{ cm}^3 \text{ mol}^{-1}$ is the partial molar volume of water in a large volume of ethanol. Thus the partial molar volume of a substance in a mixture of defined composition is the increase in volume that occurs when a substance is added to a sufficiently large sample of the solution. In general, when n_A mol of A is mixed with n_B mol of B, the total volume (V) of the mixture can be obtained from Eq. 4.6 which is written similar to Eq 4.5

$$\bar{V} = n_A \bar{V}_A + n_B \bar{V}_B \quad \dots(4.6)$$

Where \bar{V}_A and \bar{V}_B are the partial molar volumes of A and B, respectively.

The reason, as to why the increase in volume on the addition of one mole of water to a large volume of ethanol, is not equal to the molar volume of water will be seen in Unit 10 of this course.

Example 1

What is the total volume of the solution, when 3.80 mol of water is mixed with 0.500 mol of ethanol? The partial molar volumes of water and ethanol at this composition are $1.80 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$ and $5.34 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$, respectively.

Solution

$$\begin{array}{ll} n(\text{H}_2\text{O}) &= 3.80 \text{ mol} & \bar{V}(\text{H}_2\text{O}) = 1.80 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \\ n(\text{C}_2\text{H}_5\text{OH}) &= 0.500 \text{ mol} & \bar{V}(\text{C}_2\text{H}_5\text{OH}) = 5.34 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1} \end{array}$$

Applying Eq. 4.6

$$\begin{aligned} V &= (3.80 \text{ mol}) \times (1.80 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}) + \\ &\quad (0.500 \text{ mol}) \times (5.34 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}) \\ &= 6.84 \times 10^{-5} \text{ m}^3 + 2.67 \times 10^{-5} \text{ m}^3 \\ &= 9.51 \times 10^{-5} \text{ m}^3 \end{aligned}$$

Let us now see how Eq. 4.5 can be used to derive an important relationship (known as Gibbs-Duhem Equation) between the changes in the chemical potentials of the two components present in a solution.

4.0 Gibbs-Duhem Equation

According to Eq. 4.5 at a given temperature and pressure, the total Gibbs free energy for a homogeneous phase is equal to the sum of the products of the chemical potentials and the number of moles of each component. Hence, the Gibbs free energy of the system can change either by the change of chemical potential of a component or its amount in the system. A general expression for

change in G at the given temperature and pressure can be obtained by differentiating Eq. 4.5

$$dG_{T,p} = \mu_1 dn_1 + n_1 d\mu_1 + \mu_2 dn_2 + n_2 d\mu_2 \quad \dots(4.7)$$

Comparing this equation with 9.70 we obtain,

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \quad \dots(4.8)$$

This equation is known as Gibbs-Duhem or equation.

$$\text{or } d\mu_1 = -(n_2/n_1) d\mu_2 \quad \dots(4.9)$$

this means that the chemical potentials for components 1 and 2 cannot be varied independently. If μ_2 increases, then μ_1 will decrease by a definite equation finds extensive applications in liquids-vapour, liquid-solid and liquid-liquid equilibrium of binary Mixtures.

Let us now see how the chemical potential varies with temperature and pressure.

Dependence of Comical Potential on Temperature and Pressure

From Eq-.3.24, $dG = Vdp - SdT$;

$$\text{Hence, } \left(\frac{\partial G}{\partial T} \right)_p = -S \quad \dots(3.21)$$

$$\text{and } \left(\frac{\partial G}{\partial P} \right)_T = -V \quad \dots(3.23)$$

We know that the chemical potential of the component i (μ_i) is given by,

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p,n_j} \quad \dots(4.10)$$

where j = all the components except i. Note that the subscript n_j means that the amounts of all components except I are kept constant.

Differentiating μ_i (given in Eq. 4.10 with respect to temperature at constant pressure and composition, we have,

$$\left(\frac{\partial \mu_i}{\partial T} \right)_{p,N} = \frac{\partial^2 G}{\partial T \partial n_i}$$

Since G is a state function.

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{p,N} = \frac{\partial^2 G}{\partial T \partial n_i} = \left(\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial T}\right)_{p,N}\right)_{T,p,n_j}$$

From Eq 3.21, $\left(\frac{\partial G}{\partial T}\right)_{p,N} = -S$

Hence, $\left(\frac{\partial \mu_i}{\partial T}\right)_{p,N} = \left(\frac{\partial}{\partial n_i} (-S)\right)_{T,p,n_j} = - \left(\frac{\partial S}{\partial n_i}\right)_{T,p,n_j} = -\bar{S}_i \quad \dots(4.11)$

Where \bar{S}_i is the partial molar entropy of the i^{th} component. Since the entropy of a substance is always positive, its chemical potential or Gibbs free energy would decrease with increase in temperature. Eq. 4.11 describes the dependence of μ_i on temperature at constant pressure and composition. Let us now derive an expression useful in describing the dependence of μ_i on pressure.

Differentiating μ_i (given in Eq. 4.10) with respect to pressure at constant temperature and composition, we have,

$$\begin{aligned} \left(\frac{\partial \mu_i}{\partial p}\right)_{T,N} &= \frac{\partial^2 G}{\partial p \partial n_i} \\ &= \left(\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial p}\right)_{T,N}\right)_{T,p,n_j} \end{aligned}$$

Eqs. 4.11 and 4.12 are obtained from Eq. 4.10 using one of the properties of total differentials. Since dG is a total differential, the second order differentials of G with respect to T and n , taken in any order are the same.

i.e., $\frac{\partial^2 G}{\partial T \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial T}$

Also the second order differentials of G with respect to p and n_i , taken in any order are the same.

Since G is a thermodynamics property, the change in G depends on the changes in the values of the variables such as T , n_i or p , n_i etc at any particular instant, but not on the way or the sequence by which such variables are changed.

From Eq 3.21, $\left(\frac{\partial G}{\partial p}\right)_T = V$

Hence, $\left(\frac{\partial \mu_i}{\partial p}\right)_{T,N} = \left(\frac{\partial}{\partial n_i} (V)\right)_{T,p,n_j} = \left(\frac{\partial V}{\partial n_i}\right)_{T,p,n_j} = \bar{V}_i$

where \bar{V}_i is the, partial molar volume of the component i. Eq. 4.12 defines the dependence of μ_i on pressure at constant temperature and composition.

5.0 CHEMICAL POTENTIAL OF A PERFECT GAS

The standard state of a perfect gas as established at a pressure of exactly 1 bar, denoted as p^θ and its Gibbs formation as G^θ . Thus the Gibbs value at any other pressure P is

$$G(p) = G^\theta + NRT \ln(P/P^\theta) \dots\dots\dots \text{I}$$

and the molar Gibbs function G/n will be

$$G_m(P) = G^\theta_m + RT \ln (P/P^\theta) \dots\dots \text{II}$$

For a pure substance, the chemical potential (μ) is given as

$$\mu = G_m(p) \dots\dots\dots \text{III}$$

Substituting equation III into II, we have

$$\mu = \mu^\theta + RT \ln (P/P^\theta)$$

The origin of the name chemical potential, is analogy between mechanical systems, where particles tend to travel in the direction of decreasing potential, and the thermodynamic tendency of systems to shift in the direction of decreasing Gibbs function.

6. 0 Fugacity

As the departures from ideality occur under quite common conditions, as in the case of real gases, the pressure (p) is replaced by some effective pressure, the fugacity (f) such that

$$\mu = \mu^\theta + RT \ln (f/p^\theta)$$

Fugacity has the same dimension with the pressure of the gas. Relating the fugacity to the pressure, and expressing it in terms of molar quantities gives

$$\int_{p^1}^p V_m dp = \mu(p) - \mu(p^1) = RT \ln(f / f^1) \dots\dots\dots A$$

where f is the fugacity, when the pressure is p and f¹ the fugacity the fugacity when the pressure is p¹.

If the gas were perfect, we could write

$$\int_{p^1}^p V_m^o dp = \mu^o(p) - \mu^o(p^1) = RT \ln(p / p^1) \dots\dots\dots B$$

where the superscript ^o denotes quantities relating to a perfect gas.

The difference between equation A and B is

$$\int_{p^1}^p (V_m - V_m^o) dp = RT \ln(f / f^1) - RT \ln(p / p^1) \text{ or}$$

$$\ln(f / p) / (f^1 / p^1) = (1 / RT) \int_{p^1}^p (V_m - V_m^o) dp$$

when f¹/p¹ approaches 1 as p¹ approaches zero, we have

$$\ln(f / p) = (1 / RT) \int_o^p (V_m - V_m^o) dp$$

The equation above is the definition of fugacity. The standard value of the chemical potential can be calculated as given below

$$\mu^0 = \mu - RT \ln(f/p) - RT \ln(p/p^0)$$

Measurement of Fugacity

The expression for the fugacity corresponding to a pressure p , can be simplified as follows:

$$V_m^\theta = RT/P - \text{for perfect gas}$$

and

$$V_m^\theta = RTZ/p - \text{for real gas}$$

which rearranges to

$$f = \gamma p$$

and

$$\gamma = \exp \int_0^p [(Z-1)/p] dp$$

The factor γ is called the fugacity coefficient. This is the recipe for determining the fugacity of a gas at any pressure.

