COURSE GUIDE

CHM 301
PHYSICAL CHEMISTRY III

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INTRODUCTION

The Physical Chemistry course (CHM 301) unlike the other aspect of Chemistry deals with physical measureable constants of a reaction system. In this course we will look at the driving force upon which reactions proceeds.

Many of the reactions you are familiar with are in 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 discoursed.

WHAT YOU WILL LEARN IN THIS COURSE

This course CHM 301, Physical Chemistry III, is a core course for students of theBachelor 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
- Relate 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

Module1 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	Enthalpyof 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

Module3 Spontaneous and Non-Spontaneous Processes

Unit 1	Free energy functions
Unit 2	Maxwell, Gibbs-Helmholtz and Calusius-Clapeyron Equation
Unit 3	Criteria for Spontaneity

Module4 Colligative Properties

Unit 1 System of Various Comparison
Unit 2 Derivation of General Expression for Chemical Equilibrium
Unit 3 Thermodynamic Quantities from EMF Values

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. Module 4 discuss colligative properties of solute and degree of freedom of a chemical substance with brief introduction to statistical thermodynamics.

Each of the units 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 coursework. 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 at10% 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 your 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 if:

- 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.

MAIN COURSE

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MODULE 1 THERMODYNAMICS, TYPES OF PROCESS, HEAT CHANGE ANDENTHALPY OF REACTIONS

INTRODUCTION

Much of chemistry is concerned with chemical reactions. In this module we will learn about one of the factors that control whether a reaction will or will not take place. This factor is called thermodynamics. Thermodynamic concepts relate to the energetics of a system. We will study energy changes in chemical reactions. A fundamental concept is that *every chemical reaction occurs with a concurrent change in energy*. Now we need to learn how to properly express these energy changes. 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 wil1 be outlined. The significance of enthalpy and enthalpy change of a system will be stated. Towards the end of this module, you will study the importance of Joule-Thomson effect. In another unit, we shall study the second law of thermodynamics. The following units will be discussed in this module:

UNIT 1 LAW OF THERMODYNAMICS

CONTENTS

1.0 INTRODUCTION

In beginning the study of thermodynamics it is important to understand the precise thermodynamic sense of the terms that are employed. In this unit, we shall introduce you to some of these terms used in thermodynamics. The definitions of work, heat, types of systems and other basic terms in thermodynamicswill be stated.

2.0 OBJECTIVES

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

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

3.0 MAIN CONTENT

3.1 Thermodynamic Terminologies

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 scaled 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.

3.2 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 bulks. 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

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

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

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

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

State of a System

The state of a system is defined when the state variables have definite values. It is necessary to specify all the state variables since these are interdependent. For example, if the system is an ideal gas, then its pressure, volume, temperature, and 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 a lid.

3.3The 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 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 Zerothlaw 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 unit8.

The Zerothlaw 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".

3.4Extensive and Intensive Variables

We have defined homogeneous and heterogeneous systems in Sec 3.0. 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.

$$\text{Volume of 0.100 Kg of ice} = \frac{Mass\ of\ ice}{Density\ of\ ice} = \frac{0.100\ Kg}{917\ Kgm^{-3}}$$

$$= 1.09\ x10^{-4}m^3$$

$$\text{Similarly, the volume of 100 Kg of water} = \frac{Mass\ of\ water}{Density\ of\ water}$$

$$= \frac{0.100\ Kg}{1.00\ \times 10^{-4}m^3}$$

$$= 1.00\ \times 10^{-3}Kgm^{-3}$$

$$\text{Total volume} = (1.09\ \times 1.00)10^{-4}Kgm^3$$

$$= 2.09\ \times 10^{-4}$$

An intensive property of a phase is independent of the amount of the phase. Thus refractive index, density and pressure are intensive properties. However, if a system consists of several phases', then some of the intensive properties may be different. For example, density is an intensive property but its value is different for ice and liquid water in equilibrium at 273.15 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.

4.0 CONCLUSION

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

i) Energy required to cooking your meals.
ii) Volume per unit mass of milk.
iii) Your body temperature.

5.0 SUMMARY

This unit introduced some basic concepts of thermodynamics. We established according to Zeroth law of thermodynamics that temperature is a fundamental and measurable property of matter.This Zeroth law justifies the concept of temperature and the use of a thermometer as a device for measuring temperature.

6.0 TUTOR-MARKED ASSIGNMENT

Specifying the state of a system means describing the condition of the system by giving the values of a sufficient set of numerical variables. We have already asserted that for an equilibrium one-phase liquid or gaseous system of one substance, the pressure is a function of three independent variables (n, T, V). We can generally choose which three independent variables to use so long as one is proportional to the size of the system. For fluid system of one substance, we could choose T, V, and n to specify the equilibrium state. We could also choose T, P, and n, or we could choose T, P, and V.

7.0 REFERENCES/FURTHER READING

Atkins, P. (2010). *The laws of thermodynamics: A very short introduction*. Oxford University Press, USA.

Atkins, P., & De Paula, J. (2013). *Elements of physical chemistry*. Oxford University Press, USA.

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Philip, M. (2003). *Advanced Chemistry (Physical and Industrial).*South Asia, Cambridge University Press.

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UNIT 2 TYPES OF PROCESSES

CONTENTS

1.0 INTRODUCTION

When the state of a system changes, it is said to have undergone a process. Thus, a process means changes 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 different types.

2.0 OBJECTIVES

By the end of this unit, you will 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 MAIN CONTENT

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.

$P_{ext} = P$ The system is static and piston does not move.

If $P_{ext} = P + dp$ The gas is compressed and the piston moves downwards infinitesimally slowly.

$P_{ext} = P$ dp The gas expands and the piston moves outwards infinitesimally slowly.

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.

3.1 Types of Processes: Work, Heat and Heat Capacity

Work, heat and energy have the same units, namely Joule (J). Energy is a 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.

$$W = F.X \qquad \dots (1.1)$$

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

- Gravitational Work: When a body of mass *m*smoved through a height *h* 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* flowthrough it, then work done per second is *Ei*and in *t s*econds 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 1 K. If, during the process, the volume of the system remains constant, then it is calledheat capacity at constant volume (C_v); if the pressure remains unchanged, it is called heat capacity at constant pressure (C_p). For one mole of a pure substance, these are called molar heat capacity at constant pressure, C_p and at constant volume, Cv. 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

$$C_v = nC_v = \frac{dq_v}{dT} \qquad \ldots (1.2)$$

$$C_p = nC_v = \frac{dq_p}{dT} \qquad \ldots (1.3)$$

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,

$$q_v = \int_{T_1}^{T_2} C_v \, dT = \int_{T_1}^{T_2} nC_v \, dT \qquad \ldots (1.4)$$

$$q_p = \int_{T_1}^{T_2} C_p \, dT = \int_{T_1}^{T_2} nC_p \, dT \qquad \ldots (1.5)$$

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 isC_p = (19.41 + 0.233 T) J mol^{-1}K^{-1}.

Molar heat capacity = Specific heat × Molar massCalculate the heat necessary to raise the temperature of 3.00 molof butane from298 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 K
T_2 = 573 K
n = 3.00 mol
C_p = (19.41 + 0.233 T) Jmol^{-1}K^{-1}

See the box below for understanding the simplification of the terms1andII.

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

$$\underbrace{3.00 \times 19.41 \int_{298}^{573} dT}_{\text{I}} \quad + \quad \underbrace{3.00 \times 0.233 \int_{298}^{573} TdT}_{\text{II}}$$

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

$$= 9.97\,X\,10^4\,J$$

$$= 99.7\,KJ$$

Hence, heat required to raise the temperature of 3.00 molof 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 exercise. Formula 1 is used in this unit in Example l and Formula 2 in Example 3.

Formula 1
If m is not required to -1

$$\int_{X_1}^{X_2} ax^m\,dx = a\int_{X_1}^{X_2} x^m\,dx = \frac{a}{m+1}\left[x^{x+1}\right]_{x_1}^{x_2} = \frac{a}{(m+1)} \quad (x^{2\ m+1} - x^{1\ m+1})$$

Where: a is a constant. This formula is used in the term marked II inExample1, where a = 3.00 × 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

$$\int_{X_1}^{X_2} a dx = \frac{a}{(0+1)}(x_2 - x_1) = (x_2 - x_1)$$

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 $JK^{-1}mol^{-1}$. 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.

[**Ans= 15780 J**]

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

E.g., (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, '1n' representation depicts a number in power of '*e*'

$$e = 1 + \frac{1}{1!} + \frac{1}{2!} + \frac{1}{3!} + \;\dots\dots$$

= 2.718 (to four digits)
For representing population of energy levels, radioactive decay etc., 'ln' is quite
useful.

3.2 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 Coldingin 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,

$$E = \mathrm{mc}^2 \qquad \ldots (1.6)$$

This means that if mass m is destroyed, then energy E is produced; c is the velocity of 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 sub particles. 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 someenergy 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 to 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 d$q$is positive (heat absorbed by the system is positive), this leads to an increase in the internal energy of the system. A negative d$q$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 d$w$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 d$w$is work done on the system, then the internal energy again increases. Hence, the net change in the internal energy is given by

$$dU = d_q + d_w \qquad \ldots.(1.7)$$

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

$$\Delta U = U_f - U_i = q + w \qquad \ldots.(1.8)$$

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 ΔUcan 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 represented by a state ***i*** where it has energy U_i in the figure 1.1. Suppose the conditions are now altered so that the system moves to ***f*** having energy U_f by the path I and then brought back to the state ***i*** by a different path II. As a consequence of first law of thermodynamics the total internal energy change, ΔU is same. Equations 1.7 and 1.8 are mathematical expressions of the first law of thermodynamics.

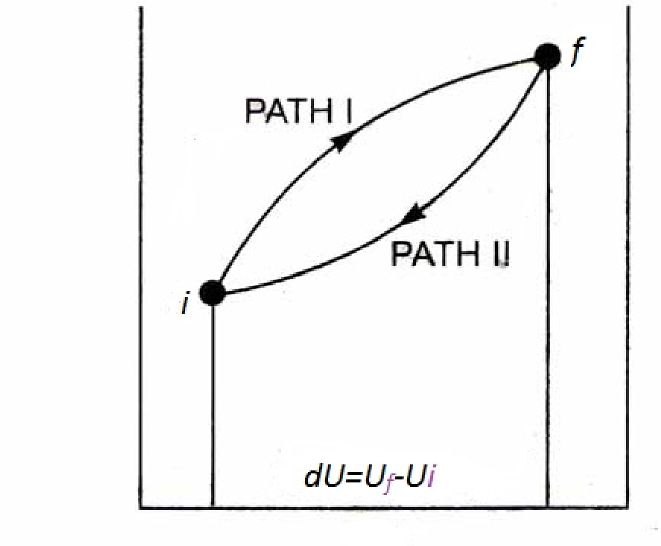

***Fig. 1.1*: Energy change through different onward paths. I and return path II.**

SELF-ASSESSMENT EXERCISE 2

Suggest a statement for the first law of thermodynamics such that the law of conservation of mass is not violated. [Ans Hint: section 3.2]

3.3 Isothermal Expansion

In this section, we are going to calculate the work done on the gas in an isothermal process. For this we must first arrive at a general expression for pressure–volume work done in an 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

$$F = P_{ext} A \qquad \ldots.(1.9)$$

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

$$dw' = \mathrm{F.dx} = P_{ext} A dx \qquad \ldots.(1.10)$$

But Ad*x*is the change in volume of the gas, d*V*. Hence

$$dw' = P_{ext}\, dV \qquad \ldots.(1.11)$$

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

$$dw' = -P_{ext}\, dV \qquad \ldots.(1.12)$$

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 d*w*is negative when the gas expands and it is positive when the gas contracts, [d*v* = + ve in expansionand d*v* = – vein compression].

Note that the value of the work (d*w*) done on the gas is obtained by reversing the sign of work (d*w*’) done by the gasor d*w*= - d*w*’

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}, = 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.

$$\left. W = -\int_{V_1}^{V_2} P_{ext}\; dV = -P_{ext}\int_{V_1}^{V_2} dV \right\} \quad \ldots$$

(1.13)

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

The symbol, ΔV, denotes the total change in volume during the process. Let us work out an example to illustrate the use of Eq. 1.13.

Example 2

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

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

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

$= -2 \times 10^5 m^3$ $(because\ 1\ bar = 1 \times 10^5 Paand\ 1\ Pam^3 = 1\ J$

$= -2 \times 10^5 \text{ J}$

It can be seen that the work done on the system is negative, this means, actually system has done work equal to 2 × 10^5 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, $P_{ext} \approx P$ andhence, Eq. 1.12 can be written as,

$$dw = -pdV \qquad \text{... (1.14)}$$

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 1discussed in Sec. 1.6.

Note that dx and Δx referto 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.

$$W = -\int_{V_1}^{V_2} pdV \qquad \text{….}(1.15)$$

Let us assume that the gas behaves ideally. Hence,

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

Using this in Eq. 1.15

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

$$= nRT - \int_{V_1}^{V_2} \frac{dV}{V} \qquad \text{….}(1.16)$$

$$= -nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{V_1}{V_2} \qquad \text{….}(1.17)$$

$$\text{Hence, W} = -2.303RT\log\frac{V_2}{V_1} = 2.303\,nRT\log\frac{V_1}{V_2} \qquad \text{….}(1.18)$$

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 Equations. 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. 1.13whereas *p* in Eq. 1.15istobe 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,
a = nRT
x_1 = V_1 x_2 = V_2 x = V

Note that Equations 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 o£ state must be used.

$$Note\ that\ -log\frac{P_1}{P_2} = log\frac{P_2}{P_1};$$

Thisfollows 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,

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

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

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

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 ($p1$ and $p2$) of the ideal gas.

For an ideal gas at constant temperature,

$$P_1V_1 = P_2V_2 \qquad ...(1.19)$$

$$\frac{V_2}{\mathrm{V}_1} = \frac{P_1}{\mathrm{P}_2} \qquad \dots (1.20)$$

$$W = -2.303\ nRT \log\frac{P_1}{P_2}$$

$$= 2.303\ nRT \log\frac{P_2}{P_1} \qquad \dots (1.21)$$

Let us illustrate the use of Eq. 1.21

Example 3

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

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

$$\mathrm{R} = 8.314\ \mathrm{JmolK^{-1}};\ \mathrm{T} = 3.00 \times 10^2 K$$

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.

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

$$n = 1.00 \times 10^2\ mol$$

Substituting the values in Eq. 1.21

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

Step (i)

$$= 2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times (61.7782 - 5.4771J)$$

Step (ii)

$$= 2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times 1.3011\ J$$

Step (iii)

$$W = 7.47 \times 10^5 J$$

Using the principles studied above, answerthe following SAQ.

4.0 CONCLUSION

- A chemical reaction takes place in a container of cross-sectional area 50.0 cm^2. As a result of the reaction, a piston is pushed out through 15 cm against an external pressure of 121 kPa. Calculate the work done by the system.
- An object is pushed in the z direction by a force given by $F_z = az + b$, where the constant a has the value 300.0Nm^{-1} and the constant b has the value 500.0 N. Find the work done in moving the object from z = 0 to z = 10.0m. [Hint: Eq. 1.10]
- a. Calculate the work done on a closed system consisting of 50.00 g of argon, assumed ideal, when it expands isothermally and reversibly from a volume of 5.000 L to a volume of 10.00 L at a temperature of 298.15 K.
- b. Calculate the integral of dP for the same process.

5.0 SUMMARY

The first law of thermodynamics does not place any restriction on the conversion of energyfrom one form to another; it simply requires that the total quantity of energy be the same before and after the conversion. It is essential to understand the meaning of the several equations derived and the meaning of such terms as isothermal, reversible and irreversible processes. These terms have definite mathematical consequences to the equations. The equations that solve each problem must be derived from the few fundamental equations mentioned thus far. Other methods of attack, such as attempting to memorize as many equations as possible, produce only panic, paralysis, and paranoia.

6.0 TUTOR-MARKED ASSIGNMENT

From this unit, we can summarize with the following principal ideas:

1. Thermodynamics is based on empirical laws.
2. The first law of thermodynamics asserts that the internal energy U is a state function if; $\Delta U = q + w$
3. where q is an amount of heat transferred to the system and w is an amount of work done on the system.
4. Heat is one way of transferring energy.
5. Work is another way of transferring energy.
6. The first law of thermodynamics provides the means to calculate amounts of work and heat transferred in various processes, including adiabatic processes.
7. The enthalpy is a state function whose change in a constant-pressure process is equal to the amount of heat transferred to the system in the process.

8. The enthalpy change of a chemical reaction can be calculated from the enthalpy changes of formation of all products and reactants.

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UNIT 3 HEAT CHANGE

CONTENTS

1.0 INTRODUCTION

One of the major effects of heat transfer is temperature change: heating increases the temperature while cooling decreases it. We assume that there is no phase change and that no work is done on or by the system. Experiments show that the transferred heat depends on three factors—the change in temperature, the mass of the system, and the substance and phase of the substance.

The heat Q transferred to cause a temperature change depends on the magnitude of the temperature change, the mass of the system, and the substance and phase involved. (a) The amount of heat transferred is directly proportional to the temperature change. To double the temperature, change of a mass m, you need to add twice the heat. (b) The amount of heat transferred is also directly proportional to the mass. To cause an equivalent temperature change in a doubled mass, you need to add twice the heat. (c) The amount of heat transferred depends on the substance and its phase. If it takes an amount Q of heat to cause a temperature change T in a given mass of copper, it will take 10.8 times that amount of heat to cause the equivalent temperature change in the same mass of water assuming no phase change in either substance.

2.0 OBJECTIVES

By the end of this unit, you will be able 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 Cp and C_V of an ideal gas equation.

3.0 MAIN CONTENT

3.1 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 Equations. 1.9 and 1.14

$$dU = dq - pdV \qquad \ldots.(1.22)$$

$$or\ dq = dU + pdV \qquad \ldots.(1.23)$$

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

$$dV - pdV = 0$$

Hence,

$$dqv - dU \qquad \ldots.(1.24)$$

For finite changes in internal energy, Eq. 1.24 becomes,

$$q_v = \Delta U \qquad \ldots.(1.25)$$

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 Equations 1.24 and 1.26

$$dU = CvdT = nC_v dT \qquad \ldots.(1.26)$$

This holds good for n molof an ideal gascan be rewritten as,

$$Cv = \frac{(\partial \mathrm{U})}{\partial T} \qquad \ldots.(1.27)$$

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

$\left(\frac{\partial U}{\partial T}\right)V$ is called the partial differentiation 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.

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

In order to obtain ΔU when an ideal gas is heated from temperature T_1 to T_2at constant volume, the integrated form of Equation 1.26 is to be used.

$$i.e\ \Delta U = \int_{T_1}^{T_2} CvdT = \int_{T_1}^{T_2} \acute{C}vdT \qquad ....(1.28)$$

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 Cvthrough Eq. 1.27. What about Cp? Is there some thermodynamic property to whichCp can be related in a similar way? For this purpose, we define the term, enthalpy, in the next section.

3.2 Enthalpy and Enthalpy Changes

Enthalpy of a system is defined by the relation,

$$H = U + pV \qquad ....(1.29)$$

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 H1, and H2 are the enthalpies of the initial and final states of a system, then the enthalpy change accompanying the process is given by,

$$\Delta H = H_2 + H \qquad ...(1.30)$$

$$= (U_2 + P_2V_2) - (U_1 + P_1V_1)$$

$$= \Delta U + (P_2V_2 - P_1V_1) \qquad ....(1.31)$$

In case of a constant pressure process $(P_1 = P_2 = P)$, Equation 1.31 can be written as,

$$\Delta H = \Delta U + p(V_2 - V_1)$$
$$\Delta H = \Delta U + p\Delta V \qquad \ldots.(1.32)$$

Rewriting Eq. 1.23 for a finite change, we get

$$q_p = \Delta U + p\Delta V \qquad \ldots.(1.33)$$

this means, the heat capacity at constant pressure is equal to the partial differential of H with respectto temperature at constant pressure. Interestingly for an ideal gas. H depends on 7" only and not on p.

Using this equation in Equation 1.32,

$$q_p = \Delta H \qquad \ldots.(1.34)$$

The subscript p in qp 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

$$dq_p = dH \ldots. (1.35)$$

Using Eq. 1.3 and assuming that there is no phase change or chemical reactionhave,

$$dH = C_p \mathrm{d}T = \mathrm{n}\acute{C}_p dT \qquad \ldots.(1.36)$$

In order to obtain ΔH value when an ideal gas is hated from temperature $T1$ to $T2$, at constant pressure, the integrated form of Eq. 1.36 is to be used.

$$\Delta H = \int_{\mathrm{T}_1}^{T_2} \mathrm{CvdT} = \int_{\mathrm{T}_1}^{\mathrm{T}_2} \mathrm{n}\ \acute{\mathrm{C}}_\mathrm{p}\ \mathrm{dT} \qquad \ldots.(1.37)$$

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 Equation 1.36, C_p can be defined as $C_p = \left(\frac{\partial H}{\partial T}\right)_T$ this means, the heat capacityat 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;
$i.e \left(\frac{\partial H}{\partial T}\right)_T = 0$ 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 evaporization 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 reactants as per the stoichiometry given in the chemical equation. We shall study enthalpy changes in detail in the next section. We shall also study the relationship between $C_p$and C_v values of an ideal gas.

3.3 Relationship Between $C_P$and C_V of an Ideal Gas

The internal energy of an ideal gas depends only on its temperature and is independent of pressure 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,

$$H = U + pV = U + RT \qquad \ldots.(1.38)$$

On differentiating we get,

$$dH = dU + RdT \ [because\ R\ is\ a\ constant]$$

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

$$\acute{C}_P dT = \acute{C}_P dT + RdT \qquad \ldots.(1.39)$$

$$\acute{C}_P = \acute{C}_V + R$$

And hence, $\acute{C}_P - \acute{C}_V = R \qquad \ldots.(1.40)$

Also, for $n$mol, $\acute{C}_P - \acute{C}_V = nR$ ….(1.41)

This means that $\acute{C}_P$ is always greater than $\acute{C}_V$ for an ideal gas. This is because when the temperature of a gas is raised at constant pressure; there will be an 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.

SELF-ASSESSMENT EXERCISE

i. Explain the difference between the change in internal energy and the change in enthalpy accompanying a chemical or physical process.

ii. A sample consisting of 2.0 mol He is expanded isothermally at 22°C from 22.8 dm^3 to 31.7 dm^3 (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH.

iii. Find the amount of heat needed to heat 3.20 mol of liquid water from 25.00^oC to 95.00^oC.

iv. The molar heat capacity of water vapor at a constant pressure of 1.000 atm is represented by $C_{P,m} = 30.54 JK^{-1} mol^{-1} + (0.01029 JK^{-2} mol^{-1})T$

v. where T is the Kelvin temperature. Find the amount of heat required to raise the temperature of 2.000 mol of water vapor from 100.0^oC to 500.0^oC.

vi. Find the amount of heat put into 5.000 mol of argon (assumed ideal) in expanding reversibly and isothermally at 298.15K from a volume of 20.00 L to 100.00 L.

4.0 CONCLUSION

The equations in this unit are quite general and are applicable to any transformation at constant pressure or at constant volume of any system of fixed mass, provided no phase changes or chemical reactions occur. For example, the enthalpy, H, was defined by: H = U + PV.

where P is the pressure and V is the volume of the system. At constant pressure, ΔH is equal to q for a simple system.

The physical explanation for the difference between C_P and C_V is that heating an ideal gas at constant volume does not work on the surroundings. In heating at constant pressure some of the heat is turned into work against the external pressure as the gas expands. A larger amount of heat is therefore required for a given change in the temperature than for a constant-volume process.

5.0 SUMMARY

In this unit, we first examine a process where the system has a constant volume, then contrast it with a system at constant pressure. The heat capacity at constant pressure C_P is greater than the heat capacity at constant volume C_V, because when heat is added at constant pressure, the substance expands and work is done. Hence, for an ideal gas, the heat capacity at constant pressure is greater than that at constant volume by the amount nR.

6.0 TUTOR-MARKED ASSIGNMENT

Find the amount of heat put into 5.000 mol of argon (assumed ideal) in expanding reversibly and isothermally at 298.15K from a volume of 20.00 L to 100.00 L.

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UNIT 4 ENTHALPY OF REACTIONS

CONTENTS

1.0 INTRODUCTION

The Enthalpy of Reaction (also known as Heat of Reaction) is the change in the enthalpy of a chemical reaction that occurs at a constant pressure. It is a thermodynamic unit of measurement useful for calculating the amount of energy per mole either released or produced in a reaction. Since enthalpy is derived from pressure, volume, and internal energy, all of which are state functions, enthalpy is also a state function.

2.0 OBJECTIVES

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

- Explain Joule-Thomson Effect.
- Derive Kirchhoff’s Equation and state its significance
- Define bond enthalpy, and
- Calculate enthalpies of reactions from bond enthalpies.

3.0 MAIN CONTENT

3.1 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,

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

During expansion, d$w$and hence, d$U$are negative. That is, as the system does expansion work, its internal energy decreases. This, again, according to Eq 1.26 means that d$T$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. 1.42, $dU = dw$

Substituting for d$w$and d$U$from Eqs. 1.14 and 1.26, we get for one mole of an ideal gas,

For one mole of an ideal gas,,

$$\acute{C}_V dT = -pdV$$

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

Using this relationship in Equation, 1.43 we get

$$\acute{C}_V dT = \frac{-RTdV}{V} \qquad \ldots .(1.44)$$

Rearranging, we get,

$$\frac{\acute{C}_V dT}{T} = \frac{-RdV}{V} \qquad \ldots .(1.45)$$

Integrating Equation 1.43 between temperature limits $T1$ and $T2$ and volume limits $V1$and $V2$, we get,

$$\acute{C}_V \int_{T_1}^{T_2} \frac{dT}{T} = -R \int_{V_1}^{V_2} \frac{dV}{V} \qquad \ldots .(1.46)$$

$$\acute{C}_V \ln \frac{dT}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

$$= \left(\acute{C}_p - \acute{C}_V \right) \ln \frac{V_1}{V_2} \qquad \text{(Using Equation 1.40)}$$

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

$$\ln \frac{T_2}{T_1} = (\gamma - 1) \ln \frac{V_1}{\mathrm{V}_2}$$

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

The integrals on the left and right sides of Equation 1.46 are solved using formula 2 given in Sec. 1.6. Note that $\acute{C}_V$ 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.

Rearranging Eq. 1.47 we get,

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.

$$2 \log 10 = \log 10^2 = \log 10.0$$
$$3 \log 2 \quad = \log 2^3 = \log 8$$

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

Taking antilogarithm of both sides

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

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

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

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

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{V_1}{V_2} = \frac{P_2T_1}{P_1T_2} \qquad \ldots(1.49)$$

Substituting this in Equation 1.48

$$\frac{T_1}{T_2} = \left(\frac{P_1T_2}{P_2T_1}\right)^{\gamma-1}$$

$$T_2(P_1T_2)^{\gamma-1} = T_1(P_2T_1)^{\gamma-1}$$

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

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

For any reversible adiabatic expansion, $T2$ 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_1V_1, = p_2V_2 whereas in an adiabatic reversible process, it is $p_1V_1 = p_2V_2^{\gamma}$. 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,

$$\frac{T_2}{T_1} = \frac{P_2V_2}{P_1V_1}$$

It follows from Eq. 1.48 that:

T

$$P_2V_2V_2{}^{\gamma-1} = P_1V_1V_1{}^{\gamma-1}$$

Or $P_1V_1{}^{\gamma} = P_2V_2{}^{\gamma}$

or pV^{γ} = Constant …(1.51)

Equation 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 d$U$and d$w$for an adiabatic process are related through Eq. 1.42

Using this equation and Eq. 1.26 get for 1 molof an ideal gas,

$$dU = dw = \acute{C}_V dT$$

In case of n molof an ideal gas,

$$dU = dw = nC_v dT \qquad \ldots (1.52)$$

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.

$$\Delta U = W = n\acute{C}_V \int_{T_1}^{T_2} dT$$

$$= n\acute{C}_v (T_2 - T_1) = n\acute{C}_V \Delta T \qquad (1.53)$$

Hence, ΔU and W can be calculated when n, C_v, $T_{1,}$ and T_2 are known.

Note that $C_v$is assumed to be a constant in Eq. 1.53 in the temperature range T_1 and $T_{1.}$

Irreversible Adiabatic Expansion

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

$$W = -P_{ext} \Delta V \qquad \ldots (1.54)$$

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

$$-P_{ext} \Delta V = n\acute{C}_V \Delta T$$

Hence, $\Delta T = (T_2 - T_1) = \frac{-P_{ext}\,\Delta V}{n\acute{C}_V}$ … (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.

