PREFACE

With its grounding in the “guiding pillars of Access, Equity, Equality, Affordability and Accountability,” the New Education Policy (NEP 2020) envisions flexible curricular structures and creative combinations for studies across disciplines. Accordingly, the UGC has revised the CBCS with a new Curriculum and Credit Framework for Undergraduate Programmes (CCFUP) to further empower the flexible choice based credit system with a multidisciplinary approach and multiple/ lateral entry-exit options. It is held that this entire exercise shall leverage the potential of higher education in three-fold ways – learner’s personal enlightenment; her/his constructive public engagement; productive social contribution. Cumulatively therefore, all academic endeavours taken up under the NEP 2020 framework are aimed at synergising individual attainments towards the enhancement of our national goals.

In this epochal moment of a paradigmatic transformation in the higher education scenario, the role of an Open University is crucial, not just in terms of improving the Gross Enrolment Ratio (GER) but also in upholding the qualitative parameters. It is time to acknowledge that the implementation of the National Higher Education Qualifications Framework (NHEQF), National Credit Framework (NCrF) and its syncing with the National Skills Qualification Framework (NSQF) are best optimised in the arena of Open and Distance Learning that is truly seamless in its horizons. As one of the largest Open Universities in Eastern India that has been accredited with ‘A’ grade by NAAC in 2021, has ranked second among Open Universities in the NIRF in 2024, and attained the much required UGC 12B status, Netaji Subhas Open University is committed to both quantity and quality in its mission to spread higher education. It was therefore imperative upon us to embrace NEP 2020, bring in dynamic revisions to our Undergraduate syllabi, and formulate these Self Learning Materials anew. Our new offering is synchronised with the CCFUP in integrating domain specific knowledge with multidisciplinary fields, honing of skills that are relevant to each domain, enhancement of abilities, and of course deep-diving into Indian Knowledge Systems.

Self Learning Materials (SLM’s) are the mainstay of Student Support Services (SSS) of an Open University. It is with a futuristic thought that we now offer our learners the choice of print or e-slm’s. From our mandate of offering quality higher education in the mother tongue, and from the logistic viewpoint of balancing scholastic needs, we strive to bring out learning materials in Bengali and English. All our faculty members are constantly engaged in this academic exercise that combines subject specific academic research with educational pedagogy.We are privileged in that the expertise of academics across institutions on a national level also comes together to augment our own faculty strength in developing these learning materials. We look forward to proactive feedback from all stakeholders whose participatory zeal in the teaching-learning process based on these study materials will enable us to only get better. On the whole it has been a very challenging task, and I congratulate everyone in the preparation of these SLM’s.

I wish the venture all success.

Professor Indrajit Lahiri
Vice-Chancellor

NETAJI SUBHAS OPEN UNIVERSITY
Four Year Undergraduate Degree Programme
Under National Higher Education Qualifications Framework (NHEQF) &
Curriculum and Credit Framework for Undergraduate Programmes
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Course Title: Physical Chemistry - I
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: Editing:
Dr. Puspal Mukherjee
Assistant Professor of Chemistry, NSOU

: Course Writing :
Dr. Sintu Ganai
Assistant Professor of Chemistry, NSOU

: Format Editor :
Dr. Puspal Mukherjee
Assistant Professor
School of Sciences, NSOU

Notification

Ananya Mitra
Registrar (Additional Charge)

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Module 1: Gaseous and Liquid State of Matter

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Module 1:
Gaseous and Liquid State of Matter

Unit 1 ❐ Gaseous State: Empirical Properties of Gases

Structure

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1.3 Empirical Gas Laws

1.4 Avogadro's Law

1.5 The Equation of State and The Ideal Gas Law

1.6 Dalton's Law of Partial Pressure

1.7 Graham's Law of Diffusion

1.8 The Barometric Equation

1.9 Summary

1.10 Self-Assessment Questions

1.1 Objectives

By reading this unit you will be able to

- Explain the general properties of gases
- Determine and explain the empirical rules that governs the physical properties of the gases
- Describe the laws of ideal gases
- Understand partial pressure of the gases
- Explain diffusion and the law governing diffusion of gases
- Describe the barometric equation

1.2 Introduction

Matter generally exists in three states: solid, liquid, and gas. Solids have a definite shape and volume. Due to their rigidity, the shape and size of solids change very little when heat or force is applied. Liquids have a definite volume but no fixed shape; they take the shape of their container without requiring any force. Gases, on the other hand, have neither a definite shape nor a definite volume. A gas expands to fill the entire volume of its container, and its volume changes easily with variations in temperature and pressure.

Gases are characterized by relatively low density and high compressibility, making the gaseous state the simplest form of matter. The distance between gas molecules is large, resulting in weak intermolecular interactions. In contrast, the intermolecular distances in liquids and solids are much smaller, leading to stronger interactions. Despite differences in their chemical properties, most gases exhibit similar physical behaviour and follow general laws governing pressure, temperature, and volume. Properties such as compressibility and thermal expansion apply to nearly all gases. Additionally, all gases mix uniformly to form homogeneous mixtures.

1.3 Empirical Gas Laws

(1) Boyle's Law: The law relating the pressure applied to a gas and the resulting change in volume was discovered by Boyle in 1662 AD.