7.0 Chemical Potential of components in a mixture of Ideal Gases

The chemical potential of the components in a mixture of ideal gases can be expressed in three possible ways. First let us derive an expression for the chemical potential of a component in terms of its partial pressure.

$$\text{For an ideal gas, } pV = nRT \quad \dots(4.13)$$

Let us consider an ideal gas mixture at temperature T , total pressure p and volume V . Let the number of moles of each component be $n_1, n_2, \dots, n_i, \dots$, and the partial pressure of each component be $p_1, p_2, \dots, p_i, \dots$ respectively,

Then from Eq. 4.13, we have

$$V = \frac{nRT}{p} = (n_1 + n_2 + \dots + n_i + \dots) \frac{RT}{p} = n_t \frac{RT}{p}$$

Where n_t is the total number of moles of all the components. Differentiating V in the above equation with respect to n_i at constant temperature and pressure, we have,

$$\left(\frac{\partial V}{\partial n_i} \right)_{T, p, n_j} = \bar{V}_i = \frac{RT}{P}$$

Note that the subscript n_i denotes that the amounts of all other components except i are kept constant. But from Eq. 4.12

$$V_i = \left(\frac{\partial \mu_i}{\partial p} \right)_{T, N}$$

$$\text{Hence, } \left(\frac{\partial \mu_i}{\partial p} \right)_{T, N} = \frac{RT}{P} \quad \dots\dots\dots (4.14)$$

$$\text{or } \partial \mu_i = RT \frac{dp}{p} = RT \, d \ln p \quad \dots\dots\dots (4.15)$$

If p_i is the partial pressure of the component i and p is the total pressure of the mixture of gases, then according to Dalton's law of partial pressures,

$$p_i = \frac{n_i}{n_t} p = x_i p,$$

where x_i is the mole fraction of the component i . Taking logarithms both sides,
 $\ln p_i = \ln x_i + \ln p$

If x_i is constant we can write on differentiation of $\ln p_i$
 $d \ln p_i = d \ln p$

This means that in a gaseous mixture of constant composition, the partial pressure of a component varies as the total pressure.

Substituting for $d \ln p$ in Eq. 4.15, we have
 $d\mu = RT \, d \ln p_i$

Integrating between the limits $\mu_i(1) \rightarrow \mu_i(p_i)$ and $1 \rightarrow p_i$ we have,

$$\int_{\mu_i(1)}^{\mu_i(p_i)} d\mu_i = RT \int_1^{p_i} d \ln p_i$$

$$\left[\mu_i \right]_{\mu_i(1)}^{\mu_i(p_i)} = RT \left[\ln p_i \right]_1^{p_i}$$

$$\begin{aligned} \text{or } \mu_i(p_i) - \mu_i(1) &= RT \ln p_i - RT \ln 1 \\ \text{i.e. } \mu_i(p_i) - \mu_i(1) &= RT \ln p_i \text{ [since } \ln 1 = 0] \\ \text{or } \mu_i(p_i) &= \mu_i(1) + RT \ln p_i \end{aligned}$$

In Eq. 4.16, $\mu_i(p_i)$ is the chemical potential of the i^{th} component at temperature T when its partial pressure is p_i , and $\mu_i(1)$ is the chemical potential at the same temperature but at a partial pressure of unity. Hence, $\mu_i(1)$ is equal to $\mu_i(P_i)$ when $P_i = 1$ bar; i.e., $\mu_i(1)$ is the chemical potential under standard state at 1 bar. Thus in general, we may write Eq. 4.16 in the form,

$$\mu_i(p_i) = \mu_i^\circ(P) + RT \ln p_i$$

where $\mu_i(P_i)$ is the chemical potential of the i^{th} component at a partial pressure p_i and $\mu_i^\circ(P)$ is its standard chemical potential. Eq. 4.17 gives the chemical potential of an ideal gas i in terms of its partial pressure in a mixture. Let us now derive an expression for the chemical potential of an ideal gas in terms of its Concentration in a mixture.

In order to transform Eq. 4.17 in terms of concentration, we use the ideal gas law

$$\text{and substitute } p_i = \frac{n_i}{V} RT = c_i RT \text{ where } c_i \text{ is the concentration of the } i^{\text{th}}$$

component. Let $\mu_i(c_i)$ be the chemical potential of the i^{th} component when its concentration is c_i in the mixture of ideal gases.

$$\begin{aligned} \text{So, } \mu_i(c_i) &= \mu_i(P_i) = \mu_i^\circ(P) + RT \ln p_i \\ &= \mu_i^\circ(P) + RT \ln c_i + RT \ln RT \\ \text{or } \mu_i(c_i) &= \mu_i^\circ(c) + RT \ln c_i \end{aligned}$$

Here $\mu_i^\circ(c) = \mu_i^\circ(P) + RT \ln RT$ and is equal to the chemical potential component of the i^{th} component under standard state (when c_i is unity).

A similar expression can be derived in terms of the mole fraction (x_i) of the i^{th} component. For this purpose, we make use of Dalton's law of partial pressures, $p_i = x_i p$ where p_i is the partial pressure of the i^{th} component and p is the total pressure of the mixture of ideal gases.

Let us assume that $\mu_i(x_i)$ is the chemical potential of the i^{th} component in terms of its mole fraction in the mixture.

$$\begin{aligned} \text{Using Eq. 4.17, } \mu_i(x_i) &= \mu_i(p_i) = \mu_i^\circ(P) + RT \ln p_i \\ &= \mu_i^\circ(P) + RT \ln x_i + RT \ln p \\ \text{Hence, } \mu_i(x_i) &= \mu_i^\circ(x) + RT \ln x_i \end{aligned}$$

where $\mu_i^\circ(x) = \mu_i^\circ(p) + RT \ln p$ and is equal to the chemical potential of the component i under standard state (when $x_i = 1$). Eqs. 4.17, 4.18 and 4.17 are applicable to ideal systems only. When a system exhibits deviation from ideal behaviour, modified forms of these equations are to be used.

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 4 Colligative Properties

Unit 2 DERIVATION OF GENERAL EXPRESSION FOR CHEMICAL EQUILIBRIUM

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Expression for Chemical Equilibrium
- 4.0 Ideal gas mixtures
- 5.0 Equilibrium constant in term of concentration

2.0 Objectives

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

- explain the chemical equilibrium constant
- identify expression for an ideal gas mixture
- correlation between equilibrium constant and concentration

3.0 DERIVATION OF GENERAL EXPRESSION FOR CHEMICAL EQUILIBRIUM

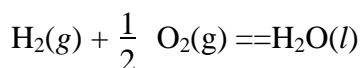
Even before derivation of equilibrium expression is attempted, we must recapitulate the following conventions in thermodynamics.

- 1) Any system, to which substances are added or from which they are taken away or in which a chemical reaction takes place, is called an open system.
- 2) A chemical reaction involving a number of substances is represented by

$$\sum_i \nu_i A_i = 0$$

Where A_i represents a chemical substance at the temperature and pressure of the reaction, and ν_i is called the stoichiometric coefficient of A_i .

ν values are positive for the products and negative for the reactants. This relationship can be explained using the following example :



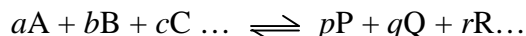
can be written as

$$(1) \text{H}_2\text{O} - (1) \text{H}_2 - \left(\frac{1}{2}\right) \text{O}_2 = 0$$

and the values of ν s are :

$$\nu_{\text{H}_2\text{O}} = 1, \nu_{\text{H}_2} = -1, \text{ and } \nu_{\text{O}_2} = \frac{1}{2}$$

Again, note that ν is positive for the products, and negative for the reactants. Let us now consider an open system represented by a general reaction :



The change in Gibb's free energy, dG , for the reaction is given by Eqs. 3.21, 3.32, 4.2 and 4.3

$$dG = Vdp - SdT + \sum_i \mu_i dn_i$$

where dn_i = change in the amount of any particular substance, 'i' and μ_i = chemical potential of that substance; all other symbols carry their usual meaning. At constant temperature and pressure, Eq. 6 reduces to:

$$dG_{T,P} = \sum_i \mu_i dn_i$$

The symbol Σ stands for summation of terms; the terms are obtained by giving different values to i .

As per Eq. 9.68 given in Sec. 9.10 of Unit 9 of this course,

$$dG = \left(\frac{\partial G}{\partial T} \right)_{p,N} dT + \left(\frac{\partial G}{\partial p} \right)_{T,N} dp + \left(\frac{\partial G}{\partial n_1} \right)_{p,T,p_2} dn_1 + \left(\frac{\partial G}{\partial n_2} \right)_{p,T,p_1} dn_2$$

Using Eqs., 9.21, 9.23 and 9.69, this expression can be written as,

$$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 \text{ Eq. 14.2}$$

Eq. 14.2 is a generalised form of the above equation.

The change in the amount of any substance ' dn_i ' can be more conveniently expressed in terms of another quantity ξ_i (pronounced as "xi") which is a measure of the extent of the reaction. For example, $\xi = 0$ for a substance 'i' means that it has not reacted at all; $\xi = 1$ means whole amount of 'i' has reacted and so on. For any reversible reaction the value of ξ should be between zero and unity.

Let us now derive an expression to specify the variation of free energy with respect to the extent of reaction. The number of moles (n_i) of a particular

substance i present at different times, as a reaction proceeds, can be expressed by the relation:

$$n_i = n_i^o + v_i \xi$$

where, n_i is the number of moles of the substance i present before the reaction starts, v_i is the stoichiometric coefficient of the same substance in the balanced chemical equation (with a proper sign) and ξ is the extent of the reaction. Note that n_i^o and v_i are constants for a substance while n_i varies as ξ changes. The change in n_i can be obtained by differentiating Eq. 4.23

$$dn_i = v_i d\xi$$

(since n_i^o and v_i are constants)

Combining Eqs. 4.22 and 4.24, we get,

$$dG_{T,p} = \sum_i^n \mu_i v_i d\xi$$

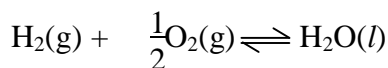
Hence, $\left(\frac{dG}{d\xi} \right)_{T,p} = \sum_i \mu_i v_i$

Eq. 4.25 represents Gibb's free energy change of the reaction ($\Delta_r G_{T,p}$) at constant temperature and pressure.