3.2 Joule-Thomson Effect

Our discussion so far centered onideal 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$p1$ and $p2$ in the two compartments. Note that $p1$ is greater than $p2$. The left hand side piston is then slowly pushed inwards so that, without changing the value of $p1$, a volume $V1$ 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 $V2$. Accurate temperature measurements are madein both compartments.

The network 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 $p2V2$ is the work done by the system and $p1V1$ 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 3of this course.

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

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

$$\mu_{JT} = \left(\frac{\partial T}{\partial \mathrm{P}}\right)_{\mathrm{H}} \qquad \ldots.(1.60)$$

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 headed and also combines with oxygen present in the air; the latter reaction causes an explosion.

3.3 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,

$$dH = C_p dT \qquad \ldots(1.61)$$

In the case of enthalpy of a reaction ($\Delta_r H$), we can rewrite Eq.1 .61 as,

$$d(\Delta_r H) = \Delta C_p dt \qquad \ldots(1.62)$$

Where: ΔC_p= (sum of C_p values of products) – (sum of C_p 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,

$$\Delta_r H_2 - \Delta_r H_1 = \int_{T_1}^{T_2} \Delta C_p \, dT \qquad ...(1.63) \qquad ....(1.63)$$

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.

$$\Delta_r U_2 - \Delta_r U_1 = \int_{T_1}^{T_2} \Delta C_V \, dT \qquad ....(1.64)$$

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 enthalpy of reaction does not change.

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

$$\Delta_r H_2 = \Delta_r H_1 + \Delta C_p \, (T_2 - T_1) \ldots (1.65)$$

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 C_p is usually expressed in the following way:

$C_p = a + bT + cT^2 + \ldots\ldots$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,

$$C\,(graphite) + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)};$$

at 298 K is l31.2 kJ. The $C_p$values are given below in the temperature range, 298 to 348 K.

Substance	**C_p/Jmol^{-1}K^{-1}**
Graphite	15.93
$H_2O_{(g)}$	30.04
$CO_{(g)}$	26.51
$H_{2(g)}$	29.04

Calculate $\Delta_r H$ at 348 K.

The 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

$$\Delta C_p = \{(1 \times C_p(\mathrm{CO}) + 1 \times C_p(\mathrm{H_2})) - (1 \times C_p(\mathrm{graphite}) + 1 \times C_p(\mathrm{H_2O}))\}\ \mathrm{JK^{-1}}$$

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

$$= \{(26.51+29.04)-(15.93+30.04)\}\ \mathrm{JK^{-1}}$$

$=9.58\ \mathrm{J\ K^{-1}}$
$=9.58\times10^{-3}\ \mathrm{kJK^{-1}}$ (Remember 1 J = 10^{-3} kJ)

ΔC_p is expressed in $\mathrm{kJK^{-1}}$, since $\Delta_r H$ at 298 K is given in kJ. Using Eq. 1.65,
$\Delta_r H$ at 348K = $\Delta_r H$ at 298 K + ΔC_p (348 - 298)
= (131.2 + 9.58 x 10^{-3} × 50) kJ
= 131.7 kJ

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

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

SELF-ASSESSMENT EXERCISE 2

For the reaction,

$$C(graphite) + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}$$

Calculate ΔC, if the molar heat capacities at constant pressure for various species vary as per the equation, $C_p = a + bT + cT^2$ where C_p is in $Jmol^{-1}K^{-1}$. 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

$H_2O_{(g)}$	30.04	9.920	8.71
$CO_{(g)}$	26.51	7.68	11.71
$H_{2(g)}$	29.04	-0.836	20.09

3.3 Bond Enthalpies andEstimation 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, ΔHatom, and is always positive. For example, the enthalpy of the followingreaction is the enthalpy of atomization of ethane gas:

$$C_2H_{6(g)} \rightarrow 2C_{(g)} + 6H_{(g)}\ \Delta H_{atom} = -2828.38\ KJ\ mol^{-1}$$

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 ΔHatom 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 kJmol^{-1}.

If graphite is considered the reference state for carbon, then the atomization can be written as follows:

$$C_{(graphite)} \rightarrow C_{(g)}\ \Delta H_{atom} = 717\ KJmol^{-1}$$

Table 1.1: Bond Enthalpies

$Bond$	$\frac{B}{KJmol^{-1}}$	$Bond$	$\frac{B}{KJmol^{-1}}$	$Bond$	$\frac{B}{KJmol^{-1}}$
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 ofsome more elements which become atomized on sublimation are givenin Table 1.2

Table 1.2: Standard Enthalpies of Atomization at 298.15 K

$\boldsymbol{Substance}$	$\boldsymbol{\Delta H^0 atom\ KJmol^{-1}}$
$C(graphite)$	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:

$$H_2O_{(g)} \rightarrow OH_{(g)} + H_{(g)} D_1 = 501.9\ kJ\ mol^{-1}$$
$$OH_{(g)} \rightarrow O_{(g)} + H_{(g)} \quad D_1 = 423.4\ kJ\ mol^{-1}$$

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 breakingall 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= (Heat required to break all the bondsin the reactants) - (heat released when the atoms form the product) ….(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.

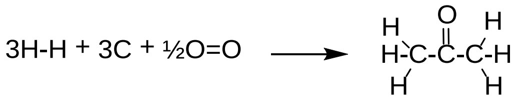
Example 4

Estimate the standard enthalpy of formation of acetone vapourand acetone liquid. (Enthalpy of vaporization of liquid acetone =29 k J mol^{-1})

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

$$3H_{2(g)} + 3C_{(graphite)} + ½O_{2(g)} \rightarrow C_2H_6CO_{(g)} \quad ...(1.67)$$

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



Step (ii): The heat required to atomize the reactants
$= 3B(H-H) + 3\Delta_{atom} H_{(grap\,hite)} + ½B(O=O)$
$= [(3\times 346) + (3\times 717) + ½(497)]KJ$
$= 3713\ KJ$

The heat released when the atoms form the product
$= 6B(C-H) + 2B(C-C) + B(C=O)$
$= -3913\ KJ$

Step (iii): $\Delta_f H^0\big(acetone(g)\big) = (3708 - 3913)KJmol^{-1}$

Hence, the standard enthalpy of formation of acetone vapouris –205 kJmol^{-1}and, the actual value is –216 kJmol^{-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. 1.68.

Note that for condensation of acetone (g),
the enthalpy change$= -\Delta H^0_{vap}(acetone) = -29KJmol^{-1}$ ... (1.68)
$C_2H_6CO_{(g)} \rightarrow C_2H_6CO_{(l)}$

Adding Equations 1.67 and 1.68 we have,
$3H_{2(g)} + 3C_{(grap\,hite)} + ½O_{2(g)} \rightarrow C_2H_6CO_{(l)}$

Hence, $\Delta_f H^0_{(acetone\ )(l)} = \Delta_f H^0_{(acetone\ )(g)} - \Delta H^0_{vap\,(acetone\ ).}$So, the standardenthalpy of formation of liquid acetone is – 234 kJmol^{-1}. Using the above principles, answer the following SAQ.

SELF-ASSESSMENT EXERCISE

i. A sample of nitrogen of mass 3.12 g at 23.0°C is allowed to expand reversibly and adiabatically from 400 cm^3 to 2.00 dm^3. What is the work done by the gas? Take $\gamma = 1.4$
ii. Calculate the final pressure of a sample of water vapour that expands reversibly and adiabatically from 8.73 Torr and 500 cm^3 to a final volume of 3.0 dm^3. Take $\gamma = 1.3$.
iii. Calculate ΔU for a process that takes 1.000 mol of argon from T = 298.15K and V = 2.000 L to T = 373.15K and V = 20.000 L. Does the result depend on whether the process is reversible?
iv. A system consisting of 2.000 mol of argon expands adiabatically and reversibly from a volume of 5.000 L and a temperature of 373.15K to a volume of 20.00 L. Find the final temperature. Assume argon to be ideal with C_V equal to 3nR/2.

v. For air at 300K and 25 atm, $\mu_{JT} = 0.173K\ atm^{-1}$. If a Joule–Thomson expansion is carried out from a pressure of 50.00 atm to a pressure of 1.00 atm, estimate the final temperature if the initial temperature is equal to 300 K.

vi. Find a formula for ΔH for the heating of a sample of a gas from temperature T_1 to temperature T_2 at constant pressure if $C_{P,m}$ is represented by

vii. $C_{P,m} = a + bT + cT^{-2}$

viii. The standard-state enthalpy change of combustion of methane at 298.15K equals −890.36 kJ mol^{-1}, with liquid water as one of the products. Find the enthalpy change of formation of methane at 298.15K using the enthalpy changes of formation of H_2O and CO_2.

4.0 CONCLUSION

One case of interest in this unit is that chemical reaction can take place adiabatically at constant pressure. In this case the enthalpy change is equal to the heat transferred, which is equal to zero. The Joule-Thomson coefficient, μ_{JT}, is defined as the limiting value $\left(\frac{\partial T}{\partial P}\right)_H$ as Δp approaches zero.

5.0 SUMMARY

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

- The Zerothlaw 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 exchangeand internal energy change in isothermal and adiabatic processes are derived. Examples are also workedout to explain the use of these formulae.
- Joule-Thomson effectis 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.

6.0 TUTOR-MARKED ASSIGNMENT

A sample of nitrogen of mass 3.12 g at 23.0°C is allowed to expand reversibly and adiabatically from 400 cm^3 to 2.00 dm^3. What is the work done by the gas? Take $\gamma = 1.4$

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MODULE 2 REVERSIBLE AND IRREVERSIBLE REACTIONS, ENTROPY OF CHANGE

INTRODUCTION

As described in the previous moduleit 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 vapoursare 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 module under the following units:

UNIT 1 REVERSIBLE, IRREVERSIBLE AND CYCLE PROCESSES

CONTENTS

1.0 INTRODUCTION

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

By the end ofthis 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 MAIN CONTENT

3.1 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 wcertainly 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

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

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

i.e., $-W_{rev} > -W_{irrev}$

Hence, $W_{rev} < W_{irrev}$

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. UsingEqs. 2.3 and 2.5, we can write,

$q_{rev} > q_{irrev}$

This means that in a non-adiabatic process, heat absorbed by a system from the surroundings is more under reversible conditions than under irreversible conditions. 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 undergoing any number of processes return to its initial state. This means that ΔU = 0; hence, the work system during all these processes should be equal to the heat absorbed by the system.

$i.e., q = q_1 + q_2 + \cdots = -(w_1 + w_2 + \cdots) = -w$

Where q and $w$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 doneon 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 molof an ideal gas at 3.00×10^2 K temperature and 6.00x10^6 Pa pressure occupies 4.16×10^{-2} 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, ΔU=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 is= -*w*

Work done by the system under reversible conditions is = -w_{rev}

Work done by the system under irreversible conditions is= -w_{irrev}

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

$$-3 > -4$$
$$and\ 3 < 4$$

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

$$q_{rev} = -w_{rev} = -2.303\, nRT \log \frac{\mathrm{V}_1}{\mathrm{V}_2}$$
$$= 2.303\, nRT \log \frac{\mathrm{V}_2}{\mathrm{V}_1}$$

$$= 2.303 \times 1.00 \times 10^2 mol \times 8.314\, Jmol^{-1}K^{-1} \times 3.00 \times 10^2 K \log \frac{0.832\ \mathrm{m}^3}{4.16 \times 10^{-2}\mathrm{m}^3}$$
$$= 7.47 \times 10^5 J$$

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

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

(b) Let us calculate $q_{\mathrm{irrev}}$and $w_{\mathrm{irrev}}$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,

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

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

$W_{rev} = -7.74 \times 10^5 J$; W_{irrev} = -2.37 × $10^5 J$
Hence, $W_{rev} < W_{irrev}$ $as\ per\ equaion$ 8.5
$q_{rev} = 7.47 \times 10^5 J$; $q_{irrev} = 2.37 \times 10^5 J$
Hence, $q_{rev} > q_{irrev}$ $as\ per\ Eg.$ 2.6

3.2 The Carnot Cycle

Carnot analyzed 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.

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

$$w_{adiabatic} = C_v\left(T_{final} - T_{initial}\right) \quad \ldots.(Eq. 1.53)$$

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

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

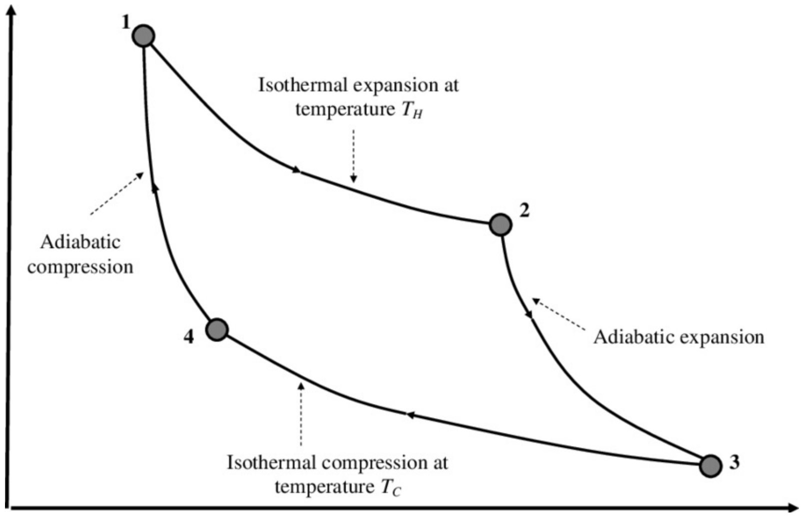

Fig. 2.1: Carnot Cycle

The Carnot cycle operation can be described by the following four steps: (1) Isothermal Expansion (2) Adiabatic Expansion (3) lsothermalCompression 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, ΔU= 0.

Hence, using Eqs. 1.8 and 1.17

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

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

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,

$$w_2 = C_v(T_C - T_H) \quad \text{... (2.10)}$$

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).

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

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

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,

$$w_4 = C_v(T_H - T_C) \quad \text{... (2.13)}$$

The net work done on the system is

$$w = w_1 + w_2 + w_3 + w_4 \quad \text{... (2.14)}$$

$$or w = RT_H \ln\frac{V_1}{V_2} + C_v(T_C - T_H) + RT_C \ln\frac{V_3}{V_4} + C_v(T_H - T_C) \quad \text{... (2.15)}$$

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

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. 1.4*8* to Step II we get,

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

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

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

Hence,

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

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

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

Using this in Eq. 2.16, $w = RT_H \ln\frac{V_1}{V_2} + RT_C \ln\frac{V_2}{V_1}$

Hence, total work done on the system = $w=R(T_H-T_C)$ In V_1/V_2 …(2.18) Total work done by the system, = $w'=-w=R(T_H-T_c)$ In V_2/V_1 ….(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 (steps1 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,

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

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

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

It may however be noted that out of the heat ($q_H = RT_H \ln V_2/V_1$ as per Eq. 2.8) absorbed from the source, only some of it is converted in to 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.

$$Efficiency(\eta) = \frac{Totalworkdonebyt\quad hesystem}{(Heat\,absorbedfromt\quad hesourceat\ \ highertemp\,.)} = \frac{w'}{q_H} \ldots (2.22)$$

Using Equations 2.9 and 2.21

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

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

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:

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

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 at temperature as high 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 the same”.

It must be pointed out that in the Carnot cycleall 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 $\times 10^2$ K and 4.00$\times 10^2$ K. Calculate its efficiency.

Solution:

$$T_H = 4.00 \ \times 10^2 K \qquad T_C = 3.00 \ \times 10^2 K$$

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

$$= 0.250$$

3.3 Thermodynamic Temperature Scale

For an engine of the type discussed above, both the efficiency and the ratio q_C/q_Hcan 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, η=l. 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 honourof Lord Kelvin, who arrived at the thermodynamic scale of temperature based on the properties of reversible heat engines.

SELF-ASSESSMENT EXERCISE

i. A certain heat engine operates between 1000 K and 500 K. (a) What is the maximum efficiency of the engine? (b) Calculate the maximum work that can be done for each 1.0 kJ of heat supplied by the hot source. (c) How much heat is discharged into the cold sink in a reversible process for each 1.0 kJ supplied by the hot source?

ii. Calculate the coefficient of performance of a Carnot heat pump operating between a high temperature of 70.0^{o}F and a low temperature of 40.0^{o}F.

4.0 CONCLUSION

According to the second law, the simplest cyclic process capable of producing a positive amount of work in the surroundings must involve at least two heat reservoirs at different temperatures. The Carnot engine operates in such a cycle; because of its simplicity it has come to be the prototype of cyclic heat engines. An important property of the Carnot cycle is the fact that it is reversible. In a cyclic transformation, reversibility requires, after the complete cycle has been traversed once in the forward sense and once in the opposite sense, that the surroundings be restored to their original condition. This means that the reservoirs and masses must be restored to their initial condition, which can only be accomplished if reversing the cycle reverses the sign of W and of Q_1 and Q_2, individually. The magnitudes of W and of the individual values of Q are not changed by running a reversible engine backwards; only the signs are changed.

5.0 SUMMARY

Carnot cycle consists of four reversible steps, and therefore is a reversible cycle. A system is subjected consecutively to the reversible changes in state:

Step 1. Isothermal expansion.	Step 2. Adiabatic expansion.
Step 3. Isothermal compression.	Step 4. Adiabatic compression.

The initial and final states and the application of the first law to each step in the
Carnot cycle shows that for the cycle, $\Delta U = 0$

6.0 TUTOR-MARKED ASSIGNMENT

7.0 REFERENCES/FURTHERREADING

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UNIT 2 ENTROPY OF CHANGE

CONTENTS

1.0 INTRODUCTION

Entropy is an important concept in the branch of physics known as thermodynamics. The idea of "irreversibility" is central to the understanding of entropy. Everyone has an intuitive understanding of irreversibility. If one watches a movie of everyday life running forward and in reverse, it is easy to distinguish between the two. The movie running in reverse shows impossible things happening – water jumping out of a glass into a pitcher above it, smoke going down a chimney, water in a glass freezing to form ice cubes, crashed cars reassembling themselves, and so on. The intuitive meaning of expressions such as "you can't unscramble an egg", or "you can't take the cream out of the coffee" is that these are irreversible processes. No matter how long you wait, the cream won't jump out of the coffee into the creamer.

In thermodynamics, one says that the "forward" processes – pouring water from a pitcher, smoke going up a chimney, etc. – are "irreversible": they cannot happen in reverse. All real physical processes involving systems in everyday life, with many atoms or molecules, are irreversible. For an irreversible process in an isolated system (a system not subject to outside influence), the thermodynamic state variable known as entropy is never decreasing. In everyday life, there may be processes in which the increase of entropy is practically unobservable, almost zero. In these cases, a movie of the process run in reverse will not seem unlikely. For example, in a 1-second video of the collision of two billiard balls, it will be hard to distinguish the forward and the backward case, because the increase of entropy during that time is relatively small. In thermodynamics, one says that this process is practically "reversible", with an entropy increase that is practically zero.

The statement of the fact that the entropy of an isolated system never decreases is known as the second law of thermodynamics.

2.0 OBJECTIVES

Bythe 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 MAIN CONTENT

3.1 Entropy

Definition of an important thermodynamic function called 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.

The following comparison may help you in understanding the transformation of Eq. 2.24 into Eq. 2.26.

$Eq. 2.24$	$Eq. 2.26$
q_H	q_2
q_C	q_1
T_H	T_2
T_C	T_1

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

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. 2.24,

$$\frac{q_2 + q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad \text{...}(2.26)$$

or $1 + \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$ …(2.27)

$$i.e., \frac{q_1}{T_1} = -\frac{q_2}{T_2}$$

$$Hence, \frac{q_1}{T_1} + \frac{q_2}{T_2} = 0 \qquad \ldots(2.28)$$

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. 2.2). If in each small Carnot cycle, heat dq_1 is absorbed at temperature T_1 and $dq_{2,}$ then for each small Carnot cycle,

$$\frac{dq_1}{T'_1} + \frac{dq_2}{T'_2} = 0 \qquad \ldots(2.30)$$

Summing these over all the cycles we can write in general, sum of $\frac{dq_i}{T_i}$ terms over all the cycles = 0 …(2.31)

Where: ‘i' stands for an individual process of expansion or contraction in each cycle. Since the summation is continuous, we can replace the summation with integration and have,

$$\oint \frac{dq_{rev}}{T} = 0 \qquad \ldots(2.32)$$

Where:

dq_{rev} is the heat absorbed reversibly at a temperature in an infinitesimal step in the cyclic proce
the integral over a whole cycle.

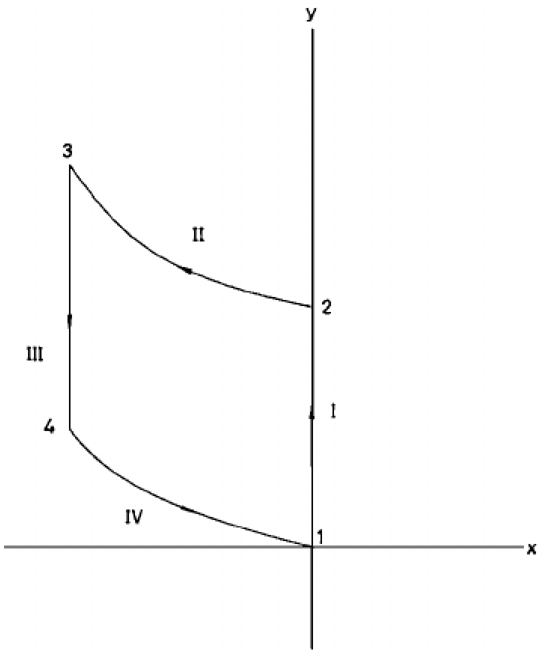

Fig. 2.2: Infinitesimal Carnot Cycle in the ($x = T - T_1, y = V - V_1$) plane.

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 process can be broken up into a large number of Carnot cycles. Startling 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.

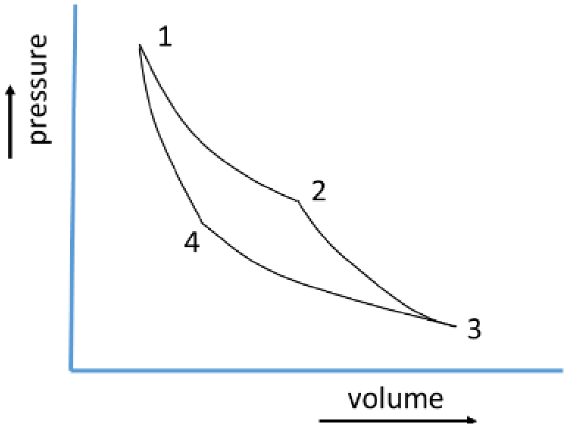

Fig. 2.3: The Cyclic Change ABA.

Hence, in the entire cycle,

$$Sum\ of\ \frac{dq_{rev}}{T}\ terms = \frac{\Sigma dq_{rev}}{T} = 0 \qquad \dots (2.33)$$

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,

$$\sum_{Cycle} dq_{rev}/T = \sum_{A\to B} dq_{rev}/T = \sum_{B\to A} dq_{rev}/T = 0 \qquad \ldots (2.34)$$

or in terms of integrals,

$$\int dq_{rev}/T = \int_A^B dq_{rev}/T + \int_A^B dq_{rev}/T = 0 \qquad \ldots (2.35)$$

and so

The symbol $\sum_{Cycle} dq_{rev}/T$ means summation of dq_{rev}/T in the entire circle.
The term $\sum_{A\to B} dq_{rev}/T$ means summation of the dq_{rev} term for the change

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

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,

$$dq_{rev}/T = dS \qquad \ldots (2.37)$$

Thus,

$$\int dS = 0 \qquad \ldots (2.38)$$

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

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

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

If we now put $d_q = TdS$ (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.

$$dU = dq + dw \quad \text{... (1.7)}$$

Hence,

$$dU = nC_V dT = TdS - pdV \quad \text{... (2.40)}$$

As per Eq. 1.29 of Unit 1, $H = U + pV$

Differentiation of this gives, $dH = dU + pdV + Vdp$ …(2.41)
Using Eq. 2.40, $dH = TdS - pdV + pdV + Vdp = TdS + VdP$ ... (2.42) 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 concernedwith 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,

$$dS = \frac{\mathrm{d}q_{\mathrm{rev}}}{\mathrm{T}}$$

This means that the entropy change in a system is to be calculated assuming the process to be reversible, irrespectiveof 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 EXERCISE 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.

3.2 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,

$$\Delta S_{1,} = \frac{q_{rev}}{T} \qquad \text{... (2.43)}$$

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

$$\Delta S_{2,} = \frac{-q_{rev}}{T} \qquad \text{... (2.44)}$$

The total entropy changeof the isolated system, ΔS_a, in this reversible expansion process isgiven by,

$$\Delta S_a = \Delta S_1 + \Delta S_2 = \frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0 \qquad \text{…(2.45)}$$

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.

$$\Delta S_b = 0 \qquad \text{... (2.46)}$$

Hence, ΔS in this cyclic process = ΔS_a +ΔS_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 changeof the system (ΔS_1) is still given by Eq. 2.43 per definition.

$$\Delta S_1 = \frac{q_{rev}}{T} \qquad \ldots (2.48)$$

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

$$\Delta S_2 = \frac{-\mathrm{q}}{\mathrm{T}} \qquad \ldots (2.49)$$

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

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

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 changeof the isolated system, ΔS_b, in this reversible compression process is given by,

$$\Delta S_b = 0 \qquad \ldots (2.51)$$

Hence, the total entropy changeof the isolated system over the whole cycle

$= \Delta S_a + \Delta S_b$

$> 0 \qquad \ldots (2.52)$

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

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

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= 2.37×10^5 J.

That is, the gas absorbs 2.37×10^5J **irreversibly** from the heat reservoir. But the heat reservoir loses 2.37×10^5 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 entropychange 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 7.47×10^5J, which is the heat absorbed under reversible conditions but not 2.37×10^5 J. The temperature of the gas is 3.00×10^2 K

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

$$= \frac{7.47 \times 10^5 J}{3.00 \times 10^2 K}$$

$$= 2490\, JK^{-1}$$

b) The heat reservoir loses 2.37×10^5 J heat reversibly,

Using Eq. 2.37, the entropy change = $\frac{-2.37 \times 10^5 J}{3.00 \times 10^2 K}$

of the heat reservoir $(\Delta S_{reservoir}) = -790\, JK^{-1}$

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

c) The total entropy changeof the isolated system

$$= \Delta S_{gas} + \Delta S_{reservoir}$$
$$= [(2490) + (-790)]\, JK^{-1}$$
$$= 1700\, JK^{-1}$$

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

To calculate the entropychange in the universe for a particular process, we should know the entropy change of the system and of the surroundings. We shall study in Secs. 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 considered reversible; this is true whether the system behaves reversibly or irreversibly. Let the temperature of the surroundings beT^{surr} .
Hence, the entropy change of the surroundings $= \frac{q^{surr}}{T^{surr}}$

This is true for all types of processes.
If a chemical reaction takes place at constant pressure with an enthalpy change,

ΔH, then $q^{surr} = - \Delta H$
Hence, the entropy change of the surroundings $= \frac{q^{surr}}{T^{surr}} = = \frac{-\Delta H}{T^{surr}}$

3.3 Statements of the Second Law of Thermodynamics

What we have studied so far in this unit can be generalized 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 asan isolated system, it follows that the entropy of the universe always increases.

2. It is impossible to transfer heat from a cold 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.

3.3 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

$\int_B^A dq_{rev}/T \quad which\ at\ constant\ temperature\ can\ be\ written\ as$

$$\frac{1}{T}\int_B^A dq_{rev} = dq_{rev}/T$$

Where: dq_{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 molof an ideal gas is isothermally and reversibly expanded from an initial state in which it has pressure $p1$ and volume $V1$ to the final state of volume $V2$ and pressure $p2$, then as shown earlier,

$$q_{rev} = \mathrm{w} = nRT\ln V_2/V_1 = \mathrm{n}RT\ln\ p_1/p_2 \ldots(2.55)$$

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

Hence, to calculate the entropy change of an ideal gas during isothermal expansion or compression, n, $V1$ and $V2$ or $p1$ and $p2$ must be known.

Example 4

1.00 molof an ideal gas is compressed isothermally and reversibly from 1.00×10^{-2} m^3 to 1.00×10^{-3} m^3. Calculate the entropy change.