In Unit 3 you have studied that $\Delta_r G_{T,p}$ is equal to the sum of the Gibb's free energy of the products minus the sum of the Gibb's free energy of the reactants.

$$\text{i.e., } \left(\frac{dG}{d\xi} \right)_{T,p} = \sum_i \mu_i v_i = \Delta_r G_{T,p}$$

Let us apply Eq. 4.26 two reactions. First, let us consider the formation of water discussed in this section.

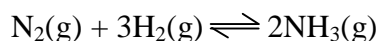


$\Delta_r G_{T,p}$ for the formation of water is given by

$$\Delta_r G_{T,p} = \mu_{\text{H}_2\text{O}} - \mu_{\text{H}_2} - \frac{1}{2} \mu_{\text{O}_2}$$

The v_i values of H_2O , H_2 and O_2 are 1, - 1 and $-\frac{1}{2}$ -, respectively.

As a second example, let us consider the formation of ammonia.



For this reaction,

$$\Delta_r G_{T,p} = 2\mu_{\text{NH}_3} - \mu_{\text{N}_2} - 3\mu_{\text{H}_2}$$

Again, note that the ν_i values of NH_3 , N_2 and H_2 are 2, -1 and -3, respectively.

From sec.3.8 of Unit 3, we know that the Gibbs free energy of the system will be minimum at equilibrium at constant temperature and pressure (see Fig. 4.1). Hence, the derivative of the Gibbs free energy function with respect to the extent of the reaction, which is the slope of the curve in Fig. 4.1, is equal to zero at equilibrium at constant temperature and pressure. In other words,

$$\left(\frac{dG}{d\xi}\right)_{T,p,eq} = \sum_i \mu_i \nu_i = \Delta_r G_{T,p} = 0$$

where 'eq' stands for equilibrium condition.

A chemical reaction will tend to proceed in a direction of decreasing free energy. At equilibrium, the reaction does not proceed in either direction, implying thereby that there would be an increase in Gibbs free energy of the system if the reaction proceeds in either direction. Hence, the Gibbs free energy of the system will be minimum at equilibrium.

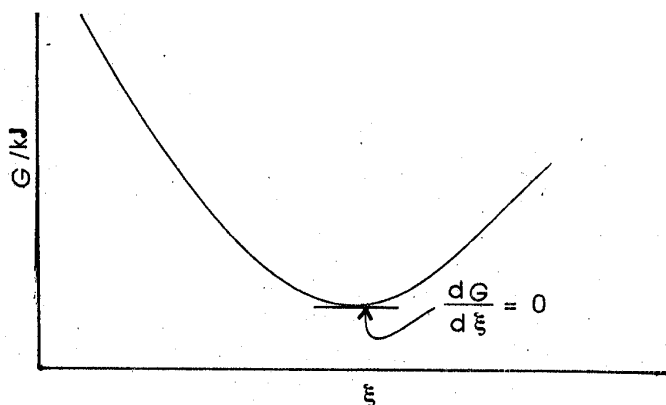


Fig. 4.1: Change of Gibbs Free Energy and the extent of chemical reaction.

Equation 4.27 is a general expression which is applicable to any reversible chemical reaction under equilibrium conditions at constant temperature and pressure. The equation simply means that the sum of the chemical potentials of the products and reactants is equal to zero at equilibrium.

Equation 4.27 would be most useful if we could express the chemical potential in terms of some experimentally determinable or known quantities. There are a number of ways to express chemical potentials. The next section discusses the

substitution for chemical potential in terms of partial pressure, mole fraction and concentration for ideal gas mixtures at equilibrium.

Try the following SAQ which is based on the above discussion.

Self Assessment Exercise 1

For the formation reaction of nitric oxide from nitrogen and oxygen gases, find the value of ν for each of the reactants and products.

4.0 CHEMICAL EQUILIBRIUM IN IDEAL GAS MIXTURES

Let us derive an expression for the equilibrium constant in terms of partial pressures for a reaction between ideal gases.

4.1 Equilibrium Constant Expression in Terms of Partial Pressure

Consider a general reaction



At constant temperature ($dT = 0$) and pressure ($dp = 0$) the free energy change for the above reaction ($A_rG_{T,p}$) is obtained by using Eq. 4.26.

$$A_rG_{T,p} = (l\mu_L + m\mu_M + \dots) - (a\mu_A + b\mu_B + \dots) \quad \dots(4.29)$$

where $\mu_L, \mu_M, \mu_A, \mu_B, \dots$, etc., are the chemical potentials of the products and reactants; and $l, m, (-a), (-b), \dots$, etc., are ν_i values. Remember that the products (such as L and M) have positive ν_i values and the reactants (such as A and B) have negative ν_i values; because of this, there is a negative sign between the two terms on the right hand side of Eq. 4.29

The chemical potential μ_i , of an ideal gas 'i' in a gaseous mixture is given by Eq. 4.17

It is quite interesting to note that Eq. 4.36 relates equilibrium constant of a reaction to the change in standard free energy that takes place during a reaction. In Unit 3 you have studied the method of calculation of Δ_rG° from the free energies of formation of the reactants and products once A_rG° is known at a particular temperature. K_p can be calculated using Eq. (4.36)

$$\mu_i(p_i) = \mu_i^\circ(p) + RT \ln p \quad \dots(4.30)$$

where $\mu_i^\circ(p)$ is the chemical potential of i in the standard state and p, is its partial pressure.

Using Eq. 4.30 in Eq. 14.10,

$$\Delta_r G_{r,p} = [(\mu_L^{\circ}(p) + RT \ln p_L) + m(\mu_M^{\circ}(p) + RT \ln p_M) + \dots] - [a(\mu_A^{\circ}(p) + RT \ln p_A) + b(\mu_B^{\circ}(p) + RT \ln p_B) \dots] \quad \dots(4.31)$$

$$\Delta_r G_{r,p} = [(l\mu_L^{\circ}(p) + m\mu_M^{\circ}(p) + \dots) - (a\mu_A^{\circ}(p) + b\mu_B^{\circ}(p) + \dots)] RT \ln \frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \quad (4.32)$$

Note that in the transformation of Eq. 4.31 to Eq. 4.32, we have used the relation:

$lRT \ln p_L = RT \ln p_L^l$; i.e., a coefficient (l) of a logarithmic term ($RT \ln p_L$) is taken inside the logarithmic term as a power,

$$\text{But } (l\mu_L^{\circ}(p) + m\mu_M^{\circ}(p) + \dots) - (a\mu_A^{\circ}(p) + b\mu_B^{\circ}(p) + \dots) = \Delta_r G_{T,p}^{\circ} \quad \dots(4.33)$$

where $\Delta_r G_{T,p}^{\circ}$ is the standard free energy change of the reaction at constant temperature and pressure.

Using Eqs. 4.32 and 4.33 we can write

$$\Delta_r G_{T,p} = \Delta_r G_{T,p}^{\circ} + RT \ln \frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \quad \dots(4.34)$$

Let us now assume that the above system is under equilibrium. Using Eqs. 4.27 and 4.34, we can write that at equilibrium,

$$\Delta_r G_{T,p} = \Delta_r G_{T,p}^{\circ} + RT \ln \left(\frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \right)_{eq} = 0$$

The subscript 'eq' stands for equilibrium values of partial pressures.

$$\text{i.e., } \Delta_r G_{T,p}^{\circ} = -RT \ln \left(\frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \right)_{eq} \quad \dots(4.35)$$

$$\text{or } \Delta_r G_{T,p}^{\circ} = -RT \ln K_p = -2.303 RT \log K_p \quad \dots(4.36)$$

where K_p is called the equilibrium constant in terms of partial pressures. The relationship is known as van't Hoff isotherm. K_p is given by the relationship,

$$K_p = \frac{p_L^l p_M^m \dots}{p_A^a p_B^b \dots} \quad \text{at equilibrium} \quad \dots(4.37)$$

$$= \frac{\text{Multiplication of } (p_i)^{v_i} \text{ terms of the products}}{\text{Multiplication of } (p_i)^{-v_i} \text{ terms of the reaction}} \quad \text{at equilibrium}$$

Note that v_i , written as power is positive for the product, NH_3 , whereas it is negative for N_2 ; and H_2 , these two being reactants.

where $p_L, p_M, p_A, p_B, \dots$, etc., are the partial pressures of L, M, A, B, ..., etc., at equilibrium. In subsequent sections, we leave out the subscript 'eq' while referring to equilibrium partial pressures. Eq. 14.18 can also be written as,

$$K_p = p_L^l \cdot p_M^m \cdot p_A^{-a} \cdot p_B^{-b} \dots \quad \dots(4.38)$$

where $p_L, p_M, p_A, p_B, \dots$ etc., are the equilibrium partial pressures and $l, m, (-a), (-b), \dots$, etc., are the respective v_i values of L, M, A, B, ..., etc. Eq. 14.19 can also be represented as,

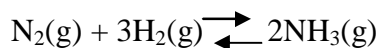
$$K_p = \prod_i p_i^{v_i} \quad \dots(4.39)$$

where the symbol Π represents the multiplication of different $p_i^{v_i}$ terms given in Eq. 4.38. Again, from Eqs. 4.27 to 4.39, we can see that the dimensions of K_p will depend upon the v_i values of the reactants and products. This particular aspect will be clear when you study the examples worked out in this unit.

Some authors prefer to give K_p as a dimensionless quantity by dividing p_i by p° where $p^\circ = 1 \text{ bar} = 10^5 \text{ Pa}$. To represent K_p as a dimensionless quantity, Eq. 14.20 is modified as,

$$K_p = \prod_i \left(\frac{p_i}{p^\circ} \right)^{v_i} \quad \dots(4.40)$$

Let us apply Eq. 4.38 to ammonia synthesis reaction.



$$K_p = (p_{\text{NH}_3})^2 (p_{\text{N}_2})^{-1} \cdot (p_{\text{H}_2})^{-3}$$

$$\text{or } K_p = \frac{p_{\text{NH}_3}^2}{p_{\text{N}_2} p_{\text{H}_2}^3}$$

Since the partial pressure are expressed in Pa unit, K_p for ammonia synthesis has the unit Pa^{-2} . If K_p for ammonia synthesis is to be dimensionless, then K_p expression is to be written following 4.40 as,

$$\text{or } K_p = \frac{p_{\text{NH}_3}^2 (p^\circ)^2}{p_{\text{N}_2} p_{\text{H}_2}^3}$$

Let us illustrate the use of Eq. 14.19 with an example.

Example 2

Suppose that, in an experiment at 1000 K, it is found that

$P_{\text{SO}_2} = 3.42 \times 10^4 \text{ Pa}$, $p_{\text{O}_2} = 3.31 \times 10^4 \text{ Pa}$ and
 $P_{\text{SO}_3} = 3.58 \times 10^4 \text{ Pa}$ for the reaction,
 $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$

Calculate the value for the equilibrium constant, K_p

Solution

At the given temperature, K_p is given by the expression

$$K_p = p_{\text{SO}_3}^2 \cdot p_{\text{SO}_2}^{-2} \cdot p_{\text{O}_2}^{-1}$$

$$\begin{aligned} \text{or } K_p &= \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \cdot P_{\text{O}_2}} = \frac{(3.58 \times 10^4 \text{ Pa})^2}{(3.42 \times 10^4 \text{ Pa})^2 \times (3.31 \times 10^4 \text{ Pa})} \\ &= 3.50 \times 10^{-4} \text{ Pa}^{-1} \end{aligned}$$

Note that the unit of K_p as per Eq. 4.58 is given by $(\text{Pa})^{\Sigma \nu}$. In the reaction discussed in Example 1, $\Sigma \nu_i = 2 - 2 - 1 = -1$. Hence, the unit K_p is Pa^{-1}

Try the following SAQ now.

Self Assessment Exercise 2

Suppose that we write the ammonia synthesis reaction in two different ways:

- i) $\frac{1}{2} \text{N}_2(\text{g}) + \text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$
- ii) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$

Would you express any difference in the expression for K_p in the two cases? (Usually, K_p values are calculated using equations of the type (ii) which have integral stoichiometric coefficients)

4.2 Equilibrium Constant Expression in Terms of Mole Fraction

Since Dalton's law tells us that partial pressure of a gas is equal to the mole fraction times the total pressure, Eq. 4.48 can be written as,

$$K_p = (x_L P_t)^l (x_M P_t)^m \dots (x_A P_t)^{-a} (x_B P_t)^{-b}$$

$$K_p = \prod_i (x_i P_t)^{n_i} \quad \dots(4.41)$$

According to Dalton's law of partial pressure, partial pressure (p_i) of an ideal gas, I, is given by,

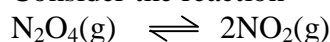
$$P_i = P_t \cdot x_i$$

Where P_t is the total pressure, and x_i is the mole fraction of the gas in a gaseous mixture.

Where, x_i = mole fraction of the species i , and p_t = total pressure.

Example 3

Consider the reaction



If a mixture of NO_2 , and N_2O_4 at equilibrium has a total pressure of 1.5×10^5 Pa, calculate the fraction of N_2O_4 that has dissociated at 303 K. K_p for the reaction is 1.4×10^4 Pa at 303 K.

Solution

Suppose that ξ is the fraction of the amount of N_2O_4 which has dissociated at equilibrium or it represents the extent of the reaction. Then $1-\xi$ is the fraction of the amount of N_2O_4 remaining at equilibrium and is proportional to the actual number of moles of N_2O_4 present at equilibrium.

From the balanced reaction, it is seen that for each mole of N_2O_4 decomposed, there are two moles of NO_2 produced. Therefore, at equilibrium, 2ξ will be proportional to the actual number of moles of NO_2 produced.

The total number of moles at equilibrium would then be proportional to $1 - \xi + 2\xi$ or $1 + \xi$

The mole fractions of the two gases at equilibrium can be written as,

$$x_{\text{NO}_2} = \frac{1 - \xi}{1 + \xi} \text{ and } x_{\text{N}_2\text{O}_4} = \frac{2\xi}{1 + \xi} \text{ where } x \text{ denotes mole fraction.}$$

$$\text{Using Eq. 4.41 } K_p = (x_{\text{NO}_2} \cdot P_t)^2 \cdot (x_{\text{N}_2\text{O}_4} \cdot P_t)^{-1}$$

$$\text{i.e., } K_p = \frac{(x_{\text{NO}_2} \cdot P_t)^2}{(x_{\text{N}_2\text{O}_4} \cdot P_t)}$$

Substituting for x_{NO_2} and $x_{\text{N}_2\text{O}_4}$ we get,

$$\frac{\left(\frac{2\xi}{1 + \xi} \cdot P_t \right)^2}{\frac{1 - \xi}{1 + \xi}}$$

$$.p_t$$

$$\text{or } K_p = \frac{4\xi^2}{(1-\xi)(1+\xi)} \cdot p_t = \frac{4\xi^2}{1-\xi^2} \cdot p_t$$

Substituting the given values, we get,

$$1.4 \times 10^4 \text{ Pa} = \frac{4\xi^2}{1-\xi^2} \times 1.5 \times 10^5 \text{ Pa.}$$

$$\text{or } \frac{1-\xi}{\xi^2} = \frac{1.5}{0.14} \times 4$$

$$\text{or } \frac{1}{\xi^2} = \frac{1.5 \times 4}{0.14}$$

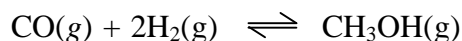
$$\text{or } \xi^2 = 0.023$$

$$\xi = 0.15$$

The fraction of N_2O_4 dissociated is thus calculated to be 0.15.

Example 4

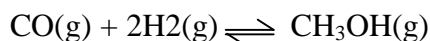
Consider the reaction,



where initially 1 mol of CO and 2 mol of H_2 were mixed together. Derive an expression for the equilibrium constant, K_p , in terms of the extent of the reaction, ξ and the total pressure, P_t .

Solution

If the extent, of the reaction at equilibrium is represented by ξ then we have,



Moles at equilibrium $1 - \xi$ $2 - 2\xi$ ξ

Mole fraction at equilibrium $\frac{1-\xi}{3-2\xi}$ $\frac{2-2\xi}{3-2\xi}$ $\frac{\xi}{3-2\xi}$

Using Eq. 14.22, $K_p = (x_{\text{CH}_3\text{OH}} \cdot p_t) \cdot (x_{\text{CO}} \cdot P_t)^{-1} \cdot (x_{\text{H}_2} \cdot p_t)^{-2}$

$$\text{i.e., } K_p = \frac{(x_{\text{CH}_3\text{OH}} \cdot p_t)}{(x_{\text{CO}} \cdot P_t) (x_{\text{H}_2} \cdot p_t)^2}$$

Hence

()

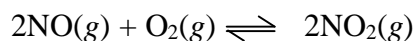
$$K_p = \frac{\frac{\xi}{3-2\xi} \cdot p_t}{\left(\frac{1-\xi}{3-2\xi} \cdot p_t\right) \left(\frac{2-2\xi}{3-2\xi} \cdot p_t\right)^2}$$

$$= \frac{\frac{(3-2\xi)^2 \cdot \xi}{(1-\xi)(2-2\xi)^2} \cdot p_t^2}{p_t^2}$$

You should be able to do the following SAQ, if you have understood the above examples.

Self Assessment Exercise 3

Express equilibrium constant K_p for the reaction,



in terms of (i) partial pressures and (ii) mole fractions of the gaseous species.

5.0 Equilibrium Constant Expression in Terms of Concentration

We know that for an ideal gas,

$$p_i = \frac{n_i RT}{V} = c_i RT$$

where c_i represents molar concentration of a gaseous substance 'i'; other symbols have their usual meaning. Hence we can express Eq. 4.38 in terms of concentrations.

$$K_p = (c_L RT)^l (c_M RT)^m \dots (c_A RT)^{-a} (c_B RT)^{-b}$$

$$= \frac{(c_L RT)^l (c_M RT)^m \dots}{(c_A RT)^a (c_B RT)^b \dots} \quad \dots(4.42)$$

$$\text{i.e., } K_p = \prod_i (c_i RT)^{\nu_i} \quad \dots(4.43)$$

Where ν_i represents the stoichiometric coefficient (along with proper sign) in the chemical equation.,

Eq. 4.42 can be written as,

$$K_p = \frac{\frac{c_L}{a} \frac{c_M}{b} \dots}{\frac{c_A}{a} \frac{c_B}{b} \dots} (RT)^{(l+m+\dots)-(a+b+\dots)}$$

$$(RT)^{\sum \nu_i}$$

$$= \frac{\frac{c_L^l c_M^m \dots}{c_A^a c_B^b \dots}}{c_A^a c_B^b \dots}$$

$$\text{i.e., } K_p = K_c (RT)^{\sum v_i} \quad \dots(4.44)$$

where K_c is defined by,

$$= \frac{\frac{c_L^l c_M^m \dots}{c_A^a c_B^b \dots}}{\text{Multiplication of } (c_i)^{-v_i} \text{ terms of the reactants}} = \frac{\text{Multiplication of } (c_i)^{v_i} \text{ terms of the products}}{\text{Multiplication of } (c_i)^{-v_i} \text{ terms of the reactants}} \quad \dots(4.45)$$

$$\text{i.e., } K_p = \prod (c_i)^{v_i} \quad \dots(4.47)$$

The dimensions of K_c depend of the v_i values of the reactants and the products. In case K_c is to be expressed as a dimensionless quantity, c , in Eq. 4.46 is to be replaced by c_i/c_o where c_o is the standard concentration and is equal to 1 mol dm^{-3} .