Solution

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

Using Eq. 2.56, $\Delta S = -2.303\, nR\log V_1/V_2$

$$= -2.303 \times 1.00\, mol \times 8.314\, JmolK^{-1}\log\frac{1.00\times10^{-2}m^3}{1.00\times10^{-3}m^3}$$

$$= -19.2\, JK^{-1}$$

Entropy Change During Adiabatic Expansion

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

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

Let n molof 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),

$$dq_{rev} = dU + pdV \qquad \ldots(2.57)$$

$Using\ Eq. 1.26, dU = nC_V dT$

Where: $C_V$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,

$$dq_{rev} = nC_V dT + nRTd\,V/V \qquad \ldots(2.58)$$

or $TdS = nC_V dT + nRT\,V/V$

Hence,

$$dS = 1/T\left[nC_V dT + nRT\frac{\mathrm{dV}}{\mathrm{V}}\right] \qquad \ldots(2.59)$$

$$= nC_V d\,T/T + nRd\,V/V \qquad \ldots(2.60)$$

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

$$\int_{\mathrm{S}_1}^{\mathrm{S}_2} \mathrm{dS} = \int_{\mathrm{T}_1}^{\mathrm{T}_2} \mathrm{n\,C_V d\,T/T} + \int_{\mathrm{V}_1}^{\mathrm{V}_2} \mathrm{nRdV/V} \ldots(2.61)$$

-

Assuming that C_V is independent of temperature, we have

$$\left.\begin{aligned} \mathrm{S}_2 - S_1 &= \Delta\mathrm{S} = \mathrm{nC_V}\ln\frac{\mathrm{T}_2}{\mathrm{T}_1} + \mathrm{nRln}\,\frac{V_2}{V_1} \quad \ldots(2.62) \\ &= 2.303n(C_V \log\frac{T_2}{T_1} + Rlog\,\frac{V_2}{V_1}) \end{aligned}\right\}$$

This is the case when we take T and V to be the variable quantities. Since for an ideal gas p, y and T arerelated 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 $T1$ to $T2$ and $p1$ to $p2$ during the process. Then these are related to the initial and final volumes $V1$ and $V2$ as

$$\frac{V_2}{V_1} = \frac{T_2 P_1}{T_1 P_2} \qquad \ldots (2.63)$$

Hence, from Eq. 2.62, we have

Δ

$$\Delta S = nC_V \ln T_2/T_1 + nR \ln T_2 P_1/T_1 P_2 \qquad \ldots (2.64)$$

$$\Delta S = nC_V \ln T_2/T_1 + nR \ln T_2 T_1 + nR \ln P_1/P_2 \qquad \ldots (2.65)$$

$$= (C_V + R) n \ln T_2/T_1 + nR \ln p_1/p_2 \qquad \ldots (2.66)$$

Since $C_p - C_V = R, C_P = R + C_\mathrm{V}$ …(2.67)

$$\left.\begin{aligned} \Delta S &= nC_P \ln T_2/T_1 + nR \ln p_1/p_2 \\ &= 2.303\, n(C_P \log T_2/T_1 + Rlog\ p_1/p_2) \end{aligned}\right\} \ldots (2.68)$$

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 molof a monoatomic gas initially at $3.00 \times 10^2\ K$and occupying $2.00 \times 10^{-3} m^3$is heated to $3.25 \times 10^2\ K$and the final volume is $4.00 \times 10^{-3} m^3$. Assuming ideal behaviour, calculate the entropy change for the process.

Solution

For a monoatomic gas $C_V = 3/2R = 3/2 \times 8.314\ \mathrm{Jmol^{-1}K^{-1}}$

$$= 12.47\ Jmol^{-1}K^{-1}$$

Using Eq. 2.62, $\Delta S = 2.303\, n(C_V \log T_2/T_1 + K \log V_2/V_1)$

$$= 2.303 \times 1.00 \left(12.47 \log \frac{3.25 \times 10^2}{3.00 \times 10^2} + 8.314 \log \frac{4.00 \times 10^{-3}}{2.00 \times 10^{-3}} \right) JK^{-1}$$

$$= 6.76\ JK^{-1}$$

SELF-ASSESSMENT EXERCISE

i. Calculate the change in entropy when 50 kJ of energy is transferred reversibly and isothermally as heat to a large block of copper at (a) 0°C, (b) 70°C.

ii. Calculate ΔS (for the system) when the state of 2.00 mol diatomic perfect gas molecules, for which $C_{p,m}$= 7/2R, is changed from 25°C and 1.50 atm to 135°C and 7.00 atm. How do you rationalize the sign of ΔS?

iii. Calculate the entropy change for the following process: A sample containing 2.000 mol of helium gas originally at 298.15K and 1.000 bar is cooled to its normal boiling temperature of 4.00 K, condensed to a liquid, and then cooled further to 2.00 K, where it undergoes another phase transition to a second liquid form, called liquid helium II. This liquid phase is suddenly vaporized by a beam of laser light, and the helium is brought to a temperature of 298.15K and a pressure of 0.500 bar.

iv. Calculate q, w, ΔU and ΔS if 1.000 mol of helium gas is heated reversibly from 25.0^{o}C to 50.0^{o}C at a constant volume. Assume that $C_{V,m}$ is equal to 3R/2 and is constant.

4.0 CONCLUSION

The statement of the first law of thermodynamics defines the internal energy and asserts as a generalization of experiment fact that it is a state function. The second law of thermodynamics establishes the entropy as a state function, but in a less direct way. Our interest in the second law stems from the fact that this law has something to say about the natural direction of a transformation. It denies the possibility of constructing a machine that causes heat to flow from a cold to a hot reservoir without any other effect. In the same way, the second law can identify the natural direction of a chemical reaction. In some situations, the second law declares that neither direction of the chemical reaction is natural; the reaction must then be at equilibrium. The application of the second law to chemical reactions is the most fruitful approach to the subject of chemical equilibrium. Fortunately, this application is easy and is done without interminable combinations of cyclic engines.

5.0 SUMMARY

- There are two principal physical statements of the second law of thermodynamics:
  (1) If a system undergoes a cyclic process it cannot turn heat put into the system completely into work done on the surroundings.

(2) Heat cannot flow spontaneously from a cooler to a hotter object if nothing else happens.

- The second law implies that no heat engine can have an efficiency as great as unity.
- The mathematical statement of the second law establishes a new state function, the entropy, denoted by S and defined through its differential by:

$$dS = \frac{\mathrm{d}q_{\mathrm{rev}}}{\mathrm{T}}$$

- The mathematical statement of the second law provides a means of calculating the entropy change of any process that begins and ends at equilibrium states.
- The second law implies that no macroscopic process can decrease the entropy of the universe.

6.0 TUTOR-MARKED ASSIGNMENT

7.0 REFERENCES/FURTHER READING

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UNIT 3 ENTROPY OF MIXING

CONTENTS

1.0 INTRODUCTION

Examining the mixing process on a molecular level gives additional insight. Suppose we were able to see the gas molecules in different colours, say the air molecules as white and the argon molecules as red. After we took the partition away, we would see white molecules start to move into the red region and, similarly, red molecules start to come into the white volume. As we watched, as the gases mixed, there would be more and more of the different colour molecules in the regions that were initially all white and all red. If we moved further away so we could no longer pick out individual molecules, we would see the growth of pink regions spreading into the initially red and white areas. In the final state, we would expect a uniform pink gas to exist throughout the volume. There might be occasional small regions which were slightly more red or slightly more white, but these fluctuations would only last for a time on the order of several molecular collisions. In this unit therefore, we will be discussing the entropy of mixing in both reversible and irreversible reactions.

2.0 OBJECTIVES

Bytheend ofthisunit,you shouldbeable to;

- deriveanexpressionusefulincalculatingentropyofmixing,
- calculatetheentropychangesinphasetransitionsand chemicalreactions,

3.0 MAIN CONTENT

3.1 Entropy ofMixing

Supposethatn_1 molesofanidealgasinitiallypresentatpressure$p$andn_2 molesof anotheridealgasalsoatthesameinitialpressure$p$aremixedat aconstant temperature, T,sothatthetotalpressureisalso$p$.Thisispossibleby usingavessel ofsuitablevolume.Letthepartialpressureofthefirstgasinthemixturebe$p_1$and thepartial pressure ofthe othergasbep_2.Thenthechangeinentropyforthefirst gasfromEq.2.56is

$\Delta S_1 = n_1 R \mathrm{In}\frac{p}{p_1}$…(2.69)

Similarly,fortheother gas,

$\Delta S_2 = n_2 R \mathrm{In}\frac{p}{p_2}$…(2.70) Thetotalentropyofmixing,ΔS_{mix}'ishence

$\Delta S_{\mathrm{mix}} = \Delta S_1 + \Delta S_2 = n_1 R \mathrm{In}\frac{p}{p_1} + n_2 R \mathrm{In}\frac{p}{p_2}$…(2.71)

Ifthemolefractionsofthegasesinthemixturearex_1 and$x_2$respectively,then accordingtoDalton'slaw ofpartialpressures,

$\Delta S_{\mathrm{mix}} = n_1 R \mathrm{In}\frac{p}{x_1 p} + n_2 R \mathrm{In}\frac{p}{x_2 p}$…(2.72)

$\Delta S_{\mathrm{mix}} = n_1 R \mathrm{In}\frac{1}{x_1} + n_2 R \mathrm{In}\frac{1}{x_2}$…(2.73)

This simplify to, $\Delta S_{\mathrm{mix}} = -(n_1 R \mathrm{In} x_1 + n_2 R \mathrm{In} x_2)$

Or, $\Delta S_{\mathrm{mix}} = -2.303R(n_1 \log x_1 + n_2 \log x_2)$ …(2.74)

Ifweknow$n_1$andn_2,ΔS_{mix}canbecalculated.Themolefractionsx_1 andx_2 are lessthanone,since $x_1 + x_2 = 1$;asa resultofthis,ΔS_{mix}will bepositive.

Note:

Partial pressure ofagas= Total pressure *mole fractionofthe gas
Hence,$p_1 = px_1$and$p_2 = px_2$

Example6

Calculatetheentropyofmixingof1.00molofH_2with2.00molofO_2assuming thatnochemicalreactionoccurs.

Solution

nH2 = 1.00 mol; nO2 = 2.00 mol

$$x_{H2} = \frac{n_{H2}}{n_{H2}+n_{O2}} = \frac{1.00\ mol}{3.00\ mol} = 0.333$$

Similarly,

$$x_{O2} = \frac{n_{O2}}{n_{H2}+n_{O2}} = \frac{2.00\ mol}{3.00\ mol} = 0.667$$

Using Eq. 2.74,

$\Delta S_{mix} = -2.303R(n_1 \log x_1 + n_2 \log x_2)$

$\Delta S_{mix} = -2.303 * 8.314(1.00 \log 0.333 + 2.00 \log 0.667)\ JK^{-1}$

$\Delta S_{mix} = 15.88\ JK^{-1}$

Onthebasisofwhatyouhave studiedinthissection,answerthefollowingSAQ.

SELF-ASSESSMENTEXERCISE5

i. Doestheentropyofmixingofidealgasesdepend ontemperature? (**Hint**:ExamineEq.2.74)

3.2EntropyChangesin PhaseTransitions

Thechangeofmatterfromonephase(solid,liquid,gas,allotropicform)into another is called phase transition. Such changes take place at definite temperaturescalledtransitiontemperatures (meltingpoints,boilingpointsetc.)at agivenpressure.Thesetransitions areaccompaniedbyabsorptionorevolutionof heat(calledlatentheat).Sinceabsorption orevolutionofheatatconstant temperatureleadstoanentropychange,theentropyoftransitionisgivenas,

$$\Delta S_{trans} = \frac{q_{rev}}{T} = \frac{\Delta H_{trans}}{T} \qquad \ldots(2.75)$$

Eq.2.75isvalidonlywhen thetransitiontakesplaceinareversiblemanner,i.e., whenthetwophasesareinequilibrium.

Thus,whenonemoleofasolidmeltstotheliquidphase,theentropyoffusionis givenby

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_f} \qquad \ldots(2.76)$$

where$T_f$isthemeltingpoint andΔH_{fus}isthemolar enthalpyoffusion.Similarly,

$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$ …(2.77)

where$T_b$istheboilingpointandΔH_{vap}isthemolar enthalpyofvaporization.

Itisobvious, since disorderliness will be reduced,thattheentropyoffreezingandcondensation(vapour changing toliquid) willbeequalto–$\Delta S_{fus}$and–ΔS_{vap},respectively.

In a similarmanner,we candefine the entropy changeaccompanyingthe transitionofasubstancefrom anallotropicformtoanother.Ifsuchatransition takes placeatatemperature$T_{trans}$and,ΔH_{trans}isthemolarenthalpy of transition, thentheentropychangeaccompanythetransitionis,

$\Delta S_{trans} = \frac{\Delta H_{trans}}{T}$ …(2.78)

Thus,inphasetransitions,ΔS valuescanbe calculated fromthecorrespondingΔH values.

Usingthematerialgivenabove,answerthefollowingSAQ.

SELF-ASSESSMENTEXERCISE6

Calculatetheentropyoffusionofbenzenesolid,ifitsmeltingpointis279Kand itsenthalpyoffusionis10.6kJmol^{-1}. [Ans=37.99 Jmol^{-1}K^{-1}]

3.3EntropyChangesin ChemicalReactions

Given that: $\Delta S = \sum \Delta S_{products} - \sum \Delta S_{reactants}$

Let us now calculate the entropychange accompanying ageneral chemical reactionofthetype,

$aA + bB + ... \longrightarrow cC + dD + \ldots$ …(2.79)

Wedefinetheentropychangeforareaction($\Delta_r S$)asthedifferencebetween the total entropy of theproductsandthetotal entropyof thereactants.Thus,ifS_A, S_B....are theentropiesofonemoleof reactants,A,B,etc.,andS_C,S_D....,ofthe products,C,D,etc.,then;

$\Delta_r S = (cS_C + dS_D + \ldots) - (aS_A + bS_B + \ldots)$ …(2.80)

wherec,d,a,b...etc.,arethestoichiometriccoefficients inEq.2.79. Thevariation ofentropychangeforareactionwithtemperaturecanbereadilydeducedfrom Eq. 2.80 bydifferentiating with respect to temperature at constant pressure. Hence,

$$\left[\frac{\partial(\Delta_r S)}{\partial T}\right]_p = \left(c\left[\frac{\partial(\Delta S_C)}{\partial T}\right]_p + d\left[\frac{\partial(\Delta S_D)}{\partial T}\right]_p + \cdots\right) - \left(a\left[\frac{\partial(\Delta S_A}{\partial T}\right]_p + b\left[\frac{\partial(\Delta S_B}{\partial T}\right]_p + \cdots\right) \ldots(2.81)$$

Accordingto Eq.2.41
$dH = TdS + Vdp$

or Cp$\mathrm{d}T$=TdS+Vdp

Atconstantpressure(dp=0)

Cp$\mathrm{d}T$=TdS_p

or, $\left[\frac{\partial S}{\partial T}\right]_p = \frac{C_p}{T}$

Cpisthemolar heatcapacityofasubstanceatconstantpressure.

Eq.2.81 then becomes,

$$\left[\frac{\partial(\Delta_r S)}{\partial T}\right]_p = \left(\frac{[cC_{p(C)} + dC_{p(D)} + \cdots] - [aC_{p(A)} + bC_{p(B)} + \cdots]}{T}\right)$$
…(2.82)

$$\left[\frac{\partial(\Delta_r S)}{\partial T}\right]_p = \frac{\Delta C_p}{T}$$
…(2.83)

whereΔCPisthedifferencebetweentheheatcapacitiesoftheproductsand that of the reactantsatconstantpressure.

By rearranging, $d(\Delta_r S) = \Delta C_P \frac{dT}{T}$
…(2.84)

AssumethatΔrS1,andΔrS2aretheentropychangeattemperatures$T$1and$T$2and
ΔCpisindependentoftemperature.ThenEq.2.84on integrationgives,

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

$$\Delta_r S_2 - \Delta_r S_1 = C_p In \frac{T_2}{T_1} \qquad \ldots(2.86)$$

Eq.2.86isusefulindeterminingΔrSvalueofareactionatany particular temperature,ifitisknownatanyothertemperaturealongwith$C$pvalues.

Entropy valuesofsubstancescanbedeterminedusingthethirdlaw of thermodynamics;weshallstudythisinthenextunit.Theentropyvaluesofsome ofthesubstancesintheirstandardstatesat298.15KaregiveninTable2.1.These are known as standard entropy ($S°$) values. Similar to the Calculation of $\Delta_r S$ as per Eq. 2.80, we can calculate $\Delta_r S°$ 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	$S°$/JK^{-1}mol^{-1}	Substance	$S°$/JK^{-1}mol^{-1}
C(graphite)	5.7	$C_6H_{6(l)}$	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
$H_2O_{(l)}$	69.9		

Example 7

Calculate the standard entropy of formation of $H_2O_{(l)}$ at 298.15 K using Table 2.1.

Solution

$H_{2(g)} + \frac{1}{2}O_{2(g)} H_2O_{(l)} \quad \longrightarrow$

Recall: $\Delta S = \sum \Delta S_{products} - \sum \Delta S_{reactants}$

The standard entropy of formation of water ($\Delta_f S°_{(H_2O)}$) 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.

$$\Delta_f S°_{(H_2O)} = S^o_{(H_2O)} - (S^o_{(H_2)} + \frac{1}{2}S^o_{(O_2)})$$

$$= [69.9 - (130.7 + (\frac{1}{2} * 205.1))] JK^{-1}$$

Since one mole of water is formed,

$\Delta_f S°_{(H_2O)} = -163.4 J mol^{-1} K^{-1}$

SELF-ASSESSMENT EXERCISE

i. The enthalpy of vaporization of methanol is 35.27 kJ mol^{-1} at its normal boiling point of 64.1^{o}C. Calculate (a) the entropy of vaporization of methanol at this temperature and (b) the entropy change of the surroundings.

ii. Calculate the difference in molar entropy (a) between liquid water and ice at -5°C, (b) between liquid water and its vapour at 95°C and 1.00 atm. The differences in heat capacities on melting and on vaporization are 37.3 JK^{-1} mol^{-1} and -41.9 $JK^{-1}mol^{-1}$, respectively. Distinguish between the entropy changes of the sample, the surroundings, and the total system, and discuss the spontaneity of the transitions at the two temperatures.

iii. Assume that 1.000 mol of dry air consists of 0.780 mol of nitrogen, 0.210 mol of oxygen, and 0.010 mol of argon. Find the entropy change of mixing of 1.000 mol of dry air. Disregard the fact that each substance has more than one isotope.

4.0 CONCLUSION

The definition of entropy, that it is a measure of randomness, is one of great value. Apart from the quantitative relationship, the concept is of great value in understanding chemical processes quantitatively. A measure of entropy changes gives an indication of structural changes. The process of fusion involves increase in disorder and therefore, the entropy increase. Greater the disorder, greater the entropy increase.

5.0 SUMMARY

Inthismodule,wedescribedthesecondlawofthermodynamicsandtheconceptof entropy.Westartedthemoduleindicatingthemain aspectsof reversible,irreversible andcyclicprocesses.Wethendescribed Carnotcycleandderived anequationfor calculatingitsefficiency.Usingthisequation,theconceptofentropywasarrived.Theexpressionswerederivedforcalculatingthe entropychangesindifferent physicalprocesses.Themethodofcalculationofentropy changesinchemical reactionswasindicatedtowardstheend of the module.

6.0 TUTOR-MARKED ASSIGNMENT

7.0 REFERENCES/FURTHERREADING

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MODULE 3 SPONTANEOUS AND NON-SPONTANEOUSPROCESSES

INTRODUCTION

InUnit 1and2 of module 1,westudiedtheapplicationofthefirstlaw ofthermodynamicsin calculatingtheenthalpyandinternalenergychangesofreactions. Suchenergy calculationsdonottelluswhetheragivenreactionisfeasibleornot. InModule2the conceptofentropywasintroducedthroughthesecondlawofthermodynamics ; westudiedthatthetotalentropyvalueofthesystemandthesurroundingscan helpusindecidingthespontaneity ofareaction.Butthemaindifficultyisthatit isnotalwayspossibletoestimatetheentropychangeofthe surroundings. In this module we will use these principles learnt so far to construct thermodynamic tools with which to analyze real systems. Learning to use these tools allows you to apply thermodynamics in a useful way. Someone has facetiously said that the practice of thermodynamics is like finding the right wrench with which to pound on the right screw. The module will consist of the following units:

Unit 1 Free Energy Functions
Unit 2 Maxwell, Gibbs-Helmholtz and Calusius-ClapeyronEquation
Unit 3 Criteria for Spontaneity

UNIT 1 FREE ENERGY FUNCTIONS

CONTENTS

1.0 INTRODUCTION

Inthisunit,wewillintroduce twomorethermodynamic quantitiesknownas Gibbsfreeenergy (G)andHelmholtzfreeenergy(A).Weshallalsodiscuss the importanceof theGibbsfreeenergychange(ΔG)inpredictingwhetheragiven process(physicalorchemical)willoccurspontaneously ornot.Weshallderive Maxwellrelationsand statetheir applications. We shall thenarriveat Gibbs-HelmholtzandClausius-Clapeyronequation.Weshall also explainthe applicationsof thesetwoequations.Weshallthenexamine thecriteriafor spontaneity.We shallillustratetheutilityoftheGibbsfree energyofformationof substancesincalculatingthereaction free energies.

Finally, weshallexplainthethirdlawofthermodynamicsanddiscussits applicationincalculatingtheentropiesofsubstances.

2.0 OBJECTIVES

By the end of thisunit,you shouldbe able to:

- distinguish betweenspontaneousand nonspontaneousprocesses,
- defineHelmholtzfree energy(A)and Gibbs free energy(G),
- CalculateΔAandΔGfordifferentprocesses.

3.0 MAIN CONTENT

3.1 SpontaneousandNonspontaneous Processes

Inthissection,wewillexplainhow spontaneousand nonspontaneousprocesses differ.Letustrytounderstandwhataspontaneousprocess is.We knowthat:

i) water flowsdownthehillspontaneously
ii) agasexpandsspontaneouslyintovacuum
iii) heatisconductedspontaneouslyfromthehotendofametalbartothe colder end untilthetemperatureofthebarissamethroughout
iv) agasdiffusesspontaneouslyintoanothergas.

Butthereverseof theabovechangesdoesnotoccurspontaneously.Allnatural processesoccurspontaneously. Thuswe candefinethataspontaneousora naturalprocess occursinasystembyitself.Noexternalforceisrequitedtomake theprocesscontinue.Ontheotherhand,anonspontaneousprocesswillnotoccur unlesssomeexternalforceiscontinuouslyapplied.Achemistisalways interested inknowingwhetherunderagivensetofconditions,areactionoraprocessis feasible or not.

Accordingtothesecondlawofthermodynamics,dS $\geq$ $\frac{dq}{T}$in whichtheequalityreferstoasystemundergoingareversibleprocess andthe inequalityreferstoanirreversibleprocess.Foranisolatedsystemforwhich dq=0, theaboveequationisreducedtod$S\underline{>}0$.Inanisolatedsystem,an irreversible changeisalwaysspontaneous. Thisisbecauseinsuch systems,no externalforcecaninteractwiththesystem.Thus,thetendency ofentropyofan isolatedsystemtoincreasecanbeused asacriterionforaspontaneouschange.Is this alwaystrue? Letusexaminethisquestion.Waterfreezes tocrystallineice spontaneouslyat263K.Iceisinamoreorderedstate thanwaterandtheentropy decreasesinfreezing.Howdoweexplaintheaboveprocess? Theanswertothis questionliesinthefactthatwemustalwaysconsiderthetotalentropychange, *i.e.*,theentropychanges oftheuniverse.Thisentropychangeisequaltothesum oftheentropychangesofthesystemand thesurroundings.

ΔSTotal=ΔSUniverse = ΔSsystem + ΔSsurroundings ....(3.1)

Eq.3.1isverydifficulttoapplyfortestingthespontaneityofaprocess.Thisissos inceforevaluatingthetotalentropy change,wehavetoevaluateΔSforthe surroundings also.Inmanycases,suchcalculationsareextremelydifficultand sometimesnoteven practical.Therefore,itwillbeadvantageousifwecan redevelopthecriteriaforspontaneity insuchamannerthatonlychangesinthe properties ofthesystem areconsidered.Forthispurpose,wedefinetwoenergy functionscalledHelmholtzfree energyand Gibbsfree energyinthenextsection.

Important highlight:
Any processwhichcantakeplacewithouttheapplication of externalforceisaspontaneous process.Allnaturalprocessesarespontaneous.

SELF-ASSESSMENTEXERCISE1

i. Explainwhythechangeinentropyinasystemisnotalwaysasuitablecriterion forspontaneouschange? [Ans Hint= explanation to Eq. 3.1]

3.2Helmholtz Free Energy and Gibbs Free Energy

Helmholtz free energy (A) andGibbsfreeenergy(G)aredefinedby the expressions,

$$A = U - TS \qquad \text{…(3.2)}$$

And, $G = H - TS$ …(3.3)

since, $H = U + pV$

Therefore, $G = U + pV - TS$ …(3.4)

A(denotingHelmohltzfree energy)comesfromthe GermanwordArbeit,whichmeanswork

Since*U*,*H*,*p*,*S*,*V*and*T*arestatefunctions,*A*andGarealsodependentonlyon thestateof thesystem.Insimplerwords,asysteminagivenstatehasdefinite valuesof*A* and*G*. Inthenextsectionwe shallderiveequationsuseful in calculatingchangesin*A*and G atconstanttemperature.

3.2.1 Physicalsignificanceof*A*and *G*

DifferentiatingEq.3.2,weobtain

$dA = dU - TdS - SdT$ …(3.5)

Atconstanttemperature($dT=0$),wehave

$dA = dU - TdS$…(3.6) We know(Recall fromEq.2.37)thatforareversibleprocess $TdS = dq_{rev}$

Alsoforareversibleprocessgives $dU = dq_{rev} + dw_{rev}$ SubstitutingthevaluesforTdSanddUinEq.3.6,weobtain,

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

or $dA = dw_{rev}$ ....(3.7)

or $-dA = -dw_{rev}$ ....(3.8)

Sincetheprocessiscarriedoutreversibly,$-dw_{rev}$representsthemaximumwork donebythesystem.Thisisanimportantconclusion whichstatesthatthechange inHelmholtzfreeenergyisequaltotheamountof reversibleworkdoneon the systemordecreaseinHelmholtzfreeenergy($-dA$)isthemaximum amountof workthatcanbeobtainedfromthesystem($-dw_{rev}$)duringthegivenchange.Asa result,thefunction*A*issometimesalsoreferredtoasthe ‘workfunction’ or the maximum work content of a system.

Inasimilar way,thedifferentiationofEq.3.4 yields,

$dG = dU + pdV + Vdp - SdT - TdS$....(3.9) Atconstanttemperature($dT=0$)and pressure($dp=0$),Eq.3.9isreducedto

$\mathrm{d}G=\mathrm{d}U+p\mathrm{d}V-T\mathrm{d}S$… (3.10) Once againiftheprocess is carriedout reversibly,usingEq1.7 ($\mathrm{d}U=\mathrm{d}q_{\mathrm{rev}}+\mathrm{d}w_{\mathrm{rev}}$)and$T\mathrm{d}S=dq_{rev}$,weobtainfromEq.3.10

$\mathrm{d}G=\mathrm{d}q_{rev}+\mathrm{d}w_{\mathrm{rev}}+p\mathrm{d}V-dq_{\mathrm{rev}}$

or $\mathrm{d}G=dw_{\mathrm{rev}}+p\mathrm{d}V$....(3.11)

Nowdw_{rev} consistsofexpansionwork($-p\mathrm{d}V$)andsomeotherkindofwork calledtheusefulorthenetwork,dw_{net},doneonthesystem. Replacingd$w_{\mathrm{rev}}$by $-p\mathrm{d}V+\mathrm{d}w_{net}$inEq.3.11,weobtain,

$\mathrm{d}G=-p\mathrm{d}V+\mathrm{d}w_{\mathrm{net}}+p\mathrm{d}V$

or $\mathrm{d}G=dw_{\mathrm{net}}$ ...(3.12)

or $-\mathrm{d}G=-\mathrm{d}w_{\mathrm{net}}$

ThusdecreaseinGibbsfreeenergy ($-\mathrm{d}G$)isameasureofthemaximum useful workthatcanbeobtainedfrom thesystematconstanttemperatureandpressure. Mostexperimentsinthelaboratory arecarriedoutundersuchconditions.Sothe property$G$ orthechangeassociatedwithit(ΔG)isveryimportant.

3.3Changesin *A* and*G*

Whenasystemgoesfromstate1tostate2atconstanttemperature,thechangein A canbe obtainedby integratingEq.3.6betweenthelimits $A_1\rightarrow A_2$,$U_1\rightarrow U_2$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)

ThechangeinGwhenasystemgoesfromastate1tostate2canbe obtained in a similar manner by integratingEq.3.10atconstanttemperatureand pressurebetweenthelimits $G_1\rightarrow G_2$,$U_1\rightarrow U_2$,$V_1\rightarrow V_2$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 knowthatatconstantpressure, $\Delta U+p\Delta V=\Delta H$(Eq.6.32)

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

Example1

Forthereaction, $2NO_{(g)}+O_{2(g)} \rightarrow 2NO2_{(g)}$

CalculateΔGat7.00×10^{2}K given that the entropyandenthalpychangesatthis temperature are-1.45×10^{2}Jmol^{-1}K^{-1}and-1.13×10^{2}kJmol^{-1}respectively.

Solution

$\Delta H=-1.13\times l0^{2}\text{kJmol}^{-1}$

$\Delta S =-1.45\times10^{2}\text{JK}^{-1}\text{mol}^{-1}=1.45\times10^{2}\times l0^{-3}\text{kJK}^{-1}\text{mol}^{-1}$

$=-1.45\times10^{-1}\text{kJK}^{-1}\text{mol}^{-1}$

$T= 7.00\times10^{2}\text{K}$

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

$\Delta G =(-1.l3\times l0^{2}\text{kJmol}^{-1})-7.00\times l0^{2}\text{ K}(-l.45\times l0^{-1}\text{ kJK}^{-1}\text{mol}^{-1})$

$=-1.13\times10^{2}\text{kJmol}^{-1}+1.015\times10^{2}\text{kJmol}^{-1}$

$=-0.115\times10^{2}\text{kJmol}^{-1}$

$=-11.5\text{kJmol}^{-1}$

3.3.1 Variationof*A* and *G*withTemperature

FromEq.3.5

$dA=dU-TdS-SdT$

Since$TdS=dq$

$dA=dU-SdT \quad -dq$....(3.16) Substitutingfromthefirstlaw ofthermodynamics,

$dU=dq-pdV$in to Eq 3.16,wehave

$dA=dq-pdV-SdT-dq$

or $dA=-pdV-SdT$....(3.17)

FromEq.3.17atconstantvolume(dV=0),we have

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

or $\left[\frac{\partial A}{\partial T}\right]_V = -S$ ....(3.18)

Atconstanttemperature(dT=0),Eq.3.17 isreducedto

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

$\left[\frac{\partial A}{\partial V}\right]_T$ = -*p*....(3.19)

EquationssimilartoEq.3.18and3.19canbeobtainedinthecase ofGibbsfree energy. FromEq.3.9wehave

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

Sincedq=TdSfromSecondlawofthermodynamicsanddU=dq-pdVfrom firstlaw ofthermodynamics,

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

or $dG = Vdp - SdT$....(3.20) Atconstantpressure(*d*p =0),Eq.3.20isreducedto

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

$\left[\frac{\partial G}{\partial T}\right]_p$ = -S … (3.21)

Atconstanttemperature(d*T*=0),wehavefromEq.3.20

$(\partial G)_T = V(\partial p)_T$

....(3.22)

$\left[\frac{\partial G}{\partial p}\right]_T = V$ …(3.23)

IfG_1,andG_2arethefreeenergies ofthesystemintheinitialandthefinalstates, respectively,thenatconstanttemperature,thefreeenergychange(ΔG)isgiven by integratingEq.3.22.

$$\Delta G = \int_{G_1}^{G_2} dG = \int_{p_1}^{p_2} Vdp \quad \text{… (3.24)}$$

Where$p_1$and$p_2$aretheinitialand thefinalpressures,respectively.

For*n*moleofanidealgas,

$pV = nRT$

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

Therefore, $\Delta G = \int_{p_1}^{p_2} nRT \frac{dp}{p} = nRT \int_{p_1}^{p_2} \frac{dp}{p}$

$= nRT\, In \frac{p_2}{p_1} = 2.303nRTlog \frac{p_2}{p_1}$

Sincepressureisinverselyproportionaltovolumeforanidealgasatconstant temperature,wehave

$$\Delta G = 2.303nRTlog \frac{p_2}{p_1} = 2.303nRTlog \frac{V_1}{V_2} \quad \text{…(3.25)}$$

Example2

Calculatethefree energychangewhichoccurswhenl.00moleofanidealgas expandsreversiblyandisothermallyat3.10×10^2K fromaninitialvolumeof 5.00×$10^{-2}$$m^3$to1.00$m^3$.

Solution

n=1.00mol

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

V_1=5.00×10^{-2} m^3

$$\Delta G = 2.303nRTlog\frac{V_1}{V_2}$$

$$\Delta G = 2.303 * 1.00mol * 8.314\ Jmol^{-1}K^{-1} * 3.10x10^2 * \log\frac{5.00*10^2 m^3}{1.00\ m^3}$$

$$\Delta G = 5.93 * \ 10^3\ log\frac{1}{20}\ J$$

$$= \ -7.72\ kJ$$

Astatefunctiondependsonlyonthestateofthesystem.Itdoesnotdependonthe historyof the systemorhow thatstatehas beenachieved.

$dU= dq–pdV$

Forareversible process. dq= TdS

Hence,$dU= TdS–pdV$

Self-AssessmentExercise

i. Suggest a physical interpretation of the dependence of the Gibbs energy on the pressure.
ii. WhatisthephysicalsignificanceofdecreaseinGibbs free energy?

4.0 CONCLUSION

The word "spontaneous" applied to changes in state in a thermodynamic sense must not be given too broad a meaning. It means only that the change in state is possible. The second law of thermodynamics provides the general criterion for spontaneous processes: No process can decrease the entropy of the universe. For a closed simple system at constant pressure and temperature the Gibbs energy G cannot increase, and for a closed simple system at constant temperature and volume the Helmholtz energy A cannot increase.

5.0 SUMMARY

- The second law of thermodynamics provides the general criterion for possible processes: The entropy of the universe cannot decrease.
- This general criterion can be used to derive criteria for spontaneous processes in a system under various circumstances as found in this unit.
- The Gibbs and Helmholtz energies provide information about the maximum amount of work that can be done by a system.
- General equations for the differentials of various thermodynamic functions can be written from the first and second laws.

6.0 TUTOR-MARKED ASSIGNMENT

7.0 REFERENCES/FURTHERREADING

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UNIT 2 MAXWELL, GIBBS-HELMHOLTZ AND CLAUSIUS-CLAPEYRON EQUATION

CONTENTS

1.0 INTRODUCTION

The Clausius-Clapeyron equation relates the latent heat (heat of transformation) of vaporization or condensation to the rate of change of vapour pressure with temperature. Or, in the case of a solid-liquid transformation, it relates the latent heat of fusion or solidification to the rate of change of melting point with pressure.

Before starting this unit, it would probably be a good idea to re-read Unit 1 and 2 of this module for better understanding.

2.0OBJECTIVES

Bytheend ofthisunit,you shouldbeable to;

- derive Maxwellrelations,
- deriveGibbs-Helmholtzequation,
- explainthesignificanceofClausius-Clapeyronequation,

3.0 MAIN CONTENT

3.1 TheMaxwellRelations

Sofarwehavelearntaboutthefivefunctions U,H,S,$A$and$G$which arestate functionsandextensivevariables.Thevariousexpressionsusefulinestimating thechangesintheabovefunctionsinaclosedsystemintermsof temperature, pressure,volumeand entropyhas been presented previouslyas:

$dU = TdS - pdV$ fromEq....(2.40)

$dH=TdS+Vdp$ fromEq....(2.41)

$dA=-SdT-pdV$ fromEq....(3.17)

$dG=-SdT+Vdp$ fromEq.…(3.20)

Atconstantvolume(dV=0),Eq.2.40becomes

$(\partial U)_V=T(\partial S)_V$

or $\left[\frac{\partial U}{\partial S}\right]_V = T$ …(3.26)

and atconstantentropy(dS=0),Eq.2.40becomes

$(\partial U)_S=p(\partial V)_S$

or $\left[\frac{\partial U}{\partial V}\right]_S = -p$ …(3.27)

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

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

or $\frac{\partial^2 U}{\partial S \partial V} = -\left[\frac{\partial p}{\partial S}\right]_V$

Since U isaStatefunction,itfollowsthat

$$\frac{\partial^2 U}{\partial V \partial S} = \left[\frac{\partial^2 U}{\partial V}\right]_S$$

or $\left[\frac{\partial T}{\partial V}\right]_S = -\left[\frac{\partial p}{\partial S}\right]_V$ … (3.28)

Followingthesamemathematicalprocedureasdescribedabove,thefollowing expressionscanbeeasilyderived:

From Eq. 2.41, $\left[\frac{\partial T}{\partial p}\right]_S = \left[\frac{\partial V}{\partial S}\right]_P$ … (3.29)

From Eq. 3.17, $\left[\frac{\partial S}{\partial V}\right]_T = \left[\frac{\partial p}{\partial T}\right]_V$ … (3.30)

From Eq. 3.20, $\left[\frac{\partial S}{\partial P}\right]_T = -\left[\frac{\partial V}{\partial T}\right]_p$ … (3.31)

Eqs.3.28to3.31areknown asMaxwell relation.TheMaxwell relationsare importantbecausetheyequatetherateofchangeofaparticularquantity (which cannotbedeterminedexperimentally) with therate ofchangeofvolume,pressure ortemperature(whichcanbedeterminedexperimentally).

3.2Gibbs-Helmholtz Equation

Thedependence ofGibbsfreeenergytotemperaturecanbeexpressedinseveral ways.Startingfromthedefinition(Eq.2.3)

$G = H - TS$

or $-S = \frac{G-H}{T}$

Substituting the expression for $-S$ in Eq. 3.21, we obtained,

$$\left[\frac{\partial G}{\partial T}\right]_p = \frac{G-H}{T} \qquad \dots (3.32)$$

Sometimes it is important to know the variation of G/T on temperature. By differentiating G/T with temperature at constant pressure, we obtained

$$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_p = \frac{T\left[\frac{\partial G}{\partial T}\right]_p - G}{T^2} \qquad \dots (3.33)$$

Substituting for $\left[\frac{\partial G}{\partial T}\right]_p$ from Eq. 3.32 into Eq. 3.33, we have

$$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_p = \frac{G-H}{T^2} - \frac{G}{T^2}$$

Hence, $$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_p = \frac{G-H-G}{T^2}$$

or $$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial T}\right]_p = \frac{-H}{T^2} \qquad \dots (3.34)$$

Eq. 3.34 is the Gibbs-Helmholtz equation and can be put in other form by recalling that $d(\frac{1}{T}) = (\frac{-1}{T^2})dT$; so on replacing ∂T in Eq. 3.34 by $-T^2\partial(\frac{1}{T})$, we hav

$$\left[\frac{\partial\left(\frac{G}{T}\right)}{-T^2\partial(\frac{1}{T})}\right]_p = \frac{-H}{T^2}$$

or $$\left[\frac{\partial\left(\frac{G}{T}\right)}{\partial(\frac{1}{T})}\right]_p = H \qquad \text{... (3.35)}$$

Similar equationforHelmholtzfree energycanalso bederivedin theform

$$\left[\frac{\partial\left(\frac{A}{T}\right)}{\partial T}\right]_V = \frac{-U}{T^2} \qquad \text{... (3.36)}$$

or $$\left[\frac{\partial\left(\frac{A}{T}\right)}{\partial(\frac{1}{T})}\right]_V = U \qquad \text{... (3.37)}$$

$H=U+pV$
dH= dU+ pdV+Vdp
Butd$U$+pdV= dq= TdS
Hence,dH= TdS+Vdp

Uisathermodynamicfunction andd$U$isatotaldifferential parameter i.e.the change in$U$withrespecttoboth$V$ and$S$issame whetherwe change $U$with respectto$V$first,keeping$S$constantand thenwith respectto$S$keeping$V$constant,orvice versa.

ThedependenceofGibbsfree energyon temperature canbeexpressedinanother wayalso.Supposethe$G1$istheGibbsfreeenergyforasystemintheinitialstate andattemperatureT.Letthetemperaturechangeto$T$+d$T$and thecorresponding valueoffree energyto$G1$+d$G1$.

Similarforthefinalstateofthesystem,lettheGibbs free energiesbe$G1$and$G2$+ d$G2$attemperature$T$and$T$+dT,respectively.Atconstantpressure,Eq.3.20 reducesto

$(\partial G)_p=-S(\partial T)_p$
....(3.38)
and so$(\partial G1)_p=-S1(\partial T)_p$
....(3.39) $(\partial G2)_p=-S2(\partial T)_p$
....(3.40)

WhereS_1andS_2aretheentropiesofthesystemintheinitialandthefinalstates, respectively.Subtracting Eq. 3.39 fromEq.3.40gives
$(\partial G_2-\partial G_1)_p = -S_2(\partial T)_p - (-S_1(\partial T)_p)$

or $[\partial(G_2 - G_1)]_p = -(S_2 - S_1)(\partial T)_p)$

or $[\partial(G_2 - G_1)]_p = -(S_2 - S_1)(\partial T)_p)$

or $[\partial\Delta G)]_p = -\Delta S\,(\partial T)_p$ .... (3.41)

$$\left[\frac{\partial G}{\partial T}\right]_p = -\Delta S \qquad \text{... (3.42)}$$

AsperEq.3.15
$\Delta G=\Delta H-T\Delta S=\Delta H+T(-\Delta S)$
SubstitutingEq.3.42inEq.3.15wehave

$$\Delta G=\Delta H+T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p \ldots(3.43)$$

Eq.3.43isalsoknown asGibbs-Helmholtzequationandisapplicableforany process,reversibleorirreversible,sincethevaluesofΔGandΔHdependonly ontheinitial andfinalstatesof thesystem.Forareactionatconstantvolume, similar equationforHelmholtzfree energycanbederivedintheform:

$$\Delta A=\Delta U+T\left[\frac{\partial(\Delta A)}{\partial T}\right]_V \qquad \ldots(3.44)$$

TheGibbs-HelmholtzequationpermitsthecalculationofΔUorΔHprovidedΔA or$\Delta G$and their respectivetemperaturecoefficients,$\left[\frac{\partial G}{\partial T}\right]_p$ or $\left[\frac{\partial A}{\partial T}\right]_V$, are known.

The term $\left[\frac{\partial G}{\partial T}\right]_p$ and $\left[\frac{\partial A}{\partial T}\right]_V$ arethetemperature coefficientsofΔGandΔAat constant pressureandvolumerespectively.Thetemperaturecoefficientofaparticularparametertells ushowthat parametervarieswithrespecttotemperature.

If $\left[\frac{\partial G}{\partial T}\right]_p$ forexample is

i) Positive,it meansΔGincrease withincreasingtemperature:and
ii) negative,it meansΔGdecrease withincreasingtemperature

Also, $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = \left[\frac{\Delta G_2 - \Delta G_1}{T_2 - T_1}\right]_p$

where $\Delta G_2$and ΔG_1 are the free energy changes at temperature, T_2 and T_1 respectively.

Example3

ThefreeenergychangeΔGforaparticularprocessis-121.00kJmol^{-1}at298K and-117.00kJmol^{-1}at308K.Calculatetheenthalpychangefortheprocessat 303K.

Solution

ΔGat298K=-121.00kJmol^{-1}
ΔGat308K=-117.00kJmol^{-1}

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = \frac{\Delta G_{308} - \Delta G_{298}}{(308-298)K} = \frac{(-117.00)-(-121.00)}{308-298}$$

$=4.00\times10^{-1}$kJmol^{-1}K^{-1}

At303K,thevalueofΔGmay betakenastheaverageofat298Kand 308K.

Hence,ΔGat303K=$\frac{(-117.00)+(-121.00)}{2}$

=-119.00kJmol^{-1}

SubstitutingthevaluesintheGibbs-Helmholtzequation
$\Delta G=\Delta H+T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$
-119.00kJmol^{-1}=ΔH+303K×4.00×10^{-1}kJmol^{-1}K^{-1}

-119.00kJmol^{-1}=ΔH+121.20kJmol^{-1}

ΔH=-121.20kJmol^{-1}-119.00kJmol^{-1}=-240.20kJmol^{-1}

WhenappliedtochemicalreactionstheGibbs-Helmholtzequationwilltakethe following form:

Initialstate(Reactants) Finalstate(Products)
Free energy G_i G_f
Eq. 3.34 applies to both the initial and final states, i.e.

$$\left[\frac{\partial\left(\frac{G_i}{T}\right)}{\partial T}\right]_p = \frac{-H_i}{T^2} \text{ and } \left[\frac{\partial\left(\frac{G_f}{T}\right)}{\partial T}\right]_p = \frac{-H_f}{T^2}$$

Subtractingweget,

$$\left[\frac{\partial\left(\frac{G_f-G_i}{T}\right)}{\partial T}\right]_p = \frac{-(H_f - H_i)}{T^2}$$

or
$$\left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_p = \frac{-\Delta H}{T^2} \qquad \ldots(3.45)$$

Theaboveequationisimportantbecausefrom theknowledgeof enthalpy of reactionswecanpredictwhetherincreaseintemperaturewillfavourthereaction inonedirectionor in another direction.

3.3Clausius-ClapeyronEquation

The relationship between the variables in equilibrium between phases of one component system e.g., liquid and vapour, solid and vapour, solid and liquid etc., can also be obtained from the thermodynamics relationship called Clapeyron equation.
FromEq.3.30wehave

$$\left[\frac{\partial p}{\partial T}\right]_V = \left[\frac{\partial S}{\partial V}\right]_T$$

The aboveequationcanbeappliedtoanyclosedsystemconsistingoftwophases ofthesamesubstanceinequilibriumwitheachother.Letusconsideraclosed systeminwhichapureliquidanditsvapourareinequilibriumwitheachother.

A(liquid) A(vapour)⇌
Thevapourpressureoftheliquid(A)dependsuponthetemperature butis independentofthevolumeoftheliquidand thevapour.
Hence,

$$\left[\frac{\partial p}{\partial T}\right]_V = \frac{dp}{dT} \qquad \ldots(3.46)$$

Whenonemoleoftheliquidisvaporizedisothermally andreversiblyinsucha way thatduringtheprocess, theliquidandthevapourremaininequilibrium,the increaseinenthalpyisequaltothemolarenthalpyofvaporization (ΔH_{vap}).Since theprocess isreversible,itfollowsfromEq.2.77,

$$\Delta S = \frac{\Delta H_{vap}}{T} \qquad \ldots(3.47)$$

where$T$istemperature.

Lettheincreaseinvolumeandentropyduringthevaporization ofonemoleof liquidbe$\Delta V$and ΔS,respectively.Then wehaveatconstanttemperature(using Eq.3.47.

$$\left[\frac{\partial S}{\partial V}\right]_T = \frac{\Delta S}{\Delta V} = \frac{\Delta H_{vap}}{T\Delta V} \qquad \ldots (3.48)$$

ComparingEqs.3.30, 3.46and3.48,wehave

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T\Delta V} \qquad \ldots (3.49)$$

Eq. 3.49 was first deducedbyClapeyron(1834)andisknownasClapeyronequation.Itwaslaterextendedby Clausius (1850). This equationwasderivedfora system consistingofliquidandvapourinequilibrium.Thesameequationcan, however,bederivedforequilibriumbetween anytwophasessuchas,solidand liquid,solidandvapour, twocrystallineformsofthesamesubstanceetc.Fora system consistingofwaterinthetwophases,liquidandvapour,inequilibrium witheachother,

Water(liquid) ⇌ Water(vapour) Eq.3.49 canbewrittenas,

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T(V_g - V_l)} \qquad \ldots (3.50)$$

Where

ΔHvap=Molar enthalpyofvaporizationofwater

V_g =Molarvolumeofwater vapourattemperature$T$

V_1 =*Molar*volumeofliquidwater attemperature$T$

Forasystemconsisting oficeatitsmeltingpoint,thetwophasesinequilibrium areiceandliquidwater.

Water(ice) ⇌ Water(liquid)

Eq.3.49may bewrittenas

$$\frac{dp}{dT} = \frac{\Delta H_{fus}}{T(V_l - V_s)} \qquad \ldots (3.51)$$

Where

ΔHfus=Molar enthalpyoffusionofice

Vs=Molar volumeofwater inthesolid(ice)state

V_l=Molar volumeofwater intheliquid state

Intheliquid ⇌ vapourequilibrium, Clausius assumedthatthemolarvolumeof aliquidismuchlessthanthemolarvolumeofitsvapour; henceV_g—$V_l$canbe takenapproximatelyasV_g.Eq.3.50maybe writtenas,

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{TV_g} \qquad \dots (3.52)$$

Assumingthatthevapourbehaves ideally,

$$V_g = \frac{RT}{p} \qquad \dots (3.53)$$

SubstitutingforthevolumeV$_g$inEq.3.52, wehave

$$\frac{dp}{dT} = \frac{\Delta H_{vap}}{T} * \frac{p}{RT} = \frac{\Delta H_{vap}\, p}{RT^2} \qquad \dots (3.54)$$

Eq.3.54isknownasClausius-Clapeyronequationand canbe rewrittenas,

$$\frac{dp}{p} = \frac{\Delta H_{vap}}{R} * \frac{dT}{T^2} \qquad \dots (3.55)$$

Eq3.55canbeintegratedbetweenlimits$p_1 \rightarrow p_2$and$T_1 \rightarrow T_2$assuming thatΔHvap remainsconstantoverasmallrangeoftemperature.

$$\int_{p_1}^{p_2} \frac{dp}{p} = \frac{\Delta H_{vap}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2} \qquad \dots (3.56)$$

or $$\text{In}\frac{p_2}{p_1} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \dots (3.57)$$

or $$2.303\log\frac{p_2}{p_1} = \frac{\Delta H_{vap}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \dots (3.58)$$

or $$\log\frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right] \qquad \dots (3.59)$$

Eq. 3.57 is the integratedformofClausius-clapeyronequation

TheClausius-Clapeyronequation find several applications asgivenbelow:

1. Ifthevapourpressureofaliquidatadifferenttemperatureareknownthen itsmolar enthalpyofvaporizationcanbecalculated usingEq.3.59

2. Ifthevapourpressureofaliquidatanyonetemperatureisknownthen thatatanothertemperaturecanbecalculated using Eq.3.59.

3. Eq.3.59canalsobeusedforcalculatingtheeffectofpressureonthe boilingpointofaliquid.

Example4

Calculatethevapourpressureofwater at298K given that the molar enthalpyofvaporization ofwater initsnormalboilingpointis4.10×10^{4}Jmol^{-1}

Solution

Thestandardpressureis1.00×10^5paandtheboilingpointofwateratthispressure(knownasitsnormalboilingpoint) is373K (i.e. 100^0C).

P_1=?
$T1$ =298K P_2=1.00×10^5pa
R =8.314$Jmol^{-1}K^{-1}$$T_2$=373K
ΔHvap=4.10×$10^4$$Jmol^{-1}$

Substitutingthese valuesinClausius-Clapeyronequation(eq.3.59).

$$\log\frac{p_2}{p_1} = \frac{\Delta H_{vap}}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\frac{1.00\times10^5\text{pa}}{p_1} = \frac{4.10\text{x }10^4 J\ mol^{-1}}{2.303x\ 8.314 J\ mol^{-1}K^{-1}}\left[\frac{373\ K-298\ K}{373\ K\ x\ 298\ K}\right]$$

$\log 1.00 \times 10^5 - \log p_1 = 1.41$
$5.00 - \log p_1 = 1.41$
$\log p_1 = 5.00 - 1.41$
$\log p_1 = 3.59$
$P_1 = antilog 3.59 = 3.9\ x\ 10^3\ pa$

SELF-ASSESSMENTEXERCISE

i. Discuss the physical interpretation of anyone Maxwell relation.
ii. Estimate the standard reaction Gibbs energy of $N_{2(g)} + 3H_{2(g)} \rightarrow 2\ NH_{3(g)}$ at (a) 500 K, (b) 1000 K from their values at 298 K with enthalpy of reaction equals -46.11 $kJmol^{-1}$and gibbs free energy for the formation of ammonia being -16.45 $kJmol^{-1}$.
iii. The normal boiling temperature of chloroform is 61.7°C. Estimate the vapor pressure of chloroform at 50.0°C, given that $\Delta H_{vap,m}$ is 2.95×10^4 J mol^{-1}

4.0 CONCLUSION

We have seen that thermodynamics includes a number of useful relations that allow one variable to be replaced by another to which it is equal but which can be more easily evaluated. In this unit we obtained several such relations e.g. Maxwell relations based on expressions for the differentials of state functions. A common use of these relations is to replace a partial derivative that is hard to measure with one that can more easily be measured. The Gibbs–Helmholtz equation expresses the temperature dependence of the ratio of G/T at constant pressure, which is a composite function of T as G itself also depends on the temperature.

5.0 SUMMARY

- The four most common Maxwell relations (Eq. 3.28-3.31) are the equalities of the second derivatives of each of the four thermodynamic potentials, with respect to their thermal natural variable (temperature T; or entropy S) and their mechanical natural variable (pressure P; or volume V):
- The Gibbs–Helmholtz equation is a thermodynamic equation used for calculating changes in the Gibbs energy of a system as a function of temperature.
- Equation 3.42 tells us several things. It tells us that, in the final analysis, the ultimate driving force in nature is entropy, that is, the drive toward disorder. The system plus the surroundings is a closed isolated system so that the only spontaneous processes allowed are those which increase the entropy. Secondly, it explains why $\Delta G/T$ is more important than simply ΔG in determining how strongly spontaneous a process is. It is $-\Delta G/T$ which is related to the entropy change of the universe, not ΔG directly.

6.0 TUTOR-MARKED ASSIGNMENT

7.0 REFERENCES/FURTHERREADING

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UNIT 3 CRITERIA FOR SPONTANEITY

CONTENTS

1.0 INTRODUCTION

In this unit,we will studythe criteria for spontaneity,thirdlaw ofthermodynamicsanditsapplication incalculatingtheentropyofsubstances.

2.0OBJECTIVES

Bytheend ofthisunit,you shouldbeable to;

- explainthecriteriaforspontaneity,
- stateand explainthe thirdlaw ofthermodynamics.

3.0 MAIN CONTENT

3.1 Criteria forSpontaneity

Wehave seenthatentropycanbeused asacriterionfordeterminingthespontaneityofaprocess.We canalsoexpressthecriteriaforspontaneityin termsofotherthermodynamicproperties,namely U,H,$A$and G.

3.2 InternalEnergyChangeasaCriterion forSpontaneity

Fromthefirstlaw ofthermodynamics,weknow that

$\mathrm{d}q = \mathrm{d}U - \mathrm{d}w$(trueforirreversibleorreversible process)and since

$\mathrm{d}q_{rev} = T\mathrm{d}S$(asperEq.2.37)

$T\mathrm{d}S = \mathrm{d}U - \mathrm{d}w$(for a reversibleprocess)

Foranirreversibleprocess,$\mathrm{d}q_{\mathrm{irrev}} < \mathrm{d}q_{rev}$

Hence, $\mathrm{d}q_{\mathrm{irrev}} < T\mathrm{d}S$.

So,foranirreversibleprocess,$\mathrm{d}U - \mathrm{d}w < T\mathrm{d}S$

or$T\mathrm{d}S > \mathrm{d}U - \mathrm{d}w$

Thus foranyprocess:

$T\mathrm{d}S \geq \mathrm{d}U - \mathrm{d}w$

or $T\mathrm{d}S \geq \mathrm{d}U + (-dw)$

Ifwe consideronlythepressure-volumework($\mathrm{d}w = p\mathrm{d}V$),then

$T\mathrm{d}S \geq \mathrm{d}U + p\mathrm{d}V$

Subtracting$T\mathrm{d}S$*from*bothsides,$0 \geq \mathrm{d}U + p\mathrm{d}V - T\mathrm{d}S$

or$\mathrm{d}U + p\mathrm{d}V - T\mathrm{d}S \leq 0$
….(3.60)

...i.e.,foraprocesstobefeasible,theconditiongiveninEq.3.60mustholdgood. Atconstantvolume($\mathrm{d}V = 0$)and entropy($\mathrm{d}S = 0$),Eq.3.60thusreducesto

$(\partial U)_{V,S} \leq 0$ …(3.61)

According toEq.3.61whenthevolumeandentropyremainconstant,theinternal energyofasystemremainsconstantina reversibleprocess[$(\partial U)_{V,S} = 0$] whereas inanirreversibleprocesstheinternalenergydecreases[$(\partial U)_{V,S} < 0$].

3.3 EnthalpyChangeasaCriterion forSpontaneity

We knowthat$H=U+pV$

Differentiatingtheaboveexpression,weget $dH=dU+pdV+Vdp$

Sincefromfirst*law,*$dU=dq+dw$
$dH=dq+dw+pdV+Vdp$

Consideringonlypressure-volumeworkdoneon thesystem,wecanwriteasper Eq.1.14$dw=-pdV;$wethen have $dH= dq–pdV+pdV+Vdp$
or $dH=dq+Vdp$
or $dH–Vdp=dq$(trueforbothreversibleandirreversibleprocesses). Fora reversibleprocess$dq_{rev}=TdS$and,foranirreversibleprocess$dq_{\mathrm{irrev}}<TdS$. Thuswehaveforanyprocess

$dH-Vdp\leq TdS$…(3.62)

Atconstantpressure($dp=0$)and constantentropy($dS=0$)

Eq.3.62reducesto
$(\partial H)_{p.S}\leq 0$ …(3.63)

According to Eq. 3.63, when the pressureandentropyremain constant,the entropyofasystemremainsconstantina reversibleprocess[$(\partial H)_{p.S}<0$],whereas inanirreversibleprocesstheenthalpydecreases[$(\partial H)_{p.S}\leq 0$].