It is important to note that K_p and K_c are functions of temperature; (Unit 1)

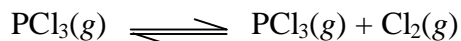
Eqs 14.18 and 14.26 are the mathematical expressions of the law of mass action.

Eq. 4.44 holds good for reactions between ideal gases.

Let us study an application of Eq. 4.45

Example 5

Calculate the equilibrium concentrations of all the species at 613 K for the reaction,



if the initial concentrations of the three gases is 0.15 M each and $K_c = 0.800 \text{ M}$ at 613 K. The volume of the vessel is 1 dm^3 .

Solution

Suppose that $x \text{ mol}$ of PCl_3 has decomposed at equilibrium. Since volume is 1 dm^3 , the concentration expressed in molarity is equal to the number of moles of a particular substance.

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

Using Eq. 4.45, we get

$$K_c = \frac{c_{\text{PCl}_3} \cdot c_{\text{Cl}_2}}{c_{\text{PCl}_5}}$$

Substituting the given values, we get,

$$0.800 \text{ M} = \frac{(0.15 + x) \cdot (0.15 + x)}{(0.15 - x)} \text{ M}$$

$$\text{or } 0.800 (0.15 - x) = (0.15 + x)^2$$

$$\text{or } x^2 + 1.1x - 0.0975 = 0$$

Using the principle of solution of standard quadratic equation, we get

$$x = 0.082 \text{ M or}$$

$$\text{or } -1.183 \text{ M}$$

The unit, mol dm^{-3} , is for denoting molarity and is represented by the letter M.
Note that concentration in

$$\text{Molarity} = \frac{\text{Number of moles}}{\text{Volume in dm}^3}$$

The unit of K_c as per Eq. 4.45 is given by $(\text{M})^{\sum \nu}$. In Example 4, $\sum \nu_i = 1 + 1 - 1 = 1$
Hence, the unit of K_c in this example is M.

The solution of a quadratic equation of the form $ax^2 + bx + C = 0$ is given by.

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

Square brackets are used to denote the concentration of a species. For example, $[\text{PCl}_5]$ is to be read as:
Concentration of PCl_5

We take $x = 0.082 \text{ M}$, since
second root of the quadratic equation gives the concentrations of PCl_3 and Cl_3 as
($0.15 \text{ M} - 1.183 \text{ M}$) = -1.033 M which is impossible. Hence, the equilibrium
concentration:

$$[\text{PCl}_3] = (0.15 - 0.082) \text{ M} = 0.068 \text{ M}$$

$$\text{and } [\text{PCl}_3] = [\text{Cl}_2] = 0.15 + 0.082 = 0.232 \text{ M}$$

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

Based on the above discussion, answer the following SAQ.

Self Assessment Exercise 4

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

5.1 EFFECT OF TEMPERATURE ON CHEMICAL EQUILIBRIUM

The equilibrium constant, K , of a reversible chemical reaction is a constant at a given temperature; but it varies with temperature. Let us derive an expression useful in bringing out the relationship between the equilibrium constant and temperature.

From Eq. 4.36, we get,

$$\Delta_r G^\circ = -RT \ln K_p$$

$$\text{or } \ln K_p = \frac{-\Delta_r G^\circ}{RT}$$

Differentiating this expression with respect to temperature,

$$\text{or } \frac{d \ln K_p}{dT} = \frac{1}{R} \frac{1}{dT} \left(\frac{\Delta_r G^\circ}{T} \right) \quad \dots(4.48)$$

Using Eq. 3.45 we can write:

$$\frac{d}{dT} \left(\frac{\Delta_r G^\circ}{T} \right) = - \frac{\Delta_r H^\circ}{T^2} \quad \dots(4.49)$$

Combining Eqs. 4.48 and 4.49, we get,

$$\frac{d \ln K_p}{dT} = \frac{\Delta_r H^\circ}{RT^2} \quad \dots(4.50)$$

Eq. 4.50 tells us that equilibrium constant varies with temperature and depends on the standard enthalpy of the reaction.

Assuming that the standard enthalpy change ($\Delta_r H^\circ$) of the reaction remains constant over a small range of temperature, the above equation on integration between limits K_{p1} , K_{p2} and T_1 , T_2 gives,

$$\int_{K_{p1}}^{K_{p2}} d\mu_i = K_p = \int_{T_1}^{T_2} \frac{\Delta_r H^\circ}{RT^2} dT$$

$$\text{or } \ln K_{p2} = \frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\frac{K_{P2}}{K_{P1}} = R \ln \left(\frac{T_2}{T_1} \right)^{\Delta_r H^\circ / R T_1 T_2}$$

$$\text{or } \ln \frac{K_{P2}}{K_{P1}} = \frac{\Delta_r H^\circ}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$= \frac{\Delta_r H^\circ (T_2 - T_1)}{2.303 R T_1 T_2} \quad \dots(4.51)$$

Eq. 4.51 correlates the equilibrium constant values K_{P1} and K_{P2} (expressed in terms of partial pressures) at two different temperatures T_1 and T_2 to the standard enthalpy of reaction.

According to Eq. 14.25, this is applicable for ideal gases,
 $K_p = K_c (RT)^{\Delta_r \nu}$

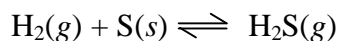
Using this equation and Eq. 14.33, it is possible to relate K values to the respective temperatures as.

$$\log \frac{K_2}{K_1} = \frac{\Delta_r U^\circ (T_2 - T_1)}{2.303 R T_1 T_2}$$

where K_1 and K_2 are the equilibrium constants (in terms of concentrations) at temperatures T_1 and T_2 and $\Delta_r U^\circ$ is the standard internal energy change of the reaction. Since reactions are generally carried out at constant pressure, Eq. 14.34 is of greater importance for us. Eq. 14.35 is known as van't Hoff's isochore.

Example 6

The equilibrium constant for the reaction



is 18.5 at 925 K and 925 at 1000 K, respectively. Calculate the standard enthalpy of the reaction. Also calculate $\Delta_r G^\circ$ and $\Delta_r S^\circ$ at 925 K.

Solution

Substituting the given values in Eq. 4.51, we get,

$$\log \frac{K_{1000}}{K_{925}} = \frac{\Delta_r H^\circ}{(2.303 \times 8.314)} \left(\frac{1}{925} - \frac{1}{1000} \right)$$

$$\text{or } \log \frac{9.25}{18.5} = \frac{\Delta_r H^\circ}{(2.303 \times 8.314)} \left(\frac{75}{925 \times 1000} \right)$$

hence $\Delta_r H^\circ = -71.1 \text{ kJ mol}^{-1}$

Using Eq. 4.36, $\Delta_r G^\circ = -2.303 \times 8.314 \times 925 \log 18.5 = -22.4 \text{ kJ mol}^{-1}$

Rearranging Eq. 3.15 of Unit 9, $\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(-71100 + 22400) \text{ J}}{925 \text{ K}}$

Self Assessment Exercise 5

For the dissociation of mercuric oxide, K_p values are 0.0196 and 0.1794 at 693 K and 723 K respectively. Calculate the standard enthalpy of the reaction.

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

Module 4 Colligative Properties

Unit 3 Thermodynamic Quantities from emf Values

- 1.0 Introduction
- 2.0 Objectives
- 3.0 Thermodynamic quantities from emf values
- 4.0 Colligative properties
- 5.0 Colligative Properties of Electrolytes
- 6.0 Phase rule
- 7.0 Statistical Thermodynamics

2.0 Objectives

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

- State the colligative properties
- Define phase rule and component
- Explain the term configuration

3.0 Thermodynamic Quantities from emf Values

We shall now study how ΔH , ΔS , and ΔG for the cell reaction can be calculated using modified forms of Nernst equation gives the relationship between ΔG and E values. Hence, if E_{cell} value is known, ΔG , for the cell reaction can be calculated.

$$- \Delta G = nFE \quad \dots(4.52)$$

Similarly, the change in entropy accompanying the cell-reaction can also be determined. In Unit 3 we have derived Eq. 3.92 which relates the temperature coefficient of the free energy

change at constant pressure, $\left(\frac{\partial (\Delta G)}{\partial T} \right)_p$ to the decrease in entropy ($-\Delta S$).

$$\left(\frac{\partial (\Delta G)}{\partial T} \right)_p = -\Delta S \quad \dots(4.53)$$

By differentiating ΔG and E_{cell} appearing in Eq. 4.52 with respect to temperature at constant pressure we can write

$$\left(\frac{\partial (\Delta G)}{\partial T} \right)_p = -nF \left(\frac{\partial E}{\partial T} \right)_p \quad \dots(4.54)$$

since n and F are constants.

Since Eqs. 3.42 and 4.54 we get.