3.4 HelmholtzFreeEnergychangeasaCriterion forSpontaneity

From $A = U–TS$wehave

$dA= dU –TdS–SdT$

Since $dU=dq+dw$

$dA= dq+dw–TdS–SdT$

$dA-dw+TdS+SdT= dq$(trueforboth reversibleand irreversibleprocesses)
Since $dq_{\mathrm{rev}}=TdS$and$dq_{\mathrm{irrev}}<TdS$
$dA–dw+TdS+SdT\leq TdS$

or$dA–dw+SdT\leq 0$(cancellingTdSfromboththerides)

Consideringonlypressure-volumeworkdoneonthesystem,

$(dw = -pdV)$,wehave

or $dA + pdV + SdT \leq 0$

Atconstantvolume(dV=0)andconstanttemperature(dT=0),theaboveform reducesto,

$$(\partial A)_{T,v} \leq 0 \qquad ...(3.64)$$

AccordingtoEq.3.64,whenthetemperatureandvolumeremainconstant,the Helmholtzfree energyofasystemremainsconstantina reversibleprocess [$(\partial A)_{T,V} = 0$], whereas inan irreversibleprocessthe Helmholtz free energy decreases[$(\partial A)_{T,V} < 0$]

3.5 GibbsFreeEnergychangeasaCriterion forSpontaneity

$G = H - TS = U + pV - TS$

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*forreversibleand irreversibleprocesses)

Since,$dq_{rev} = TdS$and$dq_{irrev} < TdS$

$dG - dw - pdV - Vdp + TdS + SdT \leq TdS$

or$dG - dw - pdV - Vdp + SdT \leq 0$(cancelling$TdS$termsbothsides)

Ifonlypressure-volumeworkisdone($dw = -pdV$),wehave $dG + pdV - pdV - Vdp + SdT \leq 0$

or $dG - Vdp + SdT \leq 0$

Atconstanttemperature(dT=0)and constantpressure(dp=0), theaboveequationreducesto

$$(\partial G)_{T,p} \leq 0 \qquad ...(3.65)$$

AccordingtoEq.3.65,whenthepressureandtemperatureremainconstant,the Gibbsfreeenergyofasystemremainsconstantinareversibleprocess[$(\partial G)_{p,T}$

=0],whereas inanirreversibleprocess,Gibbs free energydecreases[$(\partial G)_{p,T}<0$].

Thusthecriterionforspontaneity intermsofGibbs free energyisthattheprocess wouldbefeasibleifΔGisnegative.

BycombiningEqs.3.15and3.65,wecandrawsomeusefulconclusions.From Eq.3.15wehave

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

ItcanbeseenfromEqs.3.15and 3.65that

1. IfΔH isnegativeand ΔSispositive,ΔGwillbenegativeatall temperatures;hence, theprocesswouldbespontaneous atall temperatures.

2. If ΔHispositiveand$\Delta S$is negative,ΔGwillbepositiveatall temperatures; hence,theprocesswouldnotbefeasible atanytemperature.

3. IfΔHandΔS arebothpositiveornegative,ΔGwillbepositiveornegative dependinguponthetemperature.

TherearefourpossibilitiesforΔGbasedonthesignsofΔHandΔS.Theseare outlinedinTable3.1.

Table3.1: Criterionfor SpontaneousChange

Case	ΔH	ΔS	ΔG	Result
1	-	+	-	spontaneousatalltemperatures
2	-	-	-	spontaneousatlowtemperatures
			+	nonspontaneousathightemperatures
3	+	+	+	nonspontaneousatlowtemperatures
			-	spontaneousathightemperatures
4	+	-	+	nonspontaneousatalltemperatures

Table3.2: Summary ofConditionfor Spontaneity and Equilibrium

Conditions	Irreversible process (Spontaneous)	Reversible process (Equilibrium)
At constant U, V	$dS>0$	$dS=0$
At constant S, V	$-dU>0$	$-dU=0$
At constant S, p	$dH<0$	$dH=0$
At constant p, T	$dG<0$	$dG=0$

SELF-ASSESSMENTEXERCISE 5

Underwhat conditions, wouldyouexpectthefollowingreactionstooccur spontaneously

a) $N_2(g)+3H_2(g) \rightarrow 2NH_3(g)$(Thereaction isexothermic)
b) $O_2(g) \rightarrow 2O(g)$(Thereaction is endothermic)

3.6TheGibbsFreeEnergyofFormation

Itisobviousfromthedefinitionof Gibbsfreeenergy (Eqs.3.3and3.4)thatthe absolutevalueof*G*isnotdeterminable sincetheabsolutevaluesof*U*and*H*are unknown. However,inmostcases,thisisnotahandicapaswerequireonly changes inGibbs free energyforagivenprocess.Inthissection,we areinterested inshowing themethodofcalculatingthestandardGibbsfreeenergyofareaction. Beforethat,letusdefinethestandardstatesofsubstances.

Thestandardstatesof solidsandliquids correspondtotheirmoststableformat1 barpressureandthespecifiedtemperature.Foragas,thestandardstateispure gasatunitfugacity.Foridealgas,fugacityisunity whenpressureis1barata specifiedtemperature.Inall thesecases,themoststableform hasthelowestfree energy.

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

Thestandardstateconventionmaybe summarizedasgivenbelow:

Forasolid :Thepure substanceat1barexternalpressureand ata specifiedtemperature.

Foraliquid :Thepuresubstanceat1barexternalpressureand ata specifiedtemperature.
Foragas : An idealgasat1barpartialpressureand ata specified temperature.

Forasolute :An idealsolutionatone molar concentrationand ata specifiedtemperature.

ThestandardGibbsfreeenergyofformation,$\Delta_f G°$,ofasubstanceisdefinedas thechangeintheGibbsfreeenergythataccompaniestheformationofonemole ofthesubstanceinitsstandardstatefromtheelementsintheirstandardstates.

JustlikeΔfH^{o},thestandardGibbsfreeenergy offormationof allelementsby definitioniszero.ThusΔfH^{o}(CO_2)istheGibbs free energyforthereaction,

C(graphite)+O_2(g)→CO_2(g) $\Delta_r G° = -394.4 \text{kJmol}^{-1}$

Itmaybementioned thatΔfG°canbedefinedatanytemperature butgenerally thesevaluesaretabulatedat298.15K.Thevaluesof ΔfG°forsomeselected substancesat298.15KaregiveninTable3.3.

Table3.3: StandardGibbsFree EnergiesofFormationat298.15Kofsome SelectedSubstances

Substance	ΔfG°/(kJmol^{-1})	Substance	ΔfG°/(kJmol^{-1})
$H_{(g)}$	+203.3	$HF_{(g)}$	-273.2
$O_{(g)}$	+230.1	$HCl_{(g)}$	-95.3
$Cl_{(g)}$	+105.4	$HBr_{(g)}$	-53.4
$Br_{(g)}$	+82.4	$HI_{(g)}$	+1.7
$Br_{2(g)}$	+3.1	$CO_{(g)}$	-137.2
$I_{(g)}$	+70.3	$CO_{2(g)}$	-394.4
$I_{2(g)}$	+19.3	$NH_{3(g)}$	-16.5
$H_2O_{(g)}$	-228.6	$CH_{4(g)}$	-50.8
$H_2O_{(l)}$	-237.2	$C_2H_{6(g)}$	-32.9
$C_6H_{6(l)}$	+124.3	$C_2H_{4(g)}$	+68.1
$CH_3OH_{(l)}$	-166.4	$C_2H_{2(g)}$	+209.2
$C_2H_5OH_{(l)}$	-174.1		

ThetableofstandardGibbsfreeenergiesofformation canbeveryusefulfor calculatingthestandardGibbsfreeenergy ofareaction.Thisisdefinedasthe changeinGibbsfree energythataccompaniestheconversionof reactantsintheir standardstatestoproductsintheirstandardstates.Inother words,

$$\left\{\begin{array}{l}\text{StandardGibbs free}\\ \text{energyfora reaction}\end{array}\right\} = \left\{\begin{array}{l}\text{(sumof}\Delta\text{f}G°\text{valuesofproducts)–}\\ \text{(sumof}\Delta\text{f}G°\text{valuesofreactants)}\end{array}\right\}$$

$$\Delta fG° = \sum \Delta fG°_{\text{(products)}} - \sum \Delta fG°_{\text{(reactants)}} \qquad \text{… (3.66)}$$

Example5

UsingthedatainTable3.3,calculatethestandardGibbsfreeenergyforthe reaction:

$H_{(g)}+Br2_{(g)}HBr_{(g)}+Br_{(g)} \longrightarrow$

Solution

$\Delta_r G° = [\Delta fG°(HBr) + \Delta fG°(Br)] - [\Delta fG°(H) + \Delta fG°(Br_2)]$

$=\{[-53.4+82.4]-[203.3+3.l]\}$kJmol^{-1}

$=-177.4$kJmol^{-1}

Hence, hydrogen atom can spontaneouslyreactwithbrominegastogive hydrogenbromide.

3.7TheThirdLawofThermodynamics

Thesecondlaw ofthermodynamicshasbeen usedtocalculateentropychangesin various chemical and physicalprocesses.However,theabsolutevaluesofentropy havesofarremained incalculable.Wenowtry todeviseascaleofstandard entropiessothatwecanassociatedefiniteentropieswithdifferentstatesofa givensystem.

3.7.1 TheNernstHeat Theorem

We startwithGibbs-Helmholtzequation(Eq.3.43)

$$\Delta G=\Delta H+T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$$

In previous section,wementionedthatitispossibletocalculateΔHbyknowingΔG attwo differenttemperatures.Aquestionwhichremainedunansweredwaswhether we cancalculateΔGfromΔHdata.OnethingwhichisclearfromEq.3.43isthatas we approachtheabsolutezerooftemperature,ΔGandΔHmustbeequalunless

$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$ assumesaninfinitevalue.Richards,however,found,duringhis studiesontheelectromotive forcevaluesofcells,thatthequantity $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$ actuallydecreasesastemperatureislowered.Thisobservationprompted Nernstto concludethat $\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$ decreases insuchawaythatitreacheszerovalue gradually atabsolutezero temperature.ThisimpliesthatΔGandΔHnotonlyapproacheach other nearabsolutezero,butdosoasymptotically(i.e.insuchamannerthattheir curvesoverlapatthispointasinFig.3.1

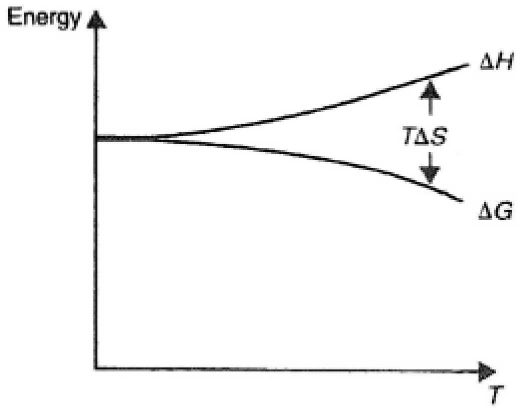

Fig.3.1□*G*and□*H*variationwithtemperature.

Mathematicallythisstatementis equivalentto:

$$\lim_{T\to 0}\frac{\partial(\Delta G)}{\partial T} = \lim_{T\to 0}\frac{\partial(\Delta H)}{\partial T} = 0 \qquad \ldots (3.67)$$

ThisisknownasNernstHeatTheorem anditisstrictlyapplicableonlytopure solids andnottoliquidsandgaseswhich arenotcapable ofexistenceatabsolute zero.

AsperEq.1.62ofUnit1

$$\left[\frac{\partial(\Delta H)}{\partial T}\right]_p = \Delta C_p$$

and again,accordingto Eq.3.42

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S$$

Here, ΔS representsthechangeinentropyaccompanyingareaction andΔCpisthe differencebetweenthetotalheat capacitiesoftheproductsandthoseofthe reactantsatconstantpressure.We canput Eq.3.67intheform,

$$\lim_{T\to 0}\Delta S = \lim_{T\to 0}\Delta C_p = 0 \qquad \ldots (3.68)$$

Inotherwords,atabsolutezero temperature,thereisnodifferencebetweentheheatcapacities of thereactantsandtheproducts atconstantpressure; thisimpliesthattheCp values ofallsubstancesat0Karesame.Later,studieshaveshown thatatthe absolutezerooftemperature,theheatcapacityofasolidshouldbezero.

i.e.,at0K,Cp=0 ...(3.69)

Asimilarargumentfortheentropychangeaccompanyingareactionleadstothe conclusionthatallsolidshave the sameentropyatabsolutezeroand,accordingto MaxPlanck,thisvalue ofentropyis 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) is equal to unity and the entropy of the substance is zero.

$S = k \ln \Omega = k \ln 1 = 0$ …(3.70)

In Eq. 3.70, 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 0K is not zero.

3.7.2 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. 1.36 of Unit 1)
Hence at constant pressure, $TdS = C_p dT$

i.e., $$dS = C_p \frac{dT}{T} \quad \ldots (3.71)$$

If we integrate Eq. 3.71 between the temperature limits 0 and T and entropy limits 0 and S, we have,

$$\int_0^S dS = \int_0^T C_p \frac{dT}{T} \quad \ldots (3.72)$$

Where S is the entropy at temperature T and by the third law, entropy at 0K (S_O) is zero.
Hence,

$$S_T - S_0 = S_T = \int_0^T C_p \, d\ln T \quad \ldots (3.73)$$

To calculate the value of S_T, the heat capacity of the substance should be known from 0K to the temperature at which the entropy is to be calculated. The heat capacities of solids are known up to about 10K to 15K. Below this temperature, the heat capacities of solids are determined using the Debye equation,

$C_p \approx C_V = aT^3$
...(3.74)

where$a$is constant;thevalueof$a$isdeterminedfromthevalueof$C_p$atsomelow temperature. Thistemperature isdenotedasT_{min};itis thelowesttemperature at which C_p ofthe solid canbemeasured conveniently. Eq.3.74 is valid for crystallinesolidsatlowtemperaturesnear0 K.Eq.3.73may bewrittenas,

$$S_T = \int_0^{T_{min}} C_p \frac{dT}{T} + \int_{T_{min}}^{T} C_p \frac{dT}{T} = \int_0^{T_{min}} aT^3 \frac{dT}{T} + \int_{T_{min}}^{T} C_p dInT \quad \ldots (3.75)$$

Eq.3.75canbesimplifiedasfollows:

$$S_T = \int_0^{T_{min}} aT^3 \frac{dT}{T} + \int_{T_{min}}^{T} C_p dInT$$

$$S_T = a\int_0^{T_{min}} T^2 dT + \int_{T_{min}}^{T} C_p dInT \qquad \text{(Since a is constant)}$$

$$S_T = \frac{a}{3}T_{min}^3 + \int_{T_{min}}^{T} C_p dInT$$

Whileusingthismethod,itmustberememberedthatanyphasechangetaking place between the temperatureszero kelvin (0 K) and T K, also contributes towardstheabsoluteentropy.Theentropyofphasechange.ΔS_{trans}isgivenby Eq. 2.75ofUnit2

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T} \quad \ldots (3.76)$$

where$\Delta H_{trans}$and$T$aretheenthalpyandtransitiontemperature,respectivelyfor thephasetransition.Thephasetransitionincludeschanges such assolidtoliquid, liquidtovapourand one allotropicformtoanother. Letusnowcalculatetheabsolutemolarentropyofasubstanceinthevapour phase at$T$K.Thisabsolutemolar entropywillbegivenbythesumoftheentropy changesinvolvedinvariousstagesasgivenbelow:

$S_T = \frac{a}{3}T_{min}^3$	entropychangeforbringing thetemperatureofthesolidfrom0KtoT_{min}
$+\int_{T_{min}}^{T} C_{p(s)} dInT$	entropychangefor heating the solid fromT_{min} to its melting point

$+\frac{\Delta H_{fus}}{T_f}$	entropy change for fusion of the solid into liquid
$+\int_{T_f}^{T_B} C_{p(l)} dInT$	entropychangefor heating the substance (in the liquid state) from its melting point to the boiling point
$+\frac{\Delta H_{vap}}{T_B}$	entropy change for the vapourization of the liquid
$+\int_{T_B}^{T} C_{p(g)} dInT$	entropy change for heating the vapour from the boiling point to the temperature T

where $C_{p(s)}$, $C_{p(l)}$, $C_{p(g)}$arethemolar heatcapacitiesofthesolid,liquidand gaseousphases,respectively;T_f andT_B arethemeltingandboilingpoints and $\Delta H_{fus}$and$\Delta H_{vap}$are themolarenthalpies offusionandvaporization, respectively. Hence,bysubstitutingin toEq.3.75thevaluesofthemolarheatcapacities,the molarenthalpiesandthetemperatures,theabsolutemolarentropyofasubstance canbecalculated.

Ifasubstanceexistsin differentallotropicmodifications,then□S_{trans} oftheallotropic transitionasgivenbyEq.2.75alsomust be addedwhilecalculatingtheabsolutemolarentropy ofasubstance.

SELF-ASSESSMENTEXERCISE

i. The following expressions have been used to establish criteria for spontaneous change: $\Delta S_{tot} > 0$, $dS_{u,v} \geq 0$ and $dU_{s,v} \leq 0$, $dA_{T,V} \leq 0$, and $dG_{T,p} \leq 0$. Discuss the origin, significance, and applicability of each criterion.

4.0 CONCLUSION

The second law of thermodynamics provides the general criterion for possible processes which can be used to derive criteria for spontaneous processes in a system under various circumstances. In addition, the third law of thermodynamics allows the entropy of any pure perfect crystalline substance consistently to be set equal to zero at absolute zero of temperature. Therefore, the second and third laws of thermodynamics imply that zero temperature on the Kelvin scale is unattainable.

5.0 SUMMARY

In this module, we have seen that;

- Foraspontaneous change,thetotal entropy ofthesystemandthesurroundings mustincrease.Ifentropyisusedasacriterionforspontaneity,itisnecessary to determinetheentropy changeforboththesystemandthesurroundings.Thisis inconvenientas onehastoconsiderthechanges takingplacebothinthesystem and thesurroundings.Therefore,acriterionforspontaneityisdevelopedin sucha mannerthatonlychangesintheproperties ofthesystem areconsidered.Forthis purpose,twomorestatefunctionscalled,Helmholtzfreeenergy(A)andGibbs freeenergy (G)aredefined.DecreaseinHelmholtzfreeenergyisequaltothe maximum amountofworkthatcanbeobtainedfromthesystemduringagiven change.ThedecreaseinGibbsfree energyisameasureofmaximumusefulwork thatcanbeobtainedfrom thesystem atconstanttemperatureandpressure.The Gibbsfree energychange (givenbytherelation$\Delta G=\Delta H-T\Delta S$)ofaphysicalor achemicalprocessisacriterionforspontaneity ofaprocess.ΔGhasanegative valueforaspontaneousprocess.

- Maxwellrelationsequatetherateofchangeofaquantity(whichcannot be determinedexperimentally)withtherateof changeofvolume,pressureor temperature.Gibbs-Helmholtz equationpermitsthecalculationofΔUorΔH providedΔAorΔGattwotemperaturesareknown.Clausius-Clapeyronequation isusefulforcalculatingthemolarenthalpyofvaporizationofliquidsifthevalues of vapourpressureattwodifferenttemperatures areknown.Thestandardfree energychange,$\Delta_r G^\circ$,isbasedontheconversionofreactantsintheirstandard statestoproductsintheirstandardstates.

- AccordingtoNernstheattheorem,ΔGandΔHnotonlybecomeequalto each otheratabsolutezero temperature,butalsoapproacheachothergradually astemperaturesnear absolutezero.Attheabsolutezero oftemperature,theentropyofeverysubstance maybecomezeroanditdoesbecomezerointhecaseof aperfectlycrystalline substance.

6.0 TUTOR-MARKED ASSIGNMENT

APPENDIX

TotalDifferentials

Let us consider a dependent variable, x, such that its value dependsonthe variables$y$and zonly,
i.e.,x=f(y,z) ...(A.I)
Foranychangein$y$andz,therewillbeachangein$x$also;alsoifthechangein$x$ (i.e.,dx)soproducedisirrespectiveofthepathfollowed,thendxiscalledtotal differential.Thevalueof d$x$intermsofchangesin$y$andzcanbeexpressedas follows:

$$dx = \left[\frac{\partial x}{\partial y}\right]_z dy + \left[\frac{\partial x}{\partial z}\right]_y dz \qquad \ldots \text{(A.2)}$$

Themeaningofthisequationisgivenbelow:

$$\begin{aligned} &Total\ change\ in\ x \\ &= \text{ changein}x\text{dueto change in y by one unit when z remains constant} \\ &+ \text{changein}x\text{dueto change in z by one unit when y remains constant} \end{aligned}$$

By comparisonyoucanrecognize thatEqs.A.1and3.67aswellasEqs.A.2and 3.68aresimilar.Theonlydifferenceisthat$x$dependsontwovariables$y$andz only,whereas$G$dependsonfourvariables$T$,P,$n$andn_2.ConsequentlyEq.3.68 containsfourtermsintherighthandside,eachterm depictingachangein$G$due toagivenchangeinaparticularvariable.

Oneofthecharacteristicsofatotal differentialisthatthesecond order differentialsofavariable suchas$x$givenabovearethesame.
i.e.,

$$\frac{\partial^2 x}{\partial y \partial z} = \frac{\partial^2 x}{\partial z \partial y} \qquad \ldots.\text{(A.3)}$$

Thismeansthatthechangein$x$issame,whetheritisvariedwith respecttozfirst and$y$next or*viceversa*

7.0 REFERENCES/FURTHERREADING

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MODULE 4 COLLIGATIVE PROPERTIES

INTRODUCTION

Inthismoduleweshallbediscussingtheprinciplesoffugacityand howitrelatestochemicalpotentialofanidealsystem.Thecolligative propertiesofsolution andphaseruleofcomponentsystemwillbe treated.Alsoabriefintroductiononstatisticalthermodynamic willbe undertaken. The module will comprise of the following units:

Unit 1 Systemof VariousComparison
Unit 2 DerivationofGeneralExpressionfor ChemicalEquilibrium
Unit 3 ThermodynamicQuantitiesfromEMFValues

UNIT 1 SYSTEM OF VARIOUS COMPARISON

CONTENTS

1.0 INTRODUCTION

The mathematical discussions in the preceding modules have been limited to systems that behave ideally; the systems were either pure ideal gases, or ideal mixtures (gaseous, liquid, solid). The question that arises is how are we to deal mathematically with non-ideal systems. These systems are handled conveniently using the concepts of fugacity and activity first introduced by G. N. Lewis which we shall see in this unit. The chemical potential of a component in a mixture is in general a function of temperature, pressure, and the composition of the mixture. These chemical potential in different types of systems can be calculated from Gibbs-Duhem equation.

2.0 OBJECTIVES

Bythe endoftheunit,studentsshouldbe ableto;

- definethe partial molarquantities
- define fugacity
- identifythe componentsofanidealgas

3.0 MAIN CONTENT

3.1 PartialMolarQuantitiesandChemical Potential

Theenthalpychangeinvolvedinthedissolutionof asoluteinaSolventisvery muchdependentontheamountsofthesoluteandsolventpresent.Similarly,other thermodynamicpropertieslikevolume,internalenergy,Helmholtzfreeenergy andGibbsfreeenergy alsodependonthecomposition ofthesystem.Untilnow however,wehaveconsideredonlytheclosedsysteminwhichtheamountsofthe reactantsand theproductsarefixed.We shallnowConsideropensysteminwhich theamountsofthecomponentsmay vary.

Ifweconsiderasinglehomogeneous phaseconsistingofonly onecomponent, thenthevalueofanextensiveproperty dividedbytheamountofthesubstance becomesthemolar property.Thesemolar propertiesareindicatedbyputtingabar abovethesymbols.

Thus,

$$\vec{V} = \frac{V}{n} \; and \; \vec{H} = \frac{H}{n}$$

where n is the amount (the number of the singlecomponent),$V$and$H$arethevolumeandtheenthalpy of$n$molof a substance. $\vec{V}$and $\vec{H}$arethemolar volumeand themolar enthalpyofthesubstance respectively.

However,if thesystem isaphaseconsistingofseveralcomponents,then the addition of one mole of any pure substance in

$$Molar\ volume\ of\ water = \frac{Molar\ mass\ of\ water}{Density\ of\ water} = \frac{1.8\ x\ 10^{-2} kg}{1.0\ x\ 10^{3}\ kgm^{-3}}$$
$$= 1.8\ x\ 10^{5} m^{3}$$
$$= 18\ cm^{3}\ (since\ 1\ cm^{3} = 10^{-6} m^{3})$$

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 18cm^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 role 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)

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. 4.1 is written from Eq. A.1 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,

$$dG = \left[\frac{\partial G}{\partial T}\right]_{p,N} dT + \left[\frac{\partial G}{\partial p}\right]_{T,N} dT + \left[\frac{\partial G}{\partial n_1}\right]_{T,p,n_2} dT + \left[\frac{\partial G}{\partial n_2}\right]_{T,p,n_1} dT$$
… (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 orT,p,n_2orT,p,n_1signify theparameters keptconstantwhileGisvariedwithrespecttoaparameternot mentionedasasubscriptoutsidethebracket.

Thepartialderivative $\left[\frac{\partial G}{\partial n_1}\right]_{T,p,n_2}$ representstherateofchangeinfree energypermoleof component1added tothesystem,whentemperature,pressureandthe amountofcomponent 2areconstant. Itisalsocalledthepartial molarfree energy (G_1) or simplychemical potential (μ_1) ofthecomponent1. The chemical potentialsofthetwocomponentsaredefinedas,

$$\left[\frac{\partial G}{\partial n_1}\right]_{T,p,n_2} = \mu_1 and \left[\frac{\partial G}{\partial n_2}\right]_{T,p,n_1} = \mu_2 \ldots(4.3)$$

Atconstanttemperature(dT=0)and constantpressure,(dp =0), Eq.4.3may be writtenas,
$dG_{T,p}= \mu_1 dn_1+\mu_2 dn_2$ ….(4.4) It is possible to define chemical potential in terms ofother thermodynamic functionsalso;butwe consideritintermsofGibbs free energyonly.

Ifasystemhasdefinitecompositionhavingn$_1$ andn$_2$ molesoftherespective components,thenonintegratingEq.4.4, wehave
$G_{T,p}=\mu_1 n_1+\mu_2 n_2$
…(4.5)

Eq.4.5describesthefree energyofasystemoftwocomponents intermsofthe partialmolarfreeenergiesof thecomponents.Similarexpressions canbewritten forotherthermodynamicquantitiesofthesystemalsointermsofthepartial molar quantities.

Theimportanceof partialmolarquantitiescanbeunderstood fromthefollowing example.WhenonemoleofWaterisaddedtoasufficientlylargevolumeofethanol,itisfoundthattheincreaseinvolumeisnotequaltothemolar volumeof water(18cm^3)butonly14cm^3.Thequantity,14cm^{3}mol^{-1} isthepartialmolar volumeofwaterinalargevolumeofethanol.Thus thepartialmolarvolumeofa substanceinamixtureofdefinedcompositionistheincreaseinvolumethatoccurswhenasubstanceisaddedtoasufficientlylargesampleofthesolution. In general,when $n_A$mol ofAismixedwith $n_B$mol ofB,the totalvolume(V)ofthe mixturecanbeobtainedfromEq.4.6whichiswrittensimilar toEq4.5

$$\vec{V} = n_A\overrightarrow{V_A} + n_B\overrightarrow{V_B} \qquad \ldots (4.6)$$

Where $\overrightarrow{V_A}$ and $\overrightarrow{V_B}$ 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 later section of this unit.

Example1
Whatisthetotalvolumeofthesolution,when3.80mol ofwaterismixedwith0.500molofethanol?Thepartialmolarvolumesofwater andethanolatthis compositionare1.80 $\times 10^{5}$ $m^3 mol^{-1}$and 5.34 $\times 10^{-5}$ m^3 mol^{-1},respectively.

Solution

$n(H_2O)$ =3.80mol $\vec{V}$ $(H_2O)=1.80\times10^{-5}m^3mol^{-1}$

$n(C_2H_5OH)$ =0.500mol $\vec{V}(C_2H_5OH)=5.34\times10^{-5}m^3mol^{-1}$

ApplyingEq.4.6

$\vec{V}=(3.80mol)\times(1.80\times10^{-5}m^3mol^{-1})+(0.500mol)\times(5.34\times10-5m^3mol^{-1})$
$=6.84\times10-5m^3+2.67\times10^{-5}m^3$
$=9.51\times10^{-5}m^3$

LetusnowseehowEq.4.5canbeusedtoderiveanimportantrelationship (knownasGibbs-Duhem Equation) betweenthechangesinthechemical potentialsofthetwocomponentspresentinasolution.

3.2 Gibbs-DuhemEquation

AccordingtoEq.4.5,atagiventemperatureandpressure,thetotal Gibbsfree energyforahomogeneous phaseisequaltothesumoftheproducts ofthe chemicalpotentialsandthenumberofmolesofeachcomponent.Hence,the Gibbsfreeenergyof thesystemcanchange eitherbythechangeof chemical potentialofacomponentoritsamountinthesystem.Ageneralexpressionforchange inGatthegiventemperatureandpressurecanbeobtainedby differentiatingEq.4.5

$\mathrm{d}G_{T,p}=\mu_1\mathrm{d}n_1+n_1\mathrm{d}\mu_1+\mu_2\mathrm{d}n_2+n_2\mathrm{d}\mu_2$
…(4.7)

At constant temperature and pressure, $\mathrm{d}G_{T,p}=0$

Eq. 4.7 then becomes,

$n_1\mathrm{d}\mu_1+n_2\mathrm{d}\mu_2=0$
…(4.8) ThisequationisknownasGibbs-Duhemorequation.

or $\mathrm{d}\mu_1 = -\left(\frac{n_2}{n_1}\right)\mathrm{d}\mu_2$
…(4.9)

thismeans thatthechemicalpotentialsforcomponents 1and2cannotbevaried independently. If $\mu_2$increases,then$\mu_1$willdecreasebyadefinite amount. Eq. 4.9finds extensiveapplicationsinliquids-vapour,liquid-solidandliquid-liquidequilibrium ofbinarymixtures.

Letusnow seehowthechemicalpotentialvarieswithtemperatureand pressure.

3.2.1 DependenceofChemicalPotentialon TemperatureandPressure

FromEq.3.20, dG=Vdp-SdT

Hence,$\left[\frac{\partial G}{\partial T}\right]_p$ = -S … (3.21)

Atconstanttemperature(dT=0),wehavefromEq.3.20

$\left[\frac{\partial G}{\partial p}\right]_T = V$ …(3.23)

We knowthatthechemicalpotentialofthecomponent$i$(μi)isgivenby,

$\mu_i = \left[\frac{\partial G}{\partial n_i}\right]_{T,p,n_j}$ … (4.10)

where$j$=allthecomponentsexcept$i$.Notethatthesubscript$n_i$meansthatthe amountsofallcomponentsexcept$i$arekeptconstant.

Differentiating$\mu_i$inEq. 4.10 withrespect to temperatureatconstant pressureand composition,wehave,

$$\left[\frac{\partial \mu_i}{\partial T}\right]_{p,N} = \frac{\partial^2 G}{\partial T \partial n_i}$$

Since$G$isastatefunction,

$$\left[\frac{\partial \mu_i}{\partial T}\right]_{p,N} = \frac{\partial^2 G}{\partial T \partial n_i} = \partial \left[\frac{1}{\partial n_i} . \left[\frac{\partial G}{\partial T}\right]_{p,N}\right]_{T,p,n_j}$$

From Eq. 3.21, $\left[\frac{\partial G}{\partial T}\right]_{p,N}$ = -S

Hence, $\left[\frac{\partial \mu_i}{\partial T}\right]_{p,N} = \left[\frac{\partial (-S)}{\partial n_i}\right]_{T,p,n_j} = -\left[\frac{\partial S}{\partial n_i}\right]_{T,p,n_j} = \overrightarrow{-S_i}$ … (4.11)

Where$\overrightarrow{-S_i}$isthepartialmolar entropyofthei^{th}component.Sincetheentropyofa substanceisalwayspositive;itschemicalpotentialorGibbsfreeenergywould decreasewithincreaseintemperature.Eq.4.11describesthedependenceofμi on temperature at constantpressureandcomposition.Letusnowderivean expressionusefulindescribingthedependenceofμionpressure.

Differentiatingμ_i (giveninEq.4.10) with respecttopressureatconstant temperatureand composition,wehave,

$$\left[\frac{\partial \mu_i}{\partial p}\right]_{T,N} = \frac{\partial^2 G}{\partial p \partial n_i} = \partial\left[\frac{1}{\partial n_i}.\left[\frac{\partial G}{\partial p}\right]_{T,N}\right]_{T,p,n_j}$$

FromEq.3.23, $\left[\frac{\partial G}{\partial p}\right]_T = V$

Hence,

$$\left[\frac{\partial \mu_i}{\partial p}\right]_{T,N} = \left[\frac{\partial V}{\partial n_i}\right]_{T,p,n_j} = \vec{V_i} \ldots \text{(4.12)}$$

Where $\vec{V_i}$isthe,partialmolar volumeofthecomponent *i*.Eq.4.12definesthe dependenceof$\mu_i$onpressureatconstanttemperatureand composition.

Eqs.4.11and4.12areobtainedfromEq.4.10usingoneof thepropertiesof totaldifferentials. Since d*G*isa total differential,the secondorderdifferentialsof*G*withrespectto*T*and*n*,takenin anyorderare thesame.

i.e., $\frac{\partial^2 G}{\partial T \partial n_i} = \frac{\partial^2 G}{\partial n_i \partial T}$

Alsothesecondorderdifferentialsof*G*withrespectto*p*andn_i,takeninanyorderare the same. Since*G*isathermodynamicsproperty,thechangein*G*dependsonthechangesinthevaluesof thevariablessuchas$T$,$n_i$or$p$,$n_i$etcatanyparticularinstant,butnotonthewayorthesequence bywhichsuchvariablesare changed.

3.3ChemicalPotentialofa PerfectGas

Thestandardstateofaperfectgasasestablishedatapressureofexactly1bar, denotedasp^{θ}anditsGibbsformationasG^{θ}.ThustheGibbsvalueatanyother Pressure, *p*,is

$G_{(p)}=G^{\square}+NRT\ell n(P/P^{\square})$……..I

and themolar Gibbs functionG/nwillbe

$G_{m(P)}=G_{m}^{\square}+RT\ell n(P/P^{\square})$……...II

Forapuresubstance,thechemicalpotential(□)isgivenas

$\square=G_{m(p)}$……………………III SubstitutingequationIIIintoII,wehave

$\square=\square^{\square}+RT\ell n(P/P^{\square})$

The originofthe namechemical potential,isanalogybetweenmechanical systems,whereparticlestend totravel inthedirectionofdecreasingpotential,and thethermodynamic tendencyofsystemstoshiftin thedirectionofdecreasing Gibbs function.

3.4 Fugacity

Asthedeparturesfromidealityoccurunderquitecommon conditions,asinthe caseof real gases,thepressure(p)isreplacedbysomeeffectivepressure,the fugacity(f)suchthat

$$\mu = \mu^{\theta} + RT\ In\left[\frac{f}{p^{\theta}}\right]$$

Fugacityhasthe samedimensionwiththepressureofthegas.Relatingthe fugacitytothepressure, and expressing itintermsofmolar quantitiesgives

$\int_{p^1}^{p} V_m\, dp = \mu_{(p)} - \mu_{(p^1)} = RT\ In\left[\frac{f}{f^1}\right]$ … A

wherefisthefugacity,whenthepressureispandf^{1}thefugacitywhenthepressure isp^1.

Ifthegaswereperfect,wecouldwrite

$\int_{p^1}^{p} V_m^0 dp = \mu_{(p)}^0 - \mu_{(p^1)}^0 = RT\ In\left[\frac{p}{p^1}\right]$……..B

wherethesuperscript $^{\mathrm{o}}$denotesquantitiesrelatingtoaperfectgas.

ThedifferencebetweenequationAand Bis

$$\int_{p^1}^{p} (V_m - V_m^0) dp = RT\ In\left[\frac{f}{f^1}\right] - RT\ In\left[\frac{p}{p^1}\right]$$

$$In\frac{\left(\frac{f}{p}\right)}{\left(\frac{f^1}{p^1}\right)} = \left(\frac{1}{RT}\right)\int_{p^1}^{p} (V_m - V_m^0) dp$$

when$\left(\frac{f^1}{p^1}\right)$approaches1asp^{1}approacheszero,wehave

$$In\left(\frac{f}{p}\right) = \left(\frac{1}{RT}\right)\int_{p^1}^{p} (V_m - V_m^0) dp$$

The equationaboveisthe definitionoffugacity.The standardvalue ofthe chemicalpotentialcanbecalculated asgivenbelow

$$\mu^{\theta} = \mu - RT\ In\left(\frac{f}{p}\right) - RT\ In\left(\frac{p}{p^{\theta}}\right)$$

Measurementof Fugacity

The expressionforthefugacitycorrespondingtoapressure,p,canbesimplifiedas follows:

$V_m^{\theta} = \frac{RT}{p}$ … for perfect gas

and

$V_m^{\theta} = \frac{RTZ}{p}$ … for real gas

whichrearrangesto

f= □p

and $\gamma = exp \int_0^p \left[\frac{(2-1)}{p}\right] dp$

Thefactor□scalledthefugacitycoefficient.Thisistherecipefordetermining thefugacityofagasatanypressure.

3.5 ChemicalPotentialofcomponentsinamixtureofIdealGases

Thechemical potentialofthecomponentsinamixtureofidealgasescanbe expressedinthree possibleways.Firstletusderiveanexpressionforthechemical potentialofacomponentintermsofitspartialpressure.

Foranidealgas,$pV=nRT$ …(4.13)

Letusconsideranidealgasmixtureattemperature$T$,totalpressurepandvolume V.Letthenumberofmolesofeachcomponentben_1,n_2,..n_i...,andthepartial pressureofeachcomponent bep_1,p_2......p_i......respectively,

ThenfromEq.4.13, wehave

$$V = \frac{nRT}{p} = (n_1 + n_2 + \cdots + n_i)\frac{RT}{p} = n_t\frac{RT}{p}$$

Wheren_t,isthetotalnumberofmolesofallthecomponents.Differentiating$V$in theaboveequationwithrespectton_i atconstanttemperatureandpressure,we have,

$$\left[\frac{\partial V}{\partial n_i}\right]_{T,p,n_j} = \vec{V_i} = \frac{RT}{p}$$

Notethatthesubscript$n_j$denotesthattheamountsofallothercomponentsexcept $i$atekeptconstant.ButfromEq.4.12

$$V_i = \left[\frac{\partial \mu_i}{\partial p}\right]_{T,N}$$

Hence,

$\left[\frac{\partial \mu_i}{\partial p}\right]_{T,N} = \frac{RT}{p}$ … (4.14)

or

$\partial \mu_i = RT\frac{dp}{p} = RT\ dInp$ … (4.15)

Ifp$_i$isthepartialpressureofthecomponent$i$and$p$isthetotalpressureofthe mixtureofgases, thenaccordingtoDalton'slaw ofpartialpressures,

$$p_i = \frac{n_i}{n_t}p = x_i p$$

where$x_i$isthemolefractionofthecomponent$i$.Takinglogarithm ofbothsides,

$$Inp_i = Inx_i + Inp$$

Ifx_i is constantwe canwriteondifferentiationofInp_i

dInp_i=dln$p$

Thismeansthatinagaseous mixtureofconstantcomposition,thepartialpressure ofacomponent variesasthetotalpressure.

Substitutingfordln$p$inEq.4.15,wehave

dμ_i=RTdlnP_i

Integratingbetweenthelimitsμ_i(l)→μ_i(p_i)and 1→$p_i$wehave,

$$\int_{\mu_i(1)}^{\mu_i(p_i)} d\mu_i = RT\int_{1}^{p_i} dInp_i$$

$$[\mu_i]_{\mu_i(1)}^{\mu_i(p_i)} = RT[Inp_i]_1^{p_i}$$

or $\mu_i(p_i)–\mu_i(1)=RT\ln p_i–RT\ln 1$

i.e $\mu_i(p_i)–\mu_i(1)=RT\ln p_i$ [sinceIn1=0]

or $\mu_i(p_i)=\mu_i(l)+RT1np_i$ … (4.16)

InEq.4.16,μ_i(p_i)isthechemicalpotentialoftheithcomponentattemperature$T$ whenitspartialpressureisp$_i$,andμ_i (1)isthechemicalpotentialatthesame temperature butatapartial pressureofunity.Hence,μ_i(1)is equaltoμ_i(P_i)

when P_i=lbar;i.e.,$\mu_i(1)$isthechemicalpotentialunder standardstateat1bar. Thus, ingeneral,wemaywriteEq.4.16intheform,

$\mu_i(p_i)=\mu^o(p)+RTInp_i$ … (4.17)

where$\mu_i(p_i)$isthechemicalpotentialoftheithcomponentatapartial pressurep_i and$\mu_i°(p)$isitsstandardchemical potential.Eq.4.17givesthechemical potential ofanidealgas$i$intermsofitspartial pressureinamixture.Letusnowderivean expression forthechemicalpotentialofanidealgasintermsofitsconcentration inamixture.

InordertotransformEq.4.17intermsofconcentration,weuse theidealgaslaw and substitute;

$$p_i = \frac{n_i}{V} = c_i \; and \; RT = c_i RT$$

where$c_i$istheconcentrationofthei^{th}component.

Letμ_i (c_i)bethechemicalpotentialofthei^{th}componentwhenits concentration is $c_i$inthemixtureofidealgases.

So, $\mu_i(c_i)=\mu_i(p_i) =\mu_i^o(p)+RT1np_i$

$=\mu_i(p)+RT1nc_i+RT\ 1nRT$

or $\mu_i(c_i)=\mu_i°(c)+RTInc_i$ … (4.18)

Here, $\mu_i°(c)=\mu_i^o(p)+RTInRT$

Thisisequal tothechemicalpotentialcomponent oftheithcomponent understandardstate(when$c_i$isunity).

Asimilarexpressioncanbederivedintermsofthemolefraction(x_i)ofthe i^{th}component. Forthispurpose,wemakeuse ofDalton'slaw ofpartialpressures,

$p_i = x_i\, p$

wherep_i isthepartialpressureoftheithcomponentand$p$isthetotal pressureofthemixtureofidea gases.

Letusassumethat$\mu_i(x_i)$isthechemicalpotentialoftheithcomponent intermsof itsmolefractioninthemixture.

UsingEq.4.17, $\mu_i(x_i)=\mu_i(p_i)=\mu_i^{O}(p)+RT1np_i$

where

$\mu_i^{O}(p)=RT1nx_i+RT1np$

Hence, $\mu_i(x_i)=\mu_i^{O}(x)+RT\,In\,x_i$ … (4.19)

where $\mu_i^{\circ}(x)=\ \mu_i^{\circ}(p)+RT\ln p$

and isequaltothechemicalpotentialofthe component*i*understandardstate(whenx_i =l).Eqs.4.17,4.18and4.19are applicabletoideal systemsonly.When asystemexhibitsdeviationfromideal behaviour,modifiedformsofthese equationsaretobeused.

SELF-ASSESSMENT EXERCISE(S)

i. The fugacity coefficient of a certain gas at 290 K and 2.1 MPa is 0.68. Calculate the difference of its molar Gibbs energy from that of a perfect gas in the same state.
ii. Calculate the change in chemical potential of a perfect gas when its pressure is increased isothermally from 92.0kPa to 252.0kPa at 50°C.

4.0 CONCLUSION

The all-important chemical potentials μ_i of components of a non-ideal solid or liquid solutions are expressed in terms of activities and activity coefficients. One defines a standard state for each component i and then defines its activity a_i so that $\square_{\square}=\square_{\square}^{\square}+RT\ell n(a_i)$ where $\square_{\square}^{\square}$ is the standard-state chemical potential of i. All standard states are at the T and P of the solution. In a non-ideal gas mixture, the fugacities, f,are defined so that the chemical potentials have the form:

$$\mu = \mu^{\theta} + RT\ In\left[\frac{f}{p^{\theta}}\right]$$

5.0 SUMMARY

- An ideal solution is a model system in which every component has its chemical potential given for all compositions by
  $\square_{\square}=\square_{\square}^{\square}+RT\ell n(x_i)$
  where μ_i is the chemical potential of the pure substance i, R is the ideal gas constant, T is the absolute temperature, and x_i is the mole fraction of the substance in the solution.

- This equation shows that at a given temperature the pressure is a measure of the chemical potential of the gas. If inequalities in pressure exist in a container of a gas, then matter will flow from the high-pressure regions (high chemical potential) to those of lower pressure (lower chemical potential) until the pressure is equalized throughout the vessel.
- The equilibrium condition, equality of the chemical potential everywhere, requires that the pressure be uniform throughout the vessel. For non-ideal gases it is the fugacity that must be uniform throughout the vessel; however, since the fugacity is a function of temperature and pressure, at a given temperature equal values of fugacity imply equal values of pressure.
- Fugacity and activity coefficients describe deviations from ideal or dilutebehaviour.

6.0 TUTOR-MARKED ASSIGNMENT

7.0 REFERENCES/FURTHERREADING

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UNIT 2 DERIVATION OF GENERAL EXPRESSION FOR CHEMICAL EQUILIBRIUM

CONTENTS

1.0 INTRODUCTION

Every chemical equilibrium can be characterized by an equilibrium constant, known as K_{eq}. The K_{eq} and K_P expressions are formulated as amounts of products divided by amounts of reactants; each amount (either a concentration or a pressure) is raised to the power of its coefficient in the balanced chemical equation.

2.0OBJECTIVES

Bytheend ofthisunit,you shouldbeable to;

- explain thechemicalequilibrium constant
- identifyexpressionforanidealgasmixture
- correlatebetweenequilibrium constantandconcentration

3.0 MAIN CONTENT

3.1 Derivation ofGeneralExpression for ChemicalEquilibrium

Even before derivationofequilibriumexpressionisattempted,wemust recapitulatethefollowingconventionsinthermodynamics.

1) Anysystem,towhichsubstancesareaddedorfromwhichtheyaretaken awayorinwhichachemicalreactiontakesplace,is called anopen system.
2) Achemicalreaction involvinganumberofsubstancesisrepresentedby

$$\sum V_i A_i = 0 \qquad \ldots (4.20)$$

Where$A_i$representsachemicalsubstanceatthetemperatureandpressure ofthe reaction,and$v_i$is calledthestoichiometriccoefficientofA_i.

v valuesare positivefortheproductsandnegativeforthereactants.This relationshipcanbe explainedusingthefollowingexample:

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$

canbewrittenas

(1) $H_2O – (1)H_2 – (\frac{1}{2})O_2 = 0$

and the values of vs are:

$v_{(H_2O)} = 1, v_{(H_2)} = -1, v_{(O2)} = -\frac{1}{2}$

Again,notethat$v$ispositivefortheproducts,andnegativeforthereactants.Let usnowconsideranopensystemrepresentedbyageneralreaction:

$aA + bB + cC \ldots \rightleftharpoons pP + qQ + rR \ldots$

ThechangeinGibb'sfree energy, dG,forthereaction isgivenbyEqs.3.20, 4.2 and 4.4

$$dG = Vdp – SdT + \Sigma\mu_i dn_i \qquad \ldots (4.21)$$

wheredn_i=changein theamountofany particularsubstance,'i'andμ_i=chemical potentialofthatsubstance;allothersymbolscarry theirusualmeaning.Atconstant temperatureand pressure,Eq.4.21reducesto:

$$dG_{T.P} = \Sigma\mu_i dn_i \qquad \ldots (4.22)$$

The symbolΣstandsforsummation ofterms; the terms are obtainedby givingdifferentvaluestoi.

AsperEq. 4.2giveninSec.3.0 ofUnit 1 module 4ofthiscourse,

$$dG = \left[\frac{\partial G}{\partial T}\right]_{p,N} dT + \left[\frac{\partial G}{\partial p}\right]_{T,N} dT + \left[\frac{\partial G}{\partial n_1}\right]_{T,p,n_2} dT + \left[\frac{\partial G}{\partial n_2}\right]_{T,p,n_1} dT$$

UsingEqs.,3.20 and 4.21,this expressioncanbe writtenas,

dG= -SdT + Vdp+ $\mu_i dn_i + \mu_2 dn_2$

Eq. 4.22isa generalisedform ofthe above equation.

Thechangeintheamountofanysubstance'dn_i'canbe moreconveniently expressedintermsofanotherquantity ξi(pronouncedas"xi")whichisameasure oftheextentofthereaction.Forexample,ξ=0forasubstance'i'meansthatit hasnotreactedatall;ξ=1meanswholeamountof 'i'hasreactedandsoon.For anyreversiblereactionthevalueofξshouldbebetweenzeroand unity.

Letusnowderiveanexpressiontospecifythevariationoffreeenergywith respecttotheextentofreaction.Thenumberofmoles(n_i)ofaparticular substance ‘i'presentatdifferenttimes,asareactionproceeds,canbeexpressedby therelation:

$n_i = n_i^0 + v_i\xi$ … (4.23)

where,n_i isthenumberofmolesofthesubstance$i$presentbeforethereaction starts,v_i isthestoichiometriccoefficientofthesamesubstanceinthebalanced chemicalequation(withapropersign)andξistheextentofthereaction.Note

that $n_i^0$and$v_i$areconstantsforasubstancewhilen_i variesasξchanges.The changein$n_i$canbeobtainedbydifferentiatingEq. 4.23.

$dn_i = v_i d\xi$ … (4.24)

(sincen_i^0andv_i,areconstants)

CombiningEqs.4.22and4.24, we get,

$$dG_{T,p} = \sum_{i}^{n} \mu_i v_i d\xi$$

Hence, $\left(\frac{dG}{d\xi}\right)_{T,p} = \sum_i \mu_i v_i$ … (4.25)

Eq.4.25representsGibb'sfreeenergychangeofthereaction($\Delta_r G_{T,p}$)atconstant temperatureand pressure.

Inmodule3youhave studiedthat$\Delta_r G_{T,p}$is equaltothesumoftheGibb's free energy oftheproductsminusthesumoftheGibb's free energyofthereactants. therefore,

$$\left(\frac{dG}{d\xi}\right)_{T,p} = \sum_i \mu_i v_i = \Delta_r G_{T,p} \qquad \ldots (4.26)$$

LetusapplyEq.4.26toreactions.First,letusconsidertheformation ofwater discussedinthissection.

$H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$

$\Delta_r G_{T,p}$fortheformationofwater isgivenby

$\Delta_r G_{T,p} = \mu(H_2O) - \mu(H_2) - \frac{1}{2}\mu\ (O_2)$

The v_i values of H_2O, H_2 and O_2 are 1, -1 and $-\frac{1}{2}$ respectively.

Asasecondexample,letusconsidertheformationofammonia.

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

Forthisreaction,

$\Delta_r G_{T,p} = 2\mu NH_3 - 1\mu N_2 - 3\mu H_2$

Again,notethatthev_i,valuesofNH_3,$N_2$and H_2are2,-1and-3,respectively.

From module3 of this course,weknowthatthe Gibb'sfreeenergyofa systemwillbe minimumat equilibriumat constant temperatureandpressure(see Fig. 4.1 where point 3 indicate equilibrium point with minimum ΔG). Hence,thederivativeofthe Gibb'sfreeenergyfunctionwith respecttotheextent ofthereaction,whichistheslopeofthecurveinFig.4.1, isequaltozeroat equilibriumatconstanttemperatureand pressure.Inother words,

$$\left(\frac{dG}{d\xi}\right)_{T,p,eq} = \sum_i \mu_i v_i = \Delta_r G_{T,p} = 0 \qquad \ldots (4.27)$$

where ‘eq’standsforequilibriumcondition.

Achemicalreactionwill tend toproceedinadirectionofdecreasingfreeenergy.At equilibrium,thereactiondoesnotproceedineitherdirection,implyingthereby thatthere wouldbeanincreaseinGibb'sfreeenergyofthesystemifthe reactionproceedsineither direction.Hence,theGibb'sfree energyofthe systemwillbe minimum at equilibrium.

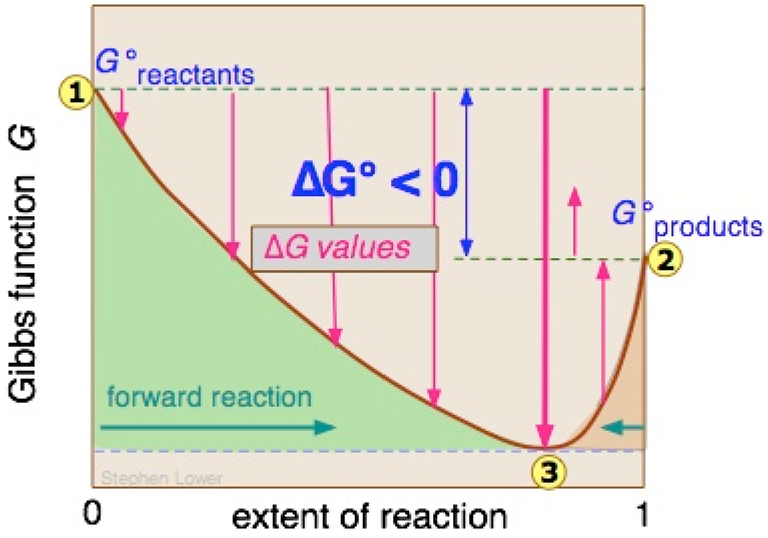

Fig.4.1:Change ofGibb'sFree Energyandthe extentofchemical reaction.

Eq.4.27 is a generalexpressionwhich isapplicable toanyreversible chemical reactionunderequilibriumconditionsatconstanttemperatureand pressure.Theequationsimplymeansthatthesumofthechemicalpotentialsof theproductsand reactantsis equaltozeroatequilibrium.

Eq.4.27wouldbemostusefulifwecouldexpress thechemicalpotentialin termsofsomeexperimentally determinableorknownquantities.Therearea numberofwaystoexpresschemicalpotentials.Thenextsectiondiscussesthe substitutionforchemicalpotentialintermsofpartialpressure,molefractionand concentrationforidealgasmixturesatequilibrium.

TrythefollowingSAQwhichisbasedontheabovediscussion.

SELF-ASSESSMENTEXERCISE1

Fortheformationreactionofnitricoxidefromnitrogenandoxygengases,find thevalueof*v*foreachofthereactantsand products.

3.2ChemicalEquilibriuminIdealGasMixtures

Let usderive anexpressionfortheequilibriumconstantintermsofpartial pressuresfora reactionbetweenidealgases.

3.2.1 EquilibriumConstantExpressioninTerms of PartialPressure

Consider ageneral reaction

$a\mathrm{A}+bB+\ldots \rightleftharpoons lL+mM+\ldots$ (4.28)

Atconstanttemperature(dT=0)andpressure (dp =0)thefree energychangefor theabovereaction($\Delta_r G_{T,p}$)isobtainedbyusingEq.4.26.

$$\Delta_r G_{T,p}=(l\mu_L+m\mu_M+\ldots)-(a\mu_A+b\mu_B+\ldots) \quad \ldots(4.29)$$

whereμ_L, μ_M, μ_A, μ_B, ...,etc.,arethechemicalpotentialsoftheproductsand reactants; and$l$,m,(-a),(-b),...,etc.,are$v_i$values.Rememberthattheproducts (suchasLandM)havepositive$v$valuesandthereactants(suchasAandB) havenegative$v$values;becauseofthis,thereisanegativesignbetween thetwo termsontherighthandsideofEq.4.29 Thechemicalpotentialμ_i,ofanideagas‘i'inagaseousmixtureisgivenbyEq. 4.17

$$\mu_i(p_i)=\mu_i^o(p)+RT\ln p_i \ldots(4.30)$$

where$\mu_i(p)$isthechemical potentialofiinthestandardstateand$p$isitspartial pressure.

UsingEq.4.30 inEq.4.29,

$$\Delta_r G_{T,p}=[l\mu_L^0(p)+lRT\ln p_L)+m\mu_m^0(p)+mRT\ln p_M)+\ldots]-[a\mu_A^0(p)+aRT\ln p_A)+b\mu_B^0(p)+bRT\ln p_B)+\ldots] \quad \ldots(4.31)$$

$$\Delta_r G_{T,p}=[(l\mu_L^0(p)+m\mu_m^0(p)+\ldots)-(a\mu_A^0(p)+b\mu_B^0(p)+\ldots)] \quad RT\ln\frac{p_L^l\cdot p_M^m}{p_A^a\cdot p_B^b} \quad ..(4.32)$$

NotethatinthetransformationofEq.4.31toEq.4.32,wehaveusedtherelation: $lRT\ln p_L = RT\ln p_L^l$

i.e.,acoefficient(l)ofalogarithmicterm($RT\ln p_L$)is taken insidethelogarithmictermasapower,

But $(l\mu_L^o(p)+m\mu_M^o(p)+\ldots)-(a\mu_A^o(p)+b\mu_B^o(p)+\ldots)=\Delta_r G_{T,p}^o$ …(4.33) where $\Delta rG^{0}_{T,p}$ isthestandardfreeenergy changeofthereactionatconstant temperatureandpressure.