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_p \quad \dots(4.55)$$

$$\Delta S = nF \left[\frac{(E_2 - E_1)}{(T_2 - T_1)} \right]_p \quad \dots(4.56)$$

In case E_2 and E_1 (the emfs of the cell at temperatures T_2 and T_1) are known, ΔS can be calculated $\left(\frac{\partial E}{\partial T} \right)_p$ is known as the temperature coefficient of emf at constant pressure.

Again Eq. 9.15 states,

$$\Delta G = \Delta H - T\Delta S$$

$$\text{or } \Delta H = \Delta G + T\Delta S \quad \dots(4.57)$$

Using Eqs. 4.25 and 4.57

$$\Delta H = nFE + TnF \left(\frac{\partial E}{\partial T} \right)_p \quad \dots(4.58)$$

Hence if E , T and $\left(\frac{\partial E}{\partial T} \right)_p$ are known, then the enthalpy change accompanying the cell reaction can be calculated.

In the light of above discussion, answer the following SAQs.

Self Assessment Exercise 6

Write down the equation relating ΔH° , ΔS° and ΔG° to ΔE° and $\left(\frac{\partial E^\circ}{\partial T} \right)_p$

4.0 Application of chemical potential to phase equilibrium

Here we consider the particles in an unreactive mixture, such as binary mixture.

4.1 Colligative Properties

Certain properties of solutions of non-volatile solutes have been observed to be dependent solely on the total number of solute particles in a given quantity of the solvent rather than on the kind of species present, such properties are known as colligative properties. There are four of them, namely:

- the depression of the vapour pressure of solvent
- the elevation of the boiling point of a solvent
- the depression of the freezing point of a solvent
- the osmotic pressure exerted by a solution of a non-volatile solute

These changes in the properties of the solvent brought about by dissolving non-volatile solutes does depends on how much of the solute there is and not on the nature and kind of the solute. For example one mole of sodium ion would depress the freezing point of a given quantity of water to the same extent as mole of sucrose or aluminum ion.

Depression in Vapour Pressure

Consider a homogenous solution of a solute A in a solvent B. Provided the solution is an ideal one the total vapour pressure of the solution is given by the equation

$$P_T = X_A P_A^{\circ} + X_B P_B^{\circ} \dots\dots\dots (I)$$

Where P_A° and P_B° are the vapour pressure of the pure solvent and pure solute respectively. X_A and X_B are the mole fractions of A and B respectively in solution. If the solute B is non-volatile, it may be assumed that its partial pressure compared to that of the pure solvent is essentially negligible. Hence the equation becomes

$$P_T = X_A P_A^{\circ} \dots\dots\dots (II)$$

Therefore the depression or decrease in the vapour pressure of the liquid is

$$\Delta P = P_A^{\circ} - P_T = P_A^{\circ} - X_A P_A^{\circ} = P_A^{\circ} (1 - X_A)$$

But $(1 - X_A) = X_B$

Therefore $\Delta P = X_B P_A^{\circ} \dots\dots\dots (III)$

At a particular temperature, P_A° is a constant and the change in the vapour pressure is thus proportional to the mole fraction of the solute, that is $\Delta P \propto X_B$.

Since $X_B = \frac{n_B}{n_A + n_B}$

The equation (III) becomes

$$\Delta P = P_A^{\circ} \left(\frac{n_B}{n_A + n_B} \right) \dots\dots\dots (IV)$$

Example:

Calculate the molecular mass of 9.21g non-volatile organic compound, dissolved in 50g of pure water at 25°C, which depresses the vapour pressure of the water from 3.16×10^3 to $3.10 \times 10^3 \text{ Nm}^{-2}$.

Solution

$$\Delta P = 3.16 \times 10^3 - 3.10 \times 10^3 \text{ Nm}^{-2} = 0.06 \times 10^3 \text{ Nm}^{-2}$$

$$P^{\circ} = 3.16 \times 10^3 \text{ Nm}^{-2}$$

$$\text{Molecular weight of H}_2\text{O} = 2 + 16 = 18$$

Mole fraction of solute X_B is

$$X_B = \frac{9.21 / M_w}{50/18 + 9.21 / M_w}$$

Where M_w is the molecular weight of solute

Therefore

$$0.06 \times 10^3 = 3.16 \times 10^3 \times \frac{9.21}{2.78M_w + 9.21}$$

$$M_w = 171$$

Elevation of Boiling Points

presence of a non-volatile solute in a volatile liquid causes a decrease on the vapour pressure of the solvent. That is the solution will require a lot more heat, compared to the pure liquid, to raise its vapour pressure to be equal to the external pressure. The result of this is that the solution will boil at a higher temperature than the original solvent, and the more concentrated the solution, the higher the boiling point, as shown in figure 4.7.1

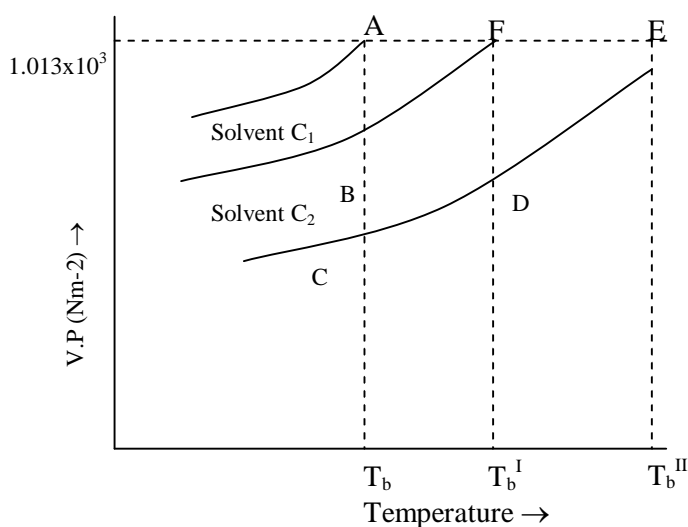


Figure 4.7.1 variation of vapour pressure with concentration
 T_b , T_b^I and T_b^{II} are the boiling points of the pure liquid and solutions containing C_1 and C_2 moles of a non-volatile solute per kilogram of the liquid respectively. If the solutions are fairly dilute the graphs for the pure liquid and the solutions are

not only parallel, they may be regarded to be fairly linear over narrow temperature ranges. Thus lines BF and CE on the graph may be regarded as straight lines.

Thus triangle ACE and ABF are similar triangles.

$$\text{Hence } \frac{AE}{AC} = \frac{AF}{AB} = \text{constant}$$

Both AC and AB represent depressions in the vapour pressure of the liquid due to the presence of the solute in the two solutions. AE and AF represent boiling point charges. It can be concluded that

$$\frac{\Delta T}{\Delta P} = \text{constant or}$$

ΔT is proportional to ΔP

But it has been shown that ΔP is proportional to the mole fraction of the solute.

Therefore

$$\Delta T \propto X_B$$

$$\text{and } \Delta T = K X_B$$

where K is the proportionally constant

if the amount of solute in solution is expressed in moles per kilogramme of solvents then the equation becomes

$$\Delta T = K_b m$$

where m is the molal concentration. The molal concentration m, can be written in terms of the weight of the solute (W) of molecular weight (M)s dissolved in weight of solvent (Ws). Thus the equation becomes

$$\Delta T_b = \frac{K_b \times W \times 1000}{M \times W_s}$$

K_b is known as the ebullioscopic constant or molal boiling point elevation constant.

Boiling point elevation measurement can be used to determine the molecular weight of a non-volatile solute if a solvent that shows a measurable increase in boiling point is used.

Example

An 0.25g compound of an unknown substance is dissolved in 25g of a solvent while K_b is 29K molal^{-1} and boils at 0.14°C higher than the pure solvent. What is the formula mass of the solute?

Solution:

$$\begin{aligned}\Delta T_b &= \frac{K_b \times W \times 1000}{M \times W_s} \\ M &= \frac{K_b \times W \times 1000}{\Delta T \times W_s} \\ &= \frac{2.9 \times 0.25 \times 1000}{0.14 \times 25} = 2.1 \times 10^2\end{aligned}$$

Depression of Freezing Point

When a cooling bath is required for temperature below the freezing point of ice, a salt-ice mixture is used, the salt depresses the freezing point of water. Thus, in an example of a general phenomenon in which added non-volatile solutes depress the freezing point of solvents on which they are contained. The greater the quantity of the solute added the greater the depression,

Considering the vapour pressure temperature curve for a pure liquid and solutions of a non-volatile solute in the liquids as shown in figure 4.7.2 below.

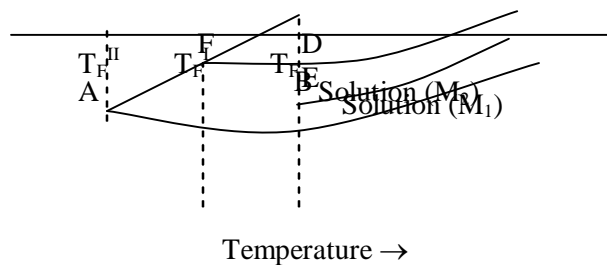


Figure 4,7.2 Vapour pressure curve of non volatile solute in the liquid

AB represents the vapour pressure of the solid at temperatures below the freezing point BC or the vapour pressure of the liquid as temperature increases. The point B where the solid and the liquid are in equilibrium in the freezing point. The temperatures T_F^I and T_F^{II} are the freezing points of the solutions containing M_1 and M_2 mole concentrations respectively. If we make the previous assumptions that the vapour pressure curves are parallel and that over short temperature ranges the vapour pressure curves are linear, then triangles ABE and FBD becomes similar triangles.

$$\text{Hence } \frac{AE}{BE} = \frac{FD}{BD} = \text{constant}$$

But DE and BE are DT_F^{II} and DP^{II} respectively and FD and BD are DT^I and DP^I respectively. Thus

$$\Delta T_f = K_f m$$

$$\text{and } \Delta DT_f = \frac{K_f \times W \times 1000}{M \times W_s}$$

Where K_f is known as the molal freezing point depression constant or cryoscopic constant. It is numerically equal to the freezing point depression when the concentration is one molal.