UsingEqs.4.32 and4.33wecanwrite

$$\Delta rG_{T,p}=\Delta rG^{0}_{T,p}+RT\,In\frac{p_L^l\cdot p_M^m}{p_A^a\cdot p_B^b} \qquad \ldots(4.34)$$

Letusnowassumethattheabovesystemisunderequilibrium.UsingEqs.4.27 and 4.34, wecanwritethatatequilibrium,

$$\Delta rG_{T,p}=\Delta rG^{0}_{T,p}+RTIn\left[\frac{p_L^l\cdot p_M^m}{p_A^a\cdot p_B^b}\right]_{eq}=0$$

Thesubscript'eq'standsforequilibriumvaluesofpartialpressures.

$$\text{i.e.,}\ \Delta rG^{0}_{T,p}=-RTIn\left[\frac{p_L^l\cdot p_M^m}{p_A^a\cdot p_B^b}\right]_{eq} \qquad \ldots(4.35)$$

or $\Delta rG^{0}_{T,p}=-RT\ InK_p=-2.303RT\log K_p$ …(4.36)

whereK_p iscalledtheequilibriumconstantintermsofpartialpressures.The relationship isknownasvan'tHoffisotherm. $K_p$isgivenbytherelationship,

$$K_p=\frac{p_L^l\cdot p_M^m}{p_A^a\cdot p_B^b}\ \text{atequilibrium} \qquad \ldots(4.37)$$

$$=\frac{multiplication\ \ of\ (p_i)^{v_i}terms\ \ of\ the\ products}{multiplication\ \ of\ (p_i)^{v_i}terms\ \ of\ the\ reactants}\quad \text{at equilibrium}$$

Notethatv_i,writtenaspowerispositivefortheproduct,NH_3,whereasitisnegativeforN_2;
andH_2, these twobeingreactants.

wherep_L,p_M,p_A,p_B,...,etc.,arethepartialpressuresof L,M,A,B,...,etc.,at equilibrium.Insubsequentsections, weleave out thesubscript'eq' whilereferring toequilibriumpartialpressures.Eq.4.37canalsobewrittenas,

$$K_p=p_L^l\cdot p_M^m \cdots p_A^{-a}\cdot p_B^{-b} \cdots\cdot \qquad \ldots(4.38)$$

wherep_L,p_M, p_A,p_B...etc.,aretheequilibriumpartialpressuresand$l$,m,(-a), (-b)...,etc.,aretherespectivecivaluesofL,M,A,B,...,etc.Eq.4.38canalso berepresentedas,

$$K_p=\prod_i p_i^{v_i} \qquad \ldots(4.39)$$

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 $p° = 1 \text{bar} = 10^5$ Pa. To represent K_p as a dimensionless quantity, Eq. 4.39 is modified as,

$$K_p = \prod_i \left(\frac{p_i}{p^0}\right)^{v_i} \qquad \ldots(4.40)$$

Let us apply Eq. 4.38 to ammonia synthesis reaction.

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

$K_p = (p_{NH_3})^2 (p_{N_2})^{-1} . (p_{H_2})^{-3}$

Or $K_p = \frac{p_{NH_3}^2}{p_{N_2} . p_{H_2}^3}$

Since the partial pressure are expressed in Pa unit, K_p for ammonia synthesis has the unit P^{-2}. If K_p for ammonia synthesis is to be dimensionless, then K_p expression is to be written following 4.40 as,

$$K_p = \frac{p_{NH_3}^2 (p^0)^2}{p_{N_2} . p_{H_2}^3}$$

Let us illustrate the use of Eq. 4.38 with an example.

Example 2

Suppose that, in an experiment at 1000 K, it is found that

$P_{SO_2} = 3.42 \times 10^4$ Pa, $p_{O_2} = 3.31 \times 10^4$ Pa and

$P_{SO_3} = 3.58 \times 10^4$ Pa for the reaction,

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

Calculate the value for the equilibrium constant, K_p

Solution

A the given temperature, K_p is given by the expression

$K_p = (p_{SO_3})^2 (p_{SO_2})^{-2} . (p_{O_2})^{-1}$

or $K_p = \frac{p^2_{SO_3}}{p^2_{SO_2}.p^1_{O_2}} = \frac{(3.58\ x\ 10^4 pa)^2}{(3.42\ x\ 10^4 pa)^2\ x\ (3.13\ x10^4 pa)} = 3.50x10^{-4}pa^{-1}$

Notethattheunitof$K_p$asperE.q4.38isgivenby$(Pa)^{\Sigma v}$.Inthe reactiondiscussedinExample 2,Σv_i= 2–2–1= –1.Hence,the unit$K_p$isPa^{-1}

TrythefollowingSAQnow.

SELF-ASSESSMENTEXERCISE2

Supposethatwewritetheammoniasynthesisreaction intwodifferentways:

i) $\frac{1}{2}N_2(g)+H_2(g) \rightleftharpoons NH_3(g)$

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

WouldyouexpressanydifferenceintheexpressionforK_p inthetwocases? (Usually,K_p valuesarecalculatedusingequationsofthetype(ii)whichhave integralstoichiometriccoefficients)

3.2.2 EquilibriumConstantExpressioninTerms ofMoleFraction

SinceDalton'slawtellsusthatpartial pressureofagasisequal tothemole fractiontimesthetotalpressure,Eq.4.38canbewrittenas,

$K_p=(x_LP_t)^l(x_MP_t)^m\ldots(x_AP_t)^{-a}(x_BP_t)^{-b}$

$K_p= \prod_i (x_i p_t)^n$ …(4.41)

Where, x_i=molefractionofthespecies$i$,andp_t=totalpressure.

AccordingtoDalton'slawofpartialpressure,partialpressure(pi)ofanidealgas ,i,isgiven by,

$Pi= P_t.x_i$

Where$P_t$is the total pressure,andxi is themole fractionofthe gas ina gaseousmixture.

Example3

Considerthereaction

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

IfamixtureofNO_2,andN_2O_4atequilibriumhasatotalpressure of1.5×10^5Pa, calculatethefractionofN_2O_4thathasdissociatedat303K.$K_p$forthereactionis 1.4×10^4Paat303K.

Solution

SupposethatξisthefractionoftheamountofN_2O_4 whichhasdissociatedat equilibrium oritrepresentstheextentofthereaction.Then1-ξisthefractionof theamountofN_2O_4remainingatequilibriumandisproportional totheactual numberofmolesofN_2O_4presentatequilibrium.

Fromthebalancedreaction,itisseenthatforeachmoleofN_2O_4 decomposed, therearetwomoles.ofNO_2 produced.Therefore,at equilibrium,2ξwillbe proportionaltotheactualnumberofmolesofNO_2produced.

Thetotalnumberofmolesatequilibriumwouldthen beproportionalto
$1-\xi+2\xi$or$1+\xi$

Themolefractionsofthetwogasesatequilibriumcanbewrittenas,

$x_{NO2}=\frac{1-\xi}{1+\xi}$ and$x_{NO2}=\frac{2\xi}{1+\xi}$
where*x*denotesmolefraction.
UsingEq.4.41, $K_p=(x_{NO2}\cdot P_t)^2.(x_{N2O4}.P_t)^{-1}$

i.e., $K_p=\frac{(x_{NO_2}p_t)^2}{x_{N_2O_4}p_t}$

Substitutingforx_{NO2}andx_{N2O4}weget,

$$K_p=\frac{\left(\frac{2\xi}{1+\xi}.p_t\right)^2}{\left(\frac{1-\xi}{1+\xi}.p_t\right)}$$

$$K_p=\frac{4\xi^2}{(1-\xi)(1+\xi)}.p_t=\frac{4\xi^2}{1-\xi^2}.p_t$$

Substitutingthegivenvalues, weget,

$$1.4x10^4\ pa=\frac{4\xi^2}{1-\xi^2}.1.5x10^5 pa$$

or $$\frac{1-\xi^2}{\xi^2}=\frac{4\ x\ 1.5x10^5}{1.4x10^4}$$

or $\xi^2=0.023$

$\xi=0.15$

ThefractionofN_2O_4dissociatedisthuscalculated tobe0.15.

Example4

Considerthereaction,

$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)}$

whereinitially1molofCOand2molofH_2 weremixedtogether.Derivean expressionfortheequilibriumconstant,K_p,intermsoftheextentofthereaction , ξand thetotalpressure, P_t.

Solution

Iftheextent,ofthereactionatequilibriumisrepresentedbyξthenwehave,

$CO_{(g)} + 2H_{2(g)} CH_3OH(g)$

$\rightleftharpoons$

Components present	$CO_{(g)}$	$2H_{2(g)}$	$CH_3OH(g)$
Molesat Equilibrium	1–ξ	2–2ξ	ξ
Molefraction atequilibrium	$\frac{1-\xi}{3-2\xi}$	$\frac{2-2\xi}{3-2\xi}$	$\frac{\xi}{3-2\xi}$

UsingEq.4.41, $K_P = (x_{CH_3OH}.p_t).(x_{CO}.p_t)^{-1}.(x_{H_2}.p_t)^{-2}$

i.e.,$K_p = \frac{(x_{CH_3OH} \cdot p_t)}{(x_{CO} \cdot p_t)(x_{H_2} . p_t)^{-2}}$

Hence, $K_p = \left(\frac{\frac{\xi}{3-2\xi} . \ p_t}{(\frac{1-\xi}{3-2\xi} . \ p_t)(\frac{2-2\xi}{3-2\xi} . p_t)^2} \right)$

$= \left(\frac{(3-2\xi)^2 \xi}{(1-\xi)(2-2\xi . p_t)^2} \right)$

YoushouldbeabletodothefollowingSAQ,ifyouhaveunderstoodtheabove examples.

SELF-ASSESSMENTEXERCISE3

Expressequilibriumconstant$K_p$forthereaction,

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

intermsof(i)partialpressuresand (ii)molefractionsofthegaseousspecies.

3.2.3 EquilibriumConstantExpressioninTerms ofConcentration

We knowthatforanidealgas

$p_i = \frac{n_i RT}{V} = c_i RT$

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.

$K_p = (c_L RT)^l (c_M RT)^m \ldots (c_A RT)^{-a} (c_B RT)^{-b}$

$$K_p = \frac{(c_L RT)^l (c_M RT)^m \ldots}{(c_A RT)^a (c_B RT)^b \ldots} \qquad \ldots(4.42)$$

$$\text{i.e.} \quad K_p = \textstyle\prod_i (c_i RT)^{v_i} \qquad \ldots (4.43)$$

Where v_i represents the stoichiometric coefficient (along with proper sign) in the chemical equation.,
Eq.4.42 can be written as,

$$K_p = \frac{(c_L)^l (c_M)^m \ldots}{(c_A)^a (c_B)^b \ldots} (RT)^{(l+m+\cdots)-(a+b+\cdots)}$$

i.e., $K_p = K_c (RT)^{\Sigma v_i}$
…(4.44)

where K_c is defined by,

$$K_c = \frac{(c_L)^l (c_M)^m \ldots}{(c_A)^a (c_B)^b \ldots} = \frac{multiplication \ \ of \ (c_i)^{v_i} terms \ of \ the \ products}{multiplication \ \ of \ (c_i)^{v_i} terms \ of \ the \ reactants} \qquad \ldots (4.45)$$

i.e., $K_p = \Pi (c_i)^{v_i}$
…(4.46)

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 4.37 and 4.45 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

Example5

Calculate the equilibriumconcentrationsofallthespeciesat613Kforthe reaction,

$PCl_5(g)$ $PCl_3(g)+Cl_2(g)$

iftheinitialconcentrationsofthe threegasesis0.15MeachandK$_C$=0.800Mat 613K.Thevolumeofthevessel is1dm^3.

Solution

Supposethat*x*molofPC1$_3$ hasdecomposedatequilibrium.Sincevolumeis1 dm^3,theconcentrationexpressedinmolarityisequaltothenumberofmolesof a particularsubstance.

	PCl_5	PCl_3	$C1_2$
Equilibriumconcentration/M	$0.15–x$	$0.15+x$	$0.15+x$

UsingEq.4.45, weget

$$K_c = \frac{c_{PCl_3}.c_{Cl_2}}{c_{PCl_5}}$$

Substituting the given values, we get,

$$0.008\ M= \frac{(0.15+x).(0.15+x)}{(0.15-x)}$$

$$0.008\ (0.15-x) = (0.15+x)^2$$

$$x^2+1.1x-0.0975 =0$$

Usingtheprincipleofsolutionofstandardquadraticequation,weget

x =0.082Mor or–1.183M

Wetake$x$=0.082M,since secondrootof thequadraticequationgivestheconcentrationsofPCl$_3$andCl$_3$as (0.15M–1.183M=–1.033)Mwhichisimpossible. Hence,theequilibrium concentration:

$[PCl_5]$=(0.15–0.082)M=0.068M

and $[PCl_3]=[Cl_2]$=0.15+0.082=0.323M

Wecanverify theanswerbysubstitutingthevaluesforconcentrationsin evaluatingK$_C$.

The unit,moldm^{-3}, isfordenotingmolarityandisrepresentedbytheletterM. Note that concentrationin

$$\text{Molarity}= \frac{\text{Numberofmoles}}{\text{Volume indm}^3}$$

TheunitofK,asperEq.4.45is given by$(M)^{\Sigma v}$

InExample 4.Σv_i= 1+ 1–1= 1

Hence,theunitofK$_c$inthisexample isM.

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, $[PCl_5]$ is to be read as: Concentration of PCl_5

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?

3.3 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,

$\Delta_r G^o = -RT\ln K_p$

or $InK_p = \frac{-\Delta_r G^0}{RT}$

Differentiating this expression with respect to temperature,

$$\frac{dIn\,K_p}{dT} = \frac{d(-\Delta_r G^0)}{RTdT} \qquad \ldots(4.47)$$

Using Eq. 3.45 we can write:

$$\left(\left(\frac{d}{dT}\right)\left(\frac{\Delta_r G^0}{T}\right)\right) = \frac{-\Delta_r H^0}{T^2} \qquad \ldots(4.48)$$

Combining Eqs. 4.47 and 4.48, we get,

$$\frac{dInK_p}{dT} = \frac{\Delta_r H^0}{RT^2} \qquad \dots (4.49)$$

Eq.4.49tellsusthatequilibriumconstantvarieswithtemperatureand dependson thestandardenthalpyofthereaction.

Assuming that thestandardenthalpy change($\Delta_r H^0$)ofthereactionremains constantoverasmall rangeoftemperature,theaboveequationonintegration betweenlimitsK_{p1},$K_{p2}$and T_1,T_2gives,

$$\int_{K_{p1}}^{K_{p2}} dInK_p = \int_{T_1}^{T_2} \frac{\Delta_r H^0}{RT^2} dT$$

$$In\frac{K_{p_2}}{K_{p_1}} = \frac{\Delta_r H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or $2.303log\frac{K_{p2}}{K_{p1}} = \frac{\Delta_r H^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$

$$log\frac{K_{p2}}{K_{p1}} = \frac{\Delta_r H^0}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad \dots (4.50)$$

AccordingtoEq.4.44.thisisapplicable forideal gases,

$K_p = Kc\,(RT)^{\Sigma v}$

UsingthisequationandEq.4.50,it ispossible relate Kvaluestotherespective temperaturesas:

$$log\frac{K_2}{K_1} = \frac{\Delta_r U^0}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \qquad \dots (4.51)$$

whereK_1 andK_2 aretheequilibriumconstants(intermsofconcentrations)attemperaturesT_1 andT_2 and$\Delta_r U^o$ isthe standardinternalenergychangeofthe reaction.Since reactionsaregenerallycarriedoutatconstantpressure,this equationisofgreaterimportance forus.Eq.4.51is knownas van't Huffsisochore

Eq.4.50correlatestheequilibriumconstantvaluesK_{P1} andK_{P2} (expressedin termsof partialpressures)attwodifferenttemperaturesT_1andT_2tothestandard enthalpyofreaction.

Example6
The equilibriumconstantforthereaction

$\rightleftharpoons H_2(g)+S(s) \quad H_2S(g)$

is18.5at925Kand9.25at1000K,respectively.Calculatethestandardenthalpy ofthereaction.Alsocalculate $\Delta_r G°$and$\Delta_r S°$at925K.

Solution
SubstitutingthegivenvaluesinEq.4.50, weget,

$$log\frac{K_{1000}}{K_{925}} = \frac{\Delta_r H^0}{2.303x8.314}\left(\frac{1000-925}{925x1000}\right)$$

$$log\frac{9.25}{18.5} = \frac{\Delta_r H^0}{19.147}\left(\frac{75}{925000}\right)$$

Hence, $\Delta_r H^0 = -71.1\ kJmol^{-1}$

Using Eq. 4.36, $\Delta_r G^O$=-RTInK_p = -2.303 RT log K_p

$\Delta_r G^O$= - *2.303 x 8.314 x 925 x log18.5 = -22.4 kJmol*$^{-1}$

Rearranging Eq. 3.15, $\Delta_r S^O = \frac{\Delta_r H^0 - \Delta_r G^0}{T} = \frac{-71100+22400}{925} = -52.65\,JK^{-1}$

SELF-ASSESSMENTEXERCISE

i. Explain how the mixing of reactants and products affects the position of chemical equilibrium.
ii. Account for Le Chatelier's principle in terms of thermodynamic quantities.

4.0 CONCLUSION

The principles of thermodynamics determine the state of chemical equilibrium for any reaction. The equilibrium constant expression of elementary chemistry is equal to a constant at constant temperature when it is expressed in terms of activities. In addition, the principle of Le Châtelier can predict how a chemical system at equilibrium responds to changes in temperature, pressure, or amounts of substances.

5.0 SUMMARY

- For a chemical reaction at equilibrium at constant temperature and pressure, we say
$$\left(\frac{dG}{d\xi}\right)_{T,p,eq} = \sum_i \mu_i v_i = \Delta_r G_{T,p} = 0$$
- The equilibrium constant is related to the standard-state Gibbs energy change of the reaction: $K = e^{-\frac{\Delta G}{RT}}$
- The Gibbs–Helmholtz equation for the temperature dependence of an equilibrium constant is: $\frac{dIn\,K_p}{dT} = \frac{\Delta_r H^0}{RT^2}$

6.0 TUTOR-MARKED ASSIGNMENT

7.0 REFERENCES/FURTHERREADING

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UNIT 3 THERMODYNAMIC QUANTITIES FROM EMF VALUES

CONTENTS

1.0 INTRODUCTION

The thermodynamic relations between the electromotive force (emf) and the various colligative properties are discussed in this unit.

2.0OBJECTIVES

Bytheend ofthisunit,you shouldbeable to;

- Statethecolligativeproperties
- Definephaserule and component
- Explainthetermconfiguration

3.0 MAIN CONTENT

3.1 ThermodynamicQuantitiesfromEMFValues

WeshallnowstudyhowΔH,ΔS,andΔGforthecellreactioncanbecalculated usingmodifiedformsofNernstequationgivestherelationship between$\Delta G$and$E$values. Hence,ifE_{cell} valueisknown,ΔG,forthecellreactioncanbecalculated.

$-\Delta G = nFE$ … (4.52)

where n is the number of equivalents and F is the quantity of electricity, known as the Faraday constant, E is the electromotive force (EMF) in volt of the cell.

Similarly, thechangeinentropyaccompanyingthecell-reactioncanalsobe determined.InModule3,wederivedEq.3.42whichrelatesthetemperaturecoefficientofthefree energy changeatconstantpressure, tothedecreaseinentropy(-ΔS) i.e.

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S \qquad \ldots (4.53)$$

BydifferentiatingΔGandE_{cell}appearinginEq.4.52withrespecttotemperature atconstantpressurewe canwrite

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -nF\left[\frac{\partial E}{\partial T}\right]_p \qquad \ldots (4.54)$$

where $n$and$F$areconstant values.
ComparingEqs.3.42and 4.54,weget.

$$\Delta S = nF\left[\frac{\partial E}{\partial T}\right]_p \qquad \ldots (4.55)$$

$$\Delta S = nF\left[\frac{E_2-E_1}{T_2-T_1}\right]_p \qquad \ldots (4.56)$$

IfE_2andE_1(i.e. the emfsofthecell)attemperaturesT_2andT_1areknown,ΔS canbe calculated. $\left[\frac{\partial E}{\partial T}\right]_p$isknownasthetemperaturecoefficientofemfat constantpressure.

Again from Eq.3.15,

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

or$\Delta H=\Delta G+T\Delta S$ … (4.57)

Substituting Eqs.4.52 and 4.55 into4.57

$$\Delta H=nFE+TnF\left[\frac{\partial E}{\partial T}\right]_p \qquad \ldots (4.58)$$

Henceif$E$,$T$and $\left[\frac{\partial E}{\partial T}\right]_p$areknown,thentheenthalpychange accompanyingthecellreactioncanbecalculated.

InthelightofabovediscussionanswerthefollowingSAQs.

SELF-ASSESSMENT EXERCISE 6

Write down the equation relating ΔH^o, ΔS^o and ΔG^o to ΔE^o and $\left[\frac{\partial E^0}{\partial T}\right]_p$ being the standard state of each parameter.

Application of Chemical Potential to Phase Equilibrium

Here we consider the particles in an unreactive mixture, such as binary mixture.

3.2 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 depend 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.

3.2.1 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

$P_T = X_A P_A^o + X_B P_B^o$ …(4.59)

Where P_A^o and P_B^o 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

$P_T = X_A P_A^o$ … (4.60)

Therefore, the depression or decrease in the vapour pressure of the liquid is □P $= P_A^o - P_T =$

$P_A^o - X_A P_A^o =$

$P_A^o(1 - X_A)$

But $(1 - X_A) = X_B$

Therefore, □P $= X_B P_A^o$ ...(4.61)

At a particular temperature, P_A^o is a constant and the change in the vapour pressure is thus proportional to the mole fraction of the solute, i.e. □P□α□X_B.

Since

$$X_B = \frac{n_B}{n_A + n_B}$$

Eq.(4.61) becomes

$$\Delta P = P_A\left[\frac{n_B}{n_A + n_B}\right] \quad \ldots (4.62)$$

Where $n_i = \frac{mass}{molar\ \ mass}$

Example 7:

Calculate the molecular mass of 9.21g non-volatile organic compound, dissolved in 50g of pure water at 25^{o}C, which depresses the vapour pressure of the water from 3.16×10^3 to 3.10×10^3 Nm^{-2}.

Solution

□P $= 3.16 \times 10^3 - 3.10 \times 10^3\ Nm^{-2} = 0.06 \times 10^3\ Nm^{-2}$

$P^o = 3.16 \times 10^3\ Nm^{-2}$

Molecular weight of $H_2O = 2 + 16 = 18$ g/mol

Mole fraction of solute X_B is

$$X_B = \frac{\frac{9.21}{M_W}}{\frac{50}{18} + \frac{9.21}{M_W}}$$

Where M_W is the molecular weight of solute

Therefore

$$\Delta P = P_A X_B$$

$$0.06x10^3 = 3.16x10^3 x\left[\frac{9.21}{2.78M_W + 9.21}\right]$$

$$M_W = 171.3\ g/mol$$

3.2.2 ElevationofBoilingPoints

Presenceof anon-volatilesoluteinavolatileliquidcausesadecrease onthe vapourpressureofthesolvent.Thatisthesolution willrequirealotmoreheat, comparedtothepureliquid,toraiseitsvapourpressure tobeequaltotheexternal pressure.Theresultofthisisthatthesolutionwillboilatahighertemperature thantheoriginalsolvent,andthemoreconcentrated thesolution,thehigherthe boilingpoint,asshowninfigure4.2.

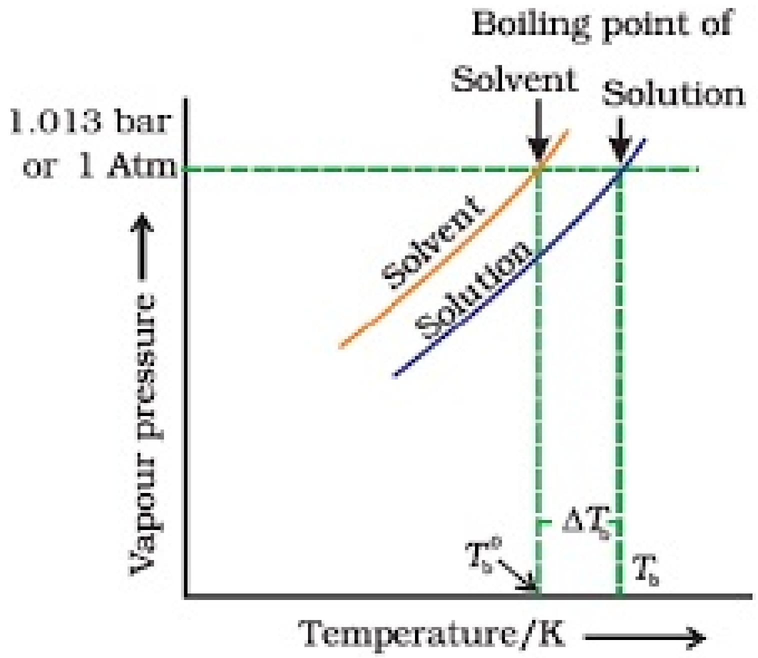

Figure 4.2: variationofvapour pressure with theboilingpointsofthepuresolventandsolutionscontaining non-volatile solute.

From the above diagram, the boiling point of the pure solvent and the solution at the same external pressure (1 atmosphere) are T_b^0 and T_b respectively whose difference amount to ΔT_b. It is evident from this curve that □$T_b$isproportionalto□P and hence;

$$\frac{\Delta T_b}{\Delta P} = constant \qquad \dots (4.63)$$

Butithasbeenshownthat□Pisproportional tothemolefractionofthesolute.

Therefore, □T_b□X_B

and □T_b=KX_B … (4.64)

whereK istheproportionalityconstant.

Again, $X_B = \frac{n_B}{n_A + n_B} \approx \frac{n_B}{n_A}$ (since the solution is very dilute)

Where n_B is the number of moles of solute and n_A is the number of moles of the solvent.

$$\frac{n_B}{n_A} = \frac{W_B/M_B}{W_A/M_A} \qquad \ldots (4.65)$$

Where W and M represent the weights and molecular weights of the respective constituents.

Hence, $\Delta T_b = K \cdot \frac{W_B/M_B}{W_A/M_A}$

$$\Delta T_b = K M_A \cdot \frac{W_B}{M_B} \cdot \frac{1}{W_A} \qquad \ldots (4.66)$$

Since M_A is constant for any solvent, both K and M_A are merged together to give a single constant, K_b.

Hence, $\Delta T_b = k_b \cdot \frac{W_B}{M_B} \cdot \frac{1}{W_A}$ … (4.68)

$k_b$isknownastheebullioscopicconstantor known molalboilingpoint elevationconstant when one mole of solute is dissolved in 1000 grams of solvent. In terms of molality, Eq. 4.68 can be written as

$$\Delta T_b = K_b \cdot \frac{W_B}{M_B} \cdot \frac{1}{W_A} x\ 1000 \qquad \ldots (4.69)$$

Where $K_b = \frac{k_B}{1000}$

The quantity $\frac{W_B}{M_B} \cdot \frac{1}{W_A} x\ 1000$ in Eq. 4.69 is known as the molality (*m*) of the solution.

Hence, $\Delta T = K_b m$ … (4.70)

Boilingpointelevationmeasurementcanbeusedtodetermine themolecular weightofanon-volatilesoluteifasolventthatshows ameasurableincreasein boilingpointisused.

Example 8:

0.25gcompoundofanunknownsubstanceisdissolvedin25gof asolvent whileK$_b$is2.9 Kmolal^{-1}andboilsat0.14^{O}C higher thanthepuresolvent.Whatis theformula massofthesolute?

Solution:

$$\Delta T_b = K_b \cdot \frac{W_B}{M_B} \cdot \frac{1}{W_A} x\ 1000$$

$$M_B = \frac{K_b x W_B x 1000}{\Delta T_b\ x\ W_A} = \frac{2.9\ x\ 0.25\ x\ 1000}{0.14\ x\ 25}$$

$$= 207.14\ g/mol$$

3.2.3 DepressionofFreezing Point

Whenacoolingbathisrequiredfortemperaturebelowthefreezingpoint ofice,asalt-icemixtureisused,thesaltdepressesthefreezingpointof water. This isanexampleofageneralphenomenoninwhichaddednon-volatilesolutes depressthefreezingpointofsolventsonwhichtheyarecontained. Thegreaterthe quantityofthesoluteaddedthegreaterthedepression.