Comparatively K_f values are much bigger than K_b values.

Osmotic Pressure

The process of diffusion of solvent molecules from a high concentration region to a lower concentration through a membrane is known as osmosis. The pressure that must be applied in order to prevent osmosis is referred to as osmotic pressure. Experimental work reveals that the osmotic pressure exerted by a solution is proportional to the concentration of solute (C) and absolute temperature (T). Then Π is proportionate to CT and hence

$$\Pi = KCT$$

The constant of proportionality is of the same magnitude as the gas constant. Hence $\Pi = CRT$

If Π is measured in Nm^{-2} , the concentration unit has to be mole m^{-3} . In principle, osmosis pressure measurements can be used to determine the molecular weight (w) of a given solute, since C can be written as

$$C = \frac{W}{M} \frac{1}{V}$$

where W is the weight of the solute dissolved in volume V. The advantage of the method is that the pressure exerted by very dilute solutions are relatively large and can therefore be measured fairly accurately.

Example

What is the molecular weight of a 15.0g of a non-volatile compound dissolved in 100cm^3 of water which extends on osmotic pressure of $2.06 \times 10^6 \text{ Nm}^{-2}$ at 298K.

Solution

$$\Pi = CRT$$

$$C = \frac{V}{M} \frac{1}{v} = \frac{150}{M} \times 10^3 \text{ mol m}^{-3}$$

$$2.06 \times 10^6 = \frac{150}{M} \times 10^3 \times 8.31 \times 298$$

$$= 180$$

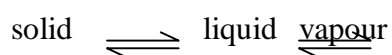
5.0 Colligative Properties of Electrolytes

Colligative properties of solutions of electrolytes are observed to be greater than those of solutions of non-electrolytes of the same molal concentration. For instance, whereas a molal solution of urea depresses the freezing point of water by about 1.86°C , one molal solutions of hydrochloric acid, nitric acid, ammonium chloride and sulphuric acid depresses the freezing point of water by 3.94 , 3.58 , 3.33 and 4.04°C respectively.

To explain these values, Van't Hoff suggested that they are obtained by multiplying 1.86 by some correcting factor referred to as the Van't Hoff factor, i . The factor i is the ratio of the observed and predicted colligative property of the electrolyte.

5.1 Phase Equilibria

When a solid such as ice, changes to liquid, solid, is in equilibrium with liquid, at any given moment during this change of state. At any given moment during the evaporation, liquid is in equilibrium with vapour. These changes of state from solid to liquid phase, and from liquid to vapour phase, may be expressed as



The equilibrium conditions for such changes, and for other changes of state such as dissolving salt in water, may be studied using fundamental principles of thermodynamics.

Phase

A change from one physical state to another is called a phase change. A phase may be defined as any homogeneous macroscopic portion of a system. A system is said to be homogeneous, or to consist of one phase if it is uniform throughout, both in chemical as well as physical composition. Since all gases are completely misable, they will always exist in a homogenous state, that is in a single phase e.g. a solution of sodium chloride in water.

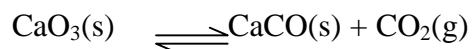
A system which is made up of more than one physical distinguishable phase, is said to be heterogonous e.g. water, which has ice cubes, on it is a homogenous system made up of two distinct phases.

Components

The composition of the system is described by using the smallest number of chemically distinct and independently variable constituents which together make up the various phases of the system. The chosen constituents are known as the components of the system. In the system ice \rightarrow water \rightarrow water vapour, the composition of all the phases can be expressed in terms of water. Water is thus described as a one-component system.

Consider the system in which solid CaCO_3 , solid CaO and gaseous CO_2 are in equilibrium. This represents a three phase system constituting of two solid and

one gaseous phases. The number of components, however, is two and not three since each of the three substances is not independent.



Hence for the calcium carbonate system, the number of components is

$$C = 3 - 1 = 2$$

Degrees of Freedom

One very important aspect of phase equilibrium is that the equilibrium state is independent of the actual amounts of the phases present provided variations in surface area are ignored. The smallest number of independent intensive thermodynamic variables that must be specified in order to describe completely the state of a system is known as the number of degree of freedom or the variance of the system. It is denoted by the symbol f . For example, 10dm^3 of pure CO_2 gas may be completely described by specifying any two of the variables; pressure, temperature and density. If any two of these variables are known, the third can be calculated such a system therefore has two degrees of freedom, or is bivariant. The water vapour system will have only one degree of freedom because of any given temperature, the pressure of vapour in equilibrium with liquid is fixed, and therefore only one variable needs to be specified to determine the state of the system.

6.0 Phase Rule

This rule was proposed by Willard Gibbs (1875 and 1876). It provides a general relationship between the number of phases, the number of components, and the degrees of freedom in a system at equilibrium. It states that for a system at

equilibrium having C components, and P phases, and in which equilibrium is only affected by the variables, pressure, temperature and concentration, the degree of freedom are given by the equation:

$$f = c - p + 2$$

The quantity two arises from the intensive variables, pressure and temperature.

Note that the phase rule only applies to systems at equilibrium.

Example

Find the number of degrees of freedom for a closed one component system , for a fixed amount of material, when.

- a. only one phase exist
- b. two phases are at equilibrium

Solution:

$$f = c - p + 2$$

- a. $p = 1$ therefore

$$f = 1 - 1 + 2 = 2 \text{ (bivariant)}$$

- b. $p = 2$ therefore

$$f = 1 - 2 + 2 = 1 \text{ (univariant)}$$

6.1 One-Component Systems

In one-component system, the smallest number of independently variable constituent substances required to form the phase is one. Examples of one-component systems are water, carbon, chloride, sulphur and bismuth.

The relationship between the vapour pressure and temperature of a substance in the solid, liquid and vapour (gaseous) phases can be represented by a phase diagram.

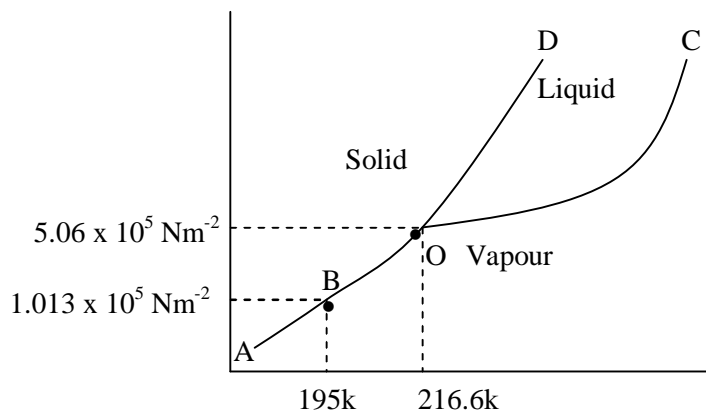


Figure 4.8.1 phase diagram for CO₂ system

O is the triple point, where solid, liquid and vapour are in equilibrium.

In point B, at 195k (sublimation temperature) and $1.013 \times 10^5 \text{ Nm}^{-2}$ pressure, a given quantity of solid CO₂ would change to the vapour without rise in temperature. CO₂ can therefore not be liquefied at ordinary atmosphere pressure.

The minimum pressure at which CO₂ will exist in liquid form is $5.06 \times 10^5 \text{ Nm}^{-2}$.

This corresponds to part of the triple point, where solid CO₂ will change to liquid (melt)s at a constant temperature of 216.6k water system.

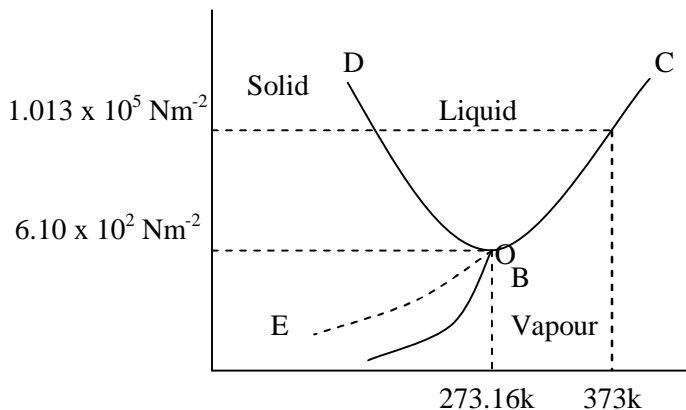


Figure 4.8.2 Phase diagram for H₂O system

The phase diagram of water is shown in figure 4.8.2. It will be seen from the diagram that at any given temperature. There is only one pressure at which liquid water and water vapour will be in equilibrium. The system is therefore univariant, with one degree of freedom. C is the critical point. AB represents the sublimation – curve for ice. Below $6.10 \times 10^2 \text{ Nm}^{-2}$ ice will form directly to vapour. B is the triple point. The curve EB represents the measurable region, along which water may be cooled below its freezing point without its solidifying.

Sulphur System

A one-component system could have more than one triple point if the solid express in more than one crystalline, or allotropic form. For example, sulphur can exist as rhombic or monoclinic sulphur, under different conditions. The transformations involved are known as solid-solid transformations. The sulphur phase diagram is as shown in figure 4.8.3. At low temperatures sulphur exists in the rhombic form. B is the triple point where rhombic sulphur, monoclinic sulphur, and sulphur vapour exist in equilibrium.

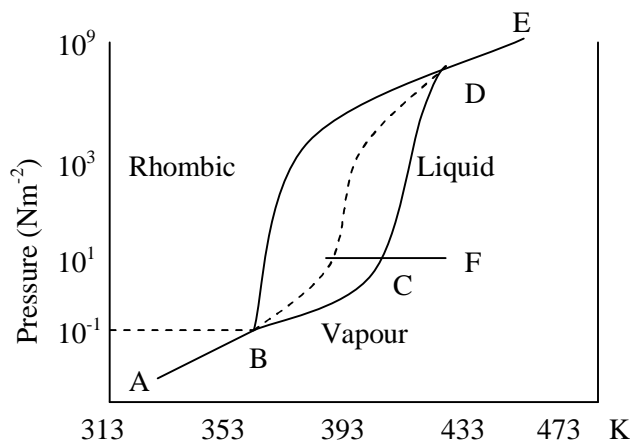


Figure 4.8.3 Phase diagram for sulphur system.

AB is thus the vapour pressure curve for rhombic sulphur. BC represents the vapour pressure curve for monoclinic sulphur. BC represents the vapour curve for monoclinic sulphur. from BO to OC, all rhombic sulphur changes to monoclinic sulphur. The point C is the triple point for monoclinic sulphur, liquid and sulphur vapour. O represents a third triple point, where rhombic, monoclinic and sulphur vapour, all exist in equilibrium.

It must be pointed out here that at point B where rhombic, monoclinic and vapour sulphur exists, we have three phases. But the system is made up of only one component. From the phase rule, the number of degree of freedom is given as $f = c - p + 2 = 1 - 3 + 2 = 0$ that is, B is an invariant point.

6.2 Two Components System

In a two component system, the smallest number of independently variable constituent substances required to form the phase is two. Examples of compounds that can be used to show such a system are those that can form alloys or form solid solutions. For example, copper and nickel, camphor and naphthalene, and bismuth and cadmium. The type of diagrams, here are for binary system, consisting of liquid solid phases and are therefore referred to as condensed system. In this, one of the variables, pressure, is kept constant. Hence the phase rule becomes $f = c - p + 1$ or $f = 3 - p$

Since pressure is kept constant the only intensive variables remaining are those of concentration and temperature. A phase diagram for a considered binary system will consist of a plot of temperature versus concentration. The concentration is most frequently expressed as mole fraction or weight percent, as shown in figure

4.8.4 for Bismuth – cadmium system.

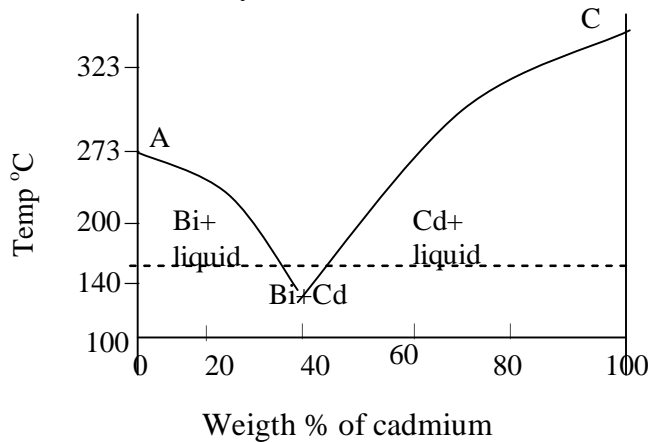


Figure 4.8.4 phase diagram for the Bi-Cd system

The degree of freedom or variance at the various areas on the phase diagram can be calculated. In the area above, ABC, there is one liquid phase and $f = 2 - 1 + 1 = 2$ (bivariant). Below AB and BC but above 140°C, there are two phases (liquid and solid) and $f = 2 - 2 + 1 = 1$ (univariant).

At the eutectic point B where there are three phases – solid bismuth, solid cadmium and liquid solution containing 40% cadmium. Here $f = 2 - 3 + 1 = 0$, and so it is the non-variant. There is only one temperature and one composition of solution at which these three phases can exist together at equilibrium at a given constant pressure.

7.0 Statistical Thermodynamics

This is based on the principle that thermodynamics observables are averages of molecular properties, and it sets about calculating these averages.

7.1 Molecular Energy Levels and the Boltzman Distribution

Consider a system composed of N particles. Although the total energy can be specified, it is not possible to define about how that energy is distributed.

Collision, take place, and result in the ceaseless redistribution of energy not only between the particles but also among their different model of motion.

Thus, on average there may be n_2 particles in a state of energy E_i , and in an equilibrium system, this average population remain constant even though there may be small momentary fluctuation around it and the identities of the particles on that state may change at every collision.

7.2 Configuration and Weights

Any individual particle may exist in states with energies $E_0, E_1, E_2, E_3, \dots$ etc. with $E_0 = 0$ and all other energies are related to it. In the sample as a whole, there will be n_0 particles in the state with energy E_0 , n_1 with E_1 and so on. The specification of the set of population n_0, n_1, n_2 , etc. is referred to as the configuration of the system.

The instantaneous configuration of the system fluctuates with time because the instantaneous populations change. For example, one might be $n_0 = N, n_1, n_2 = 0$ or $(N, 0, 0)$, corresponding to every molecules being in its ground state. Another might be $(N - 2, 2, 0)$ in which two particles are in a higher state. This can be achieved in $\frac{1}{2}N(N-1)$ different ways. If the system were free to fluctuate between the configurations, (as a result of collision), it would almost, always be found in the second.

A general configuration can be achieved in W different way, as given below

$$W = N! / n_0! n_1! n_2! \text{ Etc.}$$

where W is called the weight of the configurations and $0! = 1$

In looking for the configuration with the great weight, we have to ensure that it also satisfies the total energy criterion.

$$E = \sum_i n_i e_i$$

and is also subject to the total number criterion

$$E = \sum_i n_i$$

where E is the total energy of the system.

7.3 Most Probable Configuration

The maximum value W^* of W for a set of numbers n_o^*, n_1^*, n_2^* can be arrived at, when $\ln W$ is a maximum.

When a configuration changes, so that n_i changes to $n_i + dn_i$ and $\ln W$ changes to $\ln W + d(\ln W)$ where

$$d(\ln W) = \sum_i (\partial \ln W / \partial n_i) dn_i \dots\dots\dots I$$

At a maximum, the change $d(\ln W)$ vanishes, but the presence of the two equations involving E and N means that when n_i changes they do so subject to the constraints

$$\sum_i E_i dn_i = 0 \text{ and } \sum_i dn_i = 0$$

Multiplying the two constraints by the constants β and α respectively and then added to the equation I, gives

$$\begin{aligned} d(\ln W) &= \sum_i (\partial \ln W / \partial n_i) dn_i + \alpha \sum_i dn_i - \beta \sum_i E_i dn_i \\ &= d(\ln W) = \sum_i (\partial \ln W / \partial n_i) dn_i + \alpha \sum_i dn_i - \beta \sum_i E_i dn_i \end{aligned}$$

All the n_i are now treated as independent. This means that the only way of satisfying $d(\ln W) = 0$ is to require that for each i

$$(d \ln W / d n_i) + \alpha - \beta E_i = 0$$

Where n_i have their most probable values n_i^* . In order to solve this equation, we use Stirling's approximation in the form given below

$$\ln X! = X \ln X - X$$

In introduction of the approximation unit the expression $W = N! / n_0! n_1! n_2! \dots$, we have

$$\begin{aligned} \ln W &= \ln(N! / n_0! n_1! \dots) = \ln N! - \ln(n_0! n_1! \dots) \\ &= \ln N! - \sum_i \ln n_i! = (N \ln N - N) - \sum_i (n_i \ln n_i - n_i) \\ &= N \ln N - \sum_i n_i \ln n_i \end{aligned}$$

because the sum of the n_i is equal to N since N is a constant, differentiation with respect to n_i gives $(\partial \ln W / \partial n_i) = \sum_i \partial (n_i \ln n_i) / \partial n_i$

$$= - \sum_i [(\partial n_i / \partial n_i) \ln n_i + n_i (\partial \ln n_i / \partial n_i)] = -[\ln n_i + 1]$$

because $j \neq i$, thus $-\ln n_i + \alpha - \beta E_i = 0$ when $n_i = n_i^*$. The most probable population of the state of energy

E_i is therefore

$$n_i^* = e^{(\alpha - \beta E_i)}$$

$$\text{Since } N = \sum_i n_i^* = \sum_j e^{\alpha} e^{-\beta E_j}$$

It follows that

$$e^{\alpha} = N / \sum_j e^{-\beta E_j}$$

which leads to the boltzman distribution as given below

$$n_j^* = N e^{-n E_i / E_i} \sum_j e^{-\beta E_j}$$

The β is equal to $1/KT$, where T is the thermodynamic temperature

SUMMARY

The chemical potential of a given substance is the change in free energy of the system that results on the addition of one mole of that particular substance at a constant temperature and pressure to such a large quantity of the system that there is no appreciable change in the overall composition of the system. Gibbs-Duhem equation shows that variation in chemical potential of one of the components in a binary system affects the value of the chemical potential for another component.

In this we discussed chemical equilibrium. A general expression for the equilibrium constant was derived from the basic principles of thermodynamics. Different forms of the general expression were then utilized in understanding the equilibria of homogeneous and heterogeneous system.

Colligative properties of solute and an introduction to statistical thermodynamic were also discussed

FURTHER READING

Advanced Chemistry (Physical and Industrial) Philip Mathews Cambridge University Press 2003

Physical Chemistry PW Atkins 3rd Edition Oxford University Press 1986