Consideringthevapourpressure vs temperature curveforapureliquidandsolutions ofanon-volatilesoluteintheliquidsasshownin figure4.3 below.

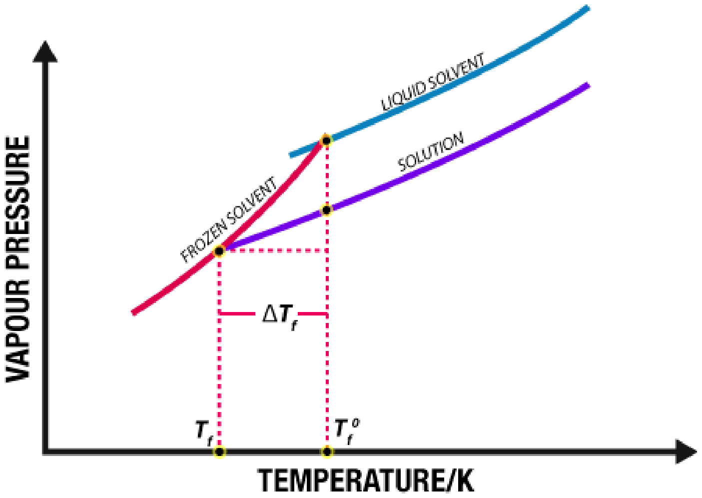

Figure 4.3:variationofvapour pressure with thefreezingpointsofthepuresolventandsolutionscontaining non-volatile solute.

From fig. 4.3, it is observed that the freezing point of a solution (T_f) is lower than that of pure solvent (T_f^0). This is again a direct consequence of the vapour pressure depression of the pure solvent by the dissolved solute. Hence, the freezing point depression of the solution is given as;

$$\Delta T_f = T_f^0 - T_f$$

Making the same assumption as for the boiling point elevation, we say

$$\frac{\Delta T_f}{\Delta P} = constant$$

$$Thus;\ \Delta T_f \ = \ K_f \ .\frac{W_B}{M_B}.\frac{1}{W_A} x\ 1000 \ldots\ (4.71)$$

Where$K_f$isknownasthemolalfreezingpointdepressionconstantorcryoscopic constant.Itisnumericallyequal tothefreezingpointdepression whenthe concentration (m) isonemolal.

Hence, $\Delta T_f = K_f m$ … (4.72)

Comparatively K_f values are much bigger than K_b values.

3.2.4 OsmoticPressure

Theprocess ofdiffusionof solventmoleculesfromahigh concentrationregionto alowerconcentrationthroughamembraneisknownasosmosis.Thepressure thatmustbeappliedinordertopreventosmosisisreferredtoasosmoticpressure. Experimental workrevealsthattheosmoticpressureexertedbyasolutionis proportionaltotheconcentrationof solute(C)andabsolutetemperature(T).Then osmotic pressure, Π, isproportionatetoCTand hence

$Π = KCT$ … (4.72)

Theconstantofproportionalityisofthesamemagnitudeasthegasconstant.

Hence Π =CRT … (4.73)

IfΠismeasuredinNm^{-2},theconcentration unithastobemolem^{-3}.In principle,osmosispressuremeasurementscanbeusedtodeterminethemolecular weight(w)ofagivensolute, since C canbewirttenas

$$C = \frac{n}{V} = \frac{W}{M.V} \quad \dots (4.74)$$

Where n is the number of mole, M is molecular weight of solvent,Wistheweightofthesolutedissolvedinvolume$V$ of solvent.Theadvantageofthe methodisthatthepresureexertedbyvery dilutesolutionsarerelativelylargeand canthereforebemeasuredfairlyaccurately.

Example 9:
Whatisthemolecularweightofa15.0 gofanon-volatilecompounddissolvedin 100 cm^{3}ofwater whichextendsonosmoticpressureof2.06x10^{6}Nm^{-2}at298 K.

Solution

$$C = \frac{n}{V} = \frac{W}{M.V} = \frac{15.0\,g}{M\,gmol^{-1}x\,0.0001\,m^3} = \frac{1.5x10^5}{M} molm^{-3}$$

Π= CRT

$$2.06x10^6 = \frac{1.5x10^5}{M} x\ 8.314\ x\ 298$$

M =180 gmol^{-1}

3.3ColligativePropertiesofElectrolytes

Colligativepropertiesofsolutionsof electrolytesareobservedtobegreaterthan thoseofsolutionsofnon-electrolytesofthesamemolal concentration.For instance, whereasamolalsolutionofurea depressesthefreezingpointofwater by about1.86^{O}C, onemolalsolutionsofhydrochloricacid,nitricacid,ammonium chlorideandsulphuricaciddepressesthefreezingpointofwaterby3.94,3.58, 3.33and 4.04^{O}Crespectively.

Toexplainthesevalues,Van'tHoffsuggested thatthey areobtainedby multiplying 1.86bysomecorrectingfactorreferredtoastheVan'tHofffactor,*i*. Thefactor,*i*, istheratiooftheobservedandpredictedcolligativeproperty ofthe electrolyte.

$$i = \frac{\Delta T_b}{(\Delta T_b)_0} = \frac{\Delta T_f}{(\Delta T_f)_0} = \frac{\pi}{(\pi)_0} = \frac{\Delta P}{(\Delta P)_0} \qquad \dots (4.75)$$

Where $(\Delta T_b)_0, (\Delta T_f)_0,\ (\pi)_0, (\Delta P)_0$ are the boiling point elevation, freezing point depression, osmotic pressure and vapour pressure depression respectively for solutions of non-electrolytes and similar terms used in the numerator are for solutions of electrolytes having the same concentration.

3.3.1 PhaseEquilibria

Whenasolidsuchasice,changestoliquid,solid,isinequilibriumwithliquid,at any givenmomentduringthischangeofstate.Atany givenmomentduringthe evaporation,liquidisinequilibriumwithvapour.Thesechangesofstatefrom solidtoliquidphase,andfromliquidtovapourphase,maybe expressedas

$\rightleftharpoons$solid $\rightleftharpoons$Liquid vapor

Theequilibriumconditionsforsuchchanges,andforotherchangesofstatesuch as dissolving saltinwater,maybestudiedusingfundamentalprinciplesof thermodynamics.

3.3.2 Phase

Achangefromonephysicalstatetoanotheriscalledaphasechange.Aphase maybedefinedasanyhomogeneousmacroscopicportionofasystem.Asystem issaidtobehomogeneous,ortoconsistofonephaseifitisuniform throughout, bothinchemicalaswellasphysical composition. Sinceall gasesarecompletely miscible, theywillalwaysexistinahomogenousstate,thatisinasinglephase e.g. asolutionofsodiumchloride inwater.

Asystemwhichismadeupofmorethanonephysical distinguishablephase,is saidtobeheterogonous e.g.water,whichhasicecubes,onitisahomogenous systemmadeup oftwodistinctphases.

3.3.4 Components

Thecomposition ofthesystem isdescribedbyusingthesmallestnumberof chemicallydistinctandindependently variableconstituentswhichtogethermake upthevariousphasesof thesystem.Thechosenconstituents areknownasthe componentsofthesystem.Inthesystemice □water□watervapour,the composition of allthephasescanbeexpressedintermsofwater.Wateristhus describedasaone-componentsystem.

ConsiderthesysteminwhichsolidCaCO$_3$,solidCaOandgaseousCO$_2$ arein equilibrium.Thisrepresentsathreephasesystemconstitutingoftwosolidand onegaseous phases.Thenumberofcomponents,however,istwoandnotthree since eachofthethree substancesisnotindependent.

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

Henceforthecalciumcarbonatesystem,thenumberofcomponentsis

C=3–1=2

3.3.5 DegreesofFreedom

Oneveryimportantaspectof phaseequilibriumisthattheequilibriumstateis independent of theactual amountsof thephasespresentprovidedvariationsin surfaceareaareignored.Thesmallestnumber of independentintensive thermodynamicvariablesthatmustbespecifiedinordertodescribecompletely thestateofasystemisknownasthenumberofdegreeoffreedomorthevariance ofthesystem.Itisdenotedbythesymbol ‘*f*’.

Forexample,10 dm^{3}ofpureCO$_2$gas maybecompletely describedbyspecifyinganytwoof thevariables;pressure, temperature anddensity.Ifanytwoofthesevariables areknown,the thirdcanbe calculatedsuchasystemthereforehastwodegreesoffreedom,orisbivariant. Thewatervapoursystem willhaveonlyonedegreeoffreedombecause of any giventemperature,thepressureofvapourinequilibrium withliquidisfixed,and therefore onlyonevariableneedstobespecifiedtodeterminethestateofthe system.

3.4 PhaseRule

Thisrulewasproposed byWillardGibbs(1875and1876).Itprovidesageneral relationshipbetweenthenumberof phases,thenumberof components,andthe degreesoffreedominasystemat equilibrium.Itstatesthatforasystemat equilibriumhaving$c$ components,and $p$phases, andinwhichequilibrium isonly affectedbythevariables,pressure,temperature andconcentration,thedegreeof freedom, f, aregivenbytheequation:
$f=c–p+2$

Thequantity2arisesfromtheintensivevariables,pressureandtemperature. Notethatthephaserule onlyappliestosystemsatequilibrium.

Example 10:
Findthenumberofdegrees offreedomforaclosedonecomponentsystem,fora fixedamountofmaterial,when.
a. onlyonephaseexist
b. twophasesareatequilibrium
Solution:

$f=c–p+2$

a. p=1therefore
f=1–1+2=(bivariant)

b. p=2therefore
f=1–2+2=1(univariant)

3.4.1 One-ComponentSystems

In one-componentsystem,thesmallestnumberofindependently variable constituent substances requiredtoformthephaseis one. Examples ofone-component systemsarewater,carbon, chloride, sulphurandbismuth.
Therelationshipbetweenthevapourpressureandtemperatureofasubstancein thesolid,liquidandvapour(gaseous)phasescanberepresentedbyaphase diagram.

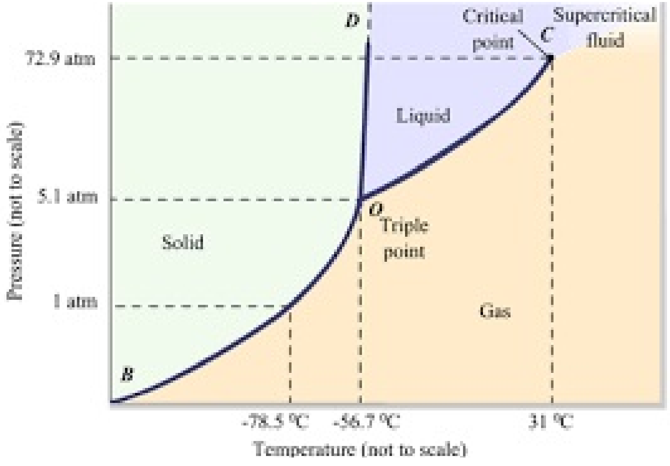

Figure4.4: PhasediagramforCO_2system

O isthetriple point,where solid,liquidand vapourareinequilibrium.
At -78.5^0C (195 K) (sublimation temperature)and1 atmpressure,a givenquantity ofsolidCO_2wouldchangetothevapourwithoutrisein temperature.CO_2canthereforenotbeliquefiedatordinary atmospherepressure. Theminimumpressure atwhichCO_2willexistinliquidformis5.1 atm. Thiscorrespondstopart ofthe triplepoint,wheresolidCO_2willchangetoliquid (melt)ataconstanttemperatureof -56.7^0C (216.6 K).

Water system

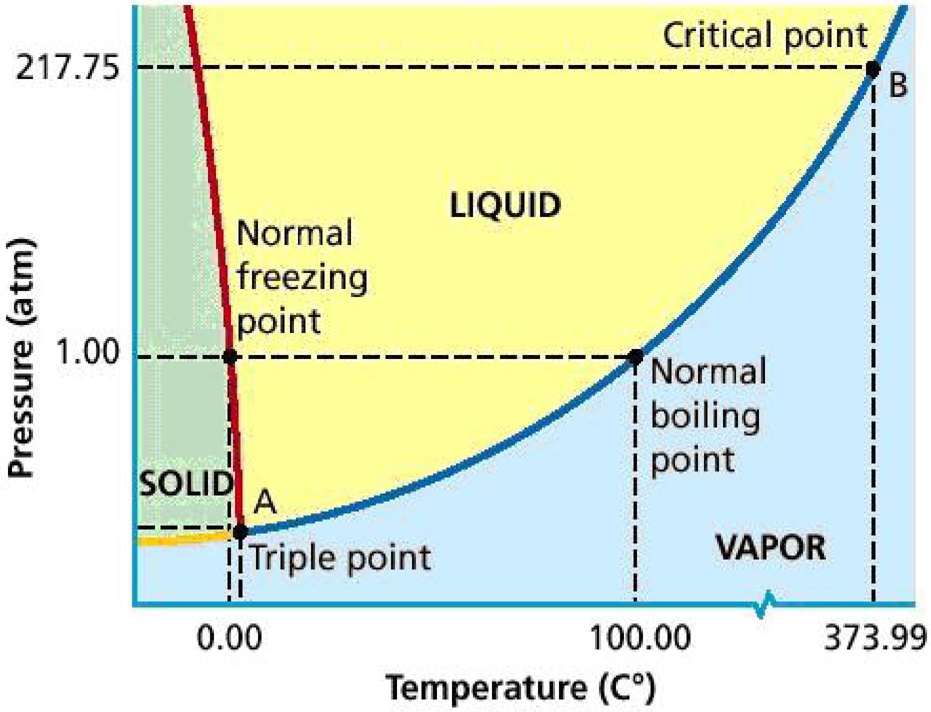

Figure4.5: Phasediagramfor H_2Osystem

Thephasediagramof waterisshowninfigure4.5.Itwillbeseenfromthe diagramthatatany giventemperature.Thereisonlyonepressure atwhichliquid water and watervapourwillbeinequilibrium.Thesystemisthereforeunivariant, with onedegreeoffreedom.Bisthecriticalpoint.Below1 atmicewillformdirectlytovapour.Aisthe triplepoint.Thecurvebelow the triple pointrepresents themeasurableregion,alongwhichwater may becooledbelowitsfreezingpointwithoutitssolidifying.

SulphurSystem

Aone-componentsystemcould have morethanonetriplepoint ifthesolid expressinmorethan onecrystalline,orallotropicform.Forexample,sulphurcan existasrhombic ormonoclinicsulphur,underdifferentconditions. The transformationsinvolvedareknown assolid-solidtransformations. Thesulphur phasediagramisasshowninfigure4.6.Atlowtemperatures sulphur existsin therhombic form. Point 1isthetriplepointwhererhombicsulphur,monoclinic sulphur,and sulphurvapourexistinequilibrium.

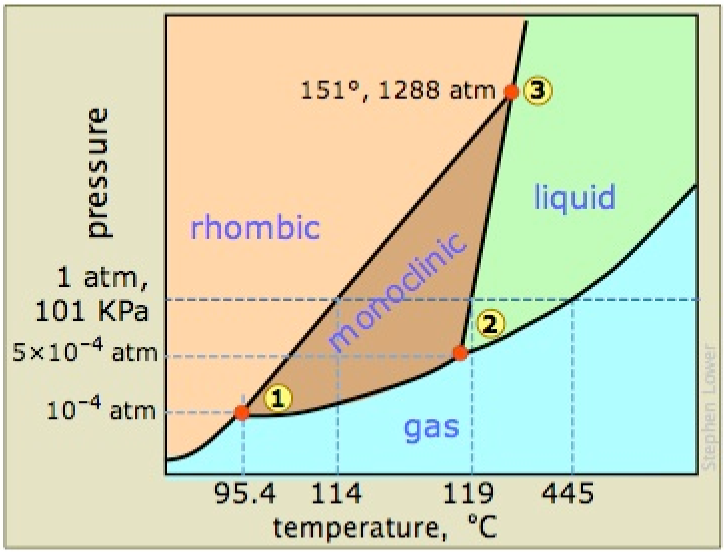

Figure4.6: Phasediagramforsulphursystem.

Curve below this point 1 isthusthevapourpressurecurveforrhombicsulphur. Curve between point 1 and 2represents the vapourpressure curveformonoclinicsulphur.Along this curve,allrhombicsulphurchangestomonoclinic sulphur. The point2isthetriplepointformonoclinicsulphur,liquidandsulphur vapour.Point 3represents athirdtriplepoint,whererhombic,monoclinic andsulphur vapour, allexistinequilibrium.

Itmustbepointedouthere thatatpoint1where rhombic,monoclinicandvapour sulphur exists,wehavethreephases.Butthesystemismadeupof onlyone component. Fromthephaserule,thenumberofdegreeoffreedomisgivenas $f=c–p+2=1–3+2=0$i.e.Point 1isaninvariantpoint.

3.4.2 TwoComponentsSystem

In atwocomponentsystem,thesmallestnumberofindependentlyvariable constituentsubstancesrequiredtoformthephaseistwo.Examplesofcompounds thatcanbeusedtoshowsuchasystemarethosethatcanformalloysorform solidsolutions.Forexample,copperandnickel,camphor andnaphthalene, and bismuth andcadmium. Thetypeofdiagrams,hereareforbinarysystem, consisting ofliquidsolidphases andare thereforereferredtoascondensed system.In this,oneofthevariables,pressure,iskeptconstant.

Hencethe phase rule becomes$f=c–p+1$or$f=3–p$
Sincepressureiskeptconstantthe onlyintensivevariables remainingare thoseof concentration andtemperature.Aphasediagramforaconsideredbinarysystem willconsistof aplotof temperatureversusconcentration.Theconcentrationis mostfrequentlyexpressedasmolefractionorweight percent,asshownin figure 4.7forBismuth–cadmiumsystem.

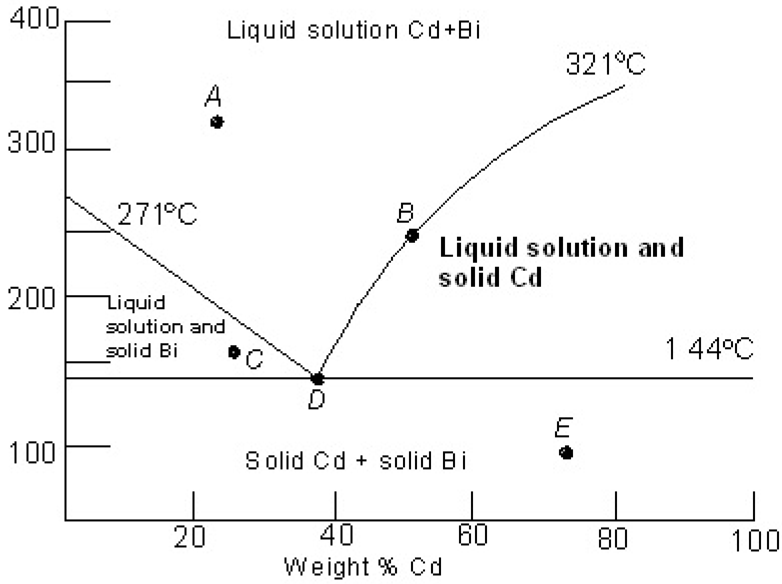

Figure4.7: PhasediagramfortheBi-Cdsystem

Thedegreeoffreedomorvarianceatthevariousareason thephasediagramcan becalculated.Intheareaabove,ABC,thereisoneliquidphaseand
$f=2–1+1 =2$(bivarant).

BelowABandBCbutabove140^{O}C,therearetwophases(liquid and solid) and
$f=2–2+1=$ 1(univariant).

Attheeutecticpoint Dwhere therearethreephases–solidbismuth,solid cadmiumandliquid solutioncontaining 40% cadmium.Heref=2–3+1 whichis 0,and soitisthenon-variant.Thereisonlyonetemperatureand one composition ofsolutionatwhichthese threephasescanexist together atequilibriumatagiven constantpressure.

3.5StatisticalThermodynamics

Thisisbasedontheprinciplethatthermodynamics observablesareaveragesof molecularproperties,anditsetsabout calculatingthese averages.

3.5.1 MolecularEnergyLevelsandtheBoltzmannDistribution

Considerasystem composedof$N$particles.Althoughthetotalenergycanbe specified,it isnotpossibletodefine abouthowthatenergyisdistributed. Collisiontakeplaceandresultintheceaselessredistribution of energynotonly betweentheparticlesbutalsoamongtheirdifferentmodeofmotion. Thus,onaveragetheremaybe$n_i$particlesinastateofenergyE_i,andinan equilibriumsystem,thisaveragepopulation remainconstanteven thoughthere maybesmallmomentaryfluctuationarounditandtheidentitiesoftheparticles onthatstatemaychangeateverycollision.

3.5.2 ConfigurationandWeights

AnyindividualparticlemayexistinstateswithenergiesE_o,E_1,E_2,E_3,…etc. with E_o=0andallotherenergiesarerelatedtoit.Inthesampleasawhole,there willbe$n_o$particlesinthestatewithenergyE_o,$n_1$withE_1andsoon.The specification ofthesetofpopulationn_o,n_1,n_2,etc.isreferredtoasthe configurationofthesystem.

Theinstantaneousconfiguration ofthesystemfluctuateswithtimebecausethe instantaneouspopulationschange.Forexample,onemightben_o=N,n_1,n_o,n_2 = 0or(N,O,O),correspondingtoeverymoleculesbeinginitsgroundstate.

Anothermightbe(N–2,2,O)inwhichtwoparticlesareinahigherstate.This canbeachievedin½N(N-1)differentways.Ifthesystem werefreetofluctuate between theconfigurations, (asaresultof collusion),itwould almost,alwaysbe foundinthesecond.
AgeneralconfigurationcanbeachievedinWdifferentways,asgivenbelow

$$W = \frac{N!}{n_0!n_1!n_2!\ldots} \qquad \ldots (4.76)$$

where$W$is calledtheweightoftheconfigurationsand 0!=1
Inlookingfortheconfigurationwiththegreatweight,wehavetoensurethatit alsosatisfiesthetotalenergycriterion.

$$E\square\square n_i e_i \qquad \ldots (4.77) i$$

andisalsosubjecttothetotalnumbercriterion

E□□n_i … (4.78)
i

whereEisthetotalenergyofthesystem.

3.5.3 MostProbableConfiguration

ThemaximumvalueW*ofWforasetofnumbers
$n_0{}^*$,$n_1{}^*$,$n_2{}^*$canbearrivedat, whenℓnW isamaximum. Whenaconfigurationchanges,sothat$n_i$changeston_i+d$n_i$andℓnW changes to
ℓnW+d (ℓn W)where

$$d(InW) = \sum_i \frac{\partial InW}{\partial n_i} dn_i \qquad \ldots (4.79)$$

Atamaximum,thechangesd(ℓnW)vanishes,butthepresenceofthetwo equationsinvolvingE and Nmeansthatwhen$n_i$changestheydososubjecttotheconstraints

□$E_i dn_i$□0and□dn_i□0
i

These constraints prevent solving Eq. 4.79 as it is because the occupation numbers are not all independent. The way to take care of the constraints into account was devised by Langrange and it is known as Langrange’s method of undetermined multipliers. This is done by multiplyingthetwoconstraintsbytheconstants -□and□respectivelyandtheaddedtotheEq. 4.79,gives

$$d(InW) = \sum_i \frac{\partial InW}{\partial n_i} dn_i + \alpha \sum_i dn_i - \beta \sum_i E_i dn_i \qquad \ldots (4.80)$$

Allthedn_iarenowtreatedasindependent.Thismeansthattheonlywayof satisfyingd(ℓnw)=0istorequirethatforeach$i$

$$\frac{\partial InW}{\partial n_i} + \alpha - \beta E_i = 0 \qquad \ldots (4.81)$$

Where$n_i$havetheirmostprobablevalues$n_i{}^*$.Inordertosolvethisequation,we use starling’sapproximationintheformgivenbelow
ℓnX!=XℓnX–X

Inintroductionoftheapproximationunittheexpression$W = \frac{N!}{n_0!n_1!n_2!\ldots}$,we have

$$InW = In\left(\frac{N!}{n_0!n_1!n_2!\ldots}\right) = In\ N! - In(n_0!\,n_1!\,n_2!\ldots)$$

=$InN!$□□$Inn_i!$□($N\ InN$□N)□□($n_i\ In\ n_i$□□n_i)

i i

$=N$□hN□□$n_i Inn_i$ … (4.82)
i

becausethesumofthe$n_i$isequal to$N$and$N$isaconstant,differentiationwith respectto$n_i$gives

$$\frac{\partial InW}{\partial n_i} = -\sum_i \frac{\partial n_i Inn_i}{\partial n_i} \quad \dots (4.83)$$

$$= -\sum_i \left[Inn_i\left(\frac{\partial n_i}{\partial n_i}\right) + n_i\left(\frac{\partial Inn_i}{\partial n_i}\right)\right]$$

$$= -[In\, n_i + 1] \quad \dots (4.84)$$

Since $In\ n_i$ in Eq. 4.84 is much larger than 1, i.e. $In\ n_i$>>1, therefore 1 can be neglected in Eq. 4.84 and on substituting Eq. 4.84 into 4.81, we have

$$-In\, n_i + \alpha - \beta E_i = 0 \quad \dots (4.85)$$

wheren_i=n_i^* (themostprobable population of the state of energy E_i)

Therefore, $n_i^* = e^{(\alpha - \beta E_i)} = e^{\alpha} e^{-\beta E_i}$ … (4.86)

Recall that $N = \sum_i n_i^* = \sum_i e^{\alpha} e^{-\beta E_i}$ … (4.87)

Dividing Eq. 4.86 by 4.87, we have

$$\frac{n_i^*}{N} = \frac{e^{\alpha} e^{-\beta E_i}}{e^{\alpha} \sum_i e^{-\beta E_i}}$$

$$\frac{n_i^*}{N} = \frac{e^{-\beta E_i}}{\sum_i e^{-\beta E_i}} = \frac{e^{-\beta E_i}}{q} \quad \dots (4.88)$$

This last equation is a central result in statistical mechanics. The denominator is referred to as the **partition function** q and is defined as

$$q = \sum_i e^{-\beta E_i}$$

The partition function represents the sum over all terms that describes the probability associated with the variable of interest, in this case E_i or the energy of level i.

Eq. 4.88 is the form of Boltzmann distribution. It quantitatively describes the probability of occupying a given energy for the dominant configuration of energy.

Where $\beta = \frac{1}{KT}$
q= partition function
K= Boltzmann constant
T= Thermodynamics temperature in Kelvin

SELF-ASSESSMENTEXERCISE

i. State and justify the thermodynamic criterion for solution-vapour equilibrium.
ii. The osmotic pressure of an aqueous solution at 288 K is 99.0 kPa. Calculate the freezing point of the solution.
iii. Describe the physical significance of partition function.

4.0 CONCLUSION

In this unit we have seen that thermodynamic relations can be used to obtain information about electrochemical systems. Phase diagrams can be used to show the phase equilibria of multicomponent systems and can be understood through the phase rule of Gibbs.

Two-component pressure–composition and temperature–composition phase diagrams give information about phases present at equilibrium. For a three-component system, a composition–composition diagram at constant temperature and pressure is plotted in an equilateral triangle.

The four principal colligative properties are freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure. In each case, the magnitude of the effect in a dilute solution is determined by the concentration of the solute but is independent of its identity.

A system of many molecules has both macroscopic and microscopic (molecular) properties. The state of the system involving macroscopic properties is called the macroscopic state or macrostate. Specification of this state for a system at equilibrium requires only a few variables. The microscopic state or microstate of a macroscopic system requires information about every atom or molecule in the system, a very large amount of information which can be well treated using statistical methods.

5.0 SUMMARY

Thechemicalpotentialof agivensubstanceisthechangeinfreeenergyofthe system thatresultsontheadditionofonemoleofthatparticularsubstanceata constanttemperatureand pressuretosuchalargequantityofthesystemthatthere isnoappreciablechangeintheoverallcomposition ofthesystem.Gibbs-Duhem equationshowsthatvariationinchemical potentialofoneofthecomponentsina binarysystemaffectsthevalueofthechemicalpotentialforanother component.

Inthismodule, wediscussed chemical equilibrium.Ageneralexpressionforthe equilibriumconstantwasderivedfrom thebasicprinciplesofthermodynamics. Differentformsofthegeneralexpression werethenutilizedinunderstandingthe equilibraofhomogeneousandheterogeneoussystem. Colligativepropertiesofsoluteandanintroduction tostatisticalthermodynamic werealso discussed

6.0 TUTOR-MARKED ASSIGNMENT

7.0 REFERENCES/FURTHERREADING

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