> *"The volume of any gas at constant temperature varies proportionally with the pressure applied to it."*

Suppose, at constant temperature, a certain amount of gas (say n moles) has volume V and pressure P. Then according to Boyle's law $V \alpha \frac{1}{P}$ at constant temperature t°C. So according to this law we can write —

$$PV=K \qquad (1)$$

K is a constant. The graph of P vs V for a fixed amount of gas at constant temperature is given by figure 1.1:

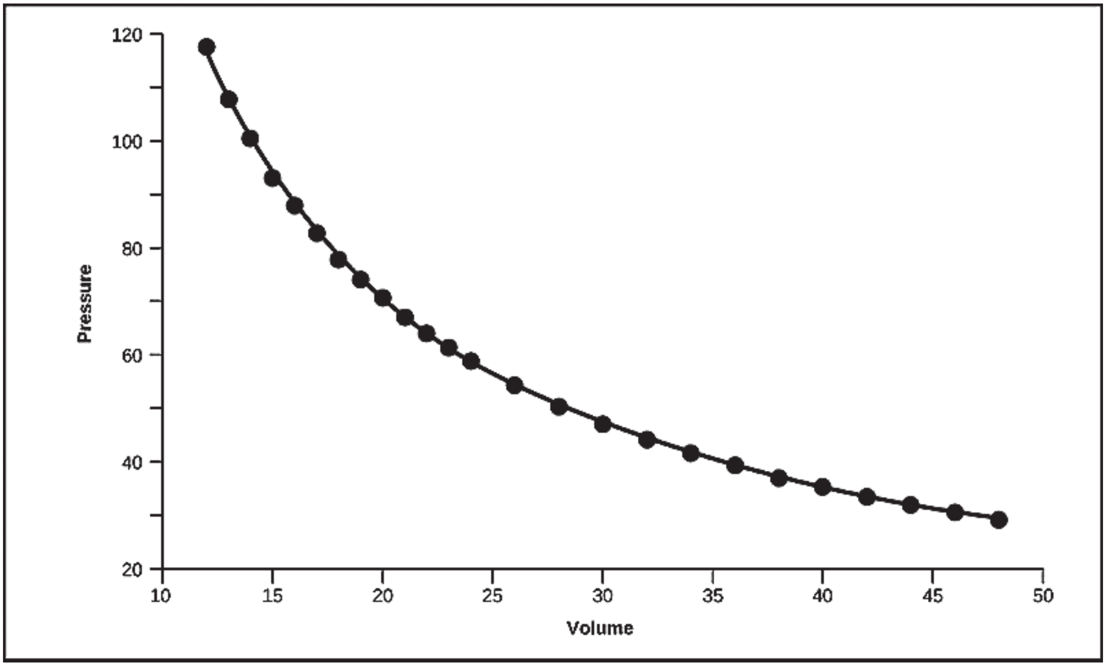


Figure 1.1: P-V Diagram according to Boyle's Law

(2) Charles's Law: Jacques Charles Formulated the original law in his unpublished work from the 1780s and it was made available by John Dalton and Gay-Lussac. Charles stated that

"The volume of a fixed mass of dry gas increases or decreases by 1/273 times the volume at 0 C for every 1 C rise or fall in temperature at constant pressure."

At a constant pressure for "n" mole of a gas, if the Volume of the gas is V_0 at 0°C and V_t at t°C then

$$V_t = V_0\left(1+\frac{t}{273}\right) = V_0\left(\frac{273+t}{273}\right) \qquad (2)$$

So, without changing the pressure, if the temperature of a gas is reduced from 0 C to -273 °C, then $\boldsymbol{V_t = 0}$ that is, the volume of the gas will be zero. In reality, any gas turns into a liquid long before this temperature is reached. This temperature of -273°C is called absolute zero temperature. Because, according to the formula, it is not possible to reduce the temperature below it. If the temperature is measured in degrees from this absolute zero, it is called the absolute temperature scale. This scale was first invented by Lord Kelvin. Hence this scale is also known as Kelvin scale and absolute temperature is expressed as K. The accurate value of absolute temperature is -273.15 °C. So t°C according to this scale is (t +273.15)K = T K. The modern statement for Charles's law is

"Volume of a given mass of gas varies directly with the absolute temperature of the gas when pressure is kept constant."

$$V \alpha T$$

$$\frac{V}{T} = \text{constant}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2} \qquad (3)$$

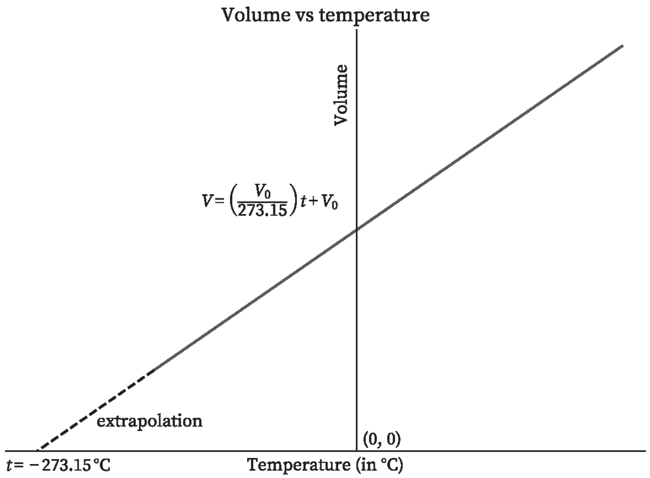


Figure 1.2: Volume vs temperature plot according to Charles's law

(3) Gay-Lussac's Law: Gay-Lussac's law of pressure-temperature was discovered between 1800 and 1802 while working on a "air thermometer" by Joseph Louis Gay-Lussac. The law states-

"The pressure of a fixed mass of dry gas increases or decreases by 1/273 times the pressure at 0 C for every 1 C rise or fall in temperature at constant volume."

So, we can write-

$$P_1 = P_0\left(1+\frac{t}{273}\right) = P_0\left(\frac{273+t}{273}\right) \qquad (4)$$

In the above equation, P_0 and P_t are the pressure of the gas at 0 C and t C. In absolute temperature scale, we can write $P \alpha T$ or

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \qquad (5)$$

In the above equation, P_1 and P_2 are pressure of the gas at T_1K and T_2K.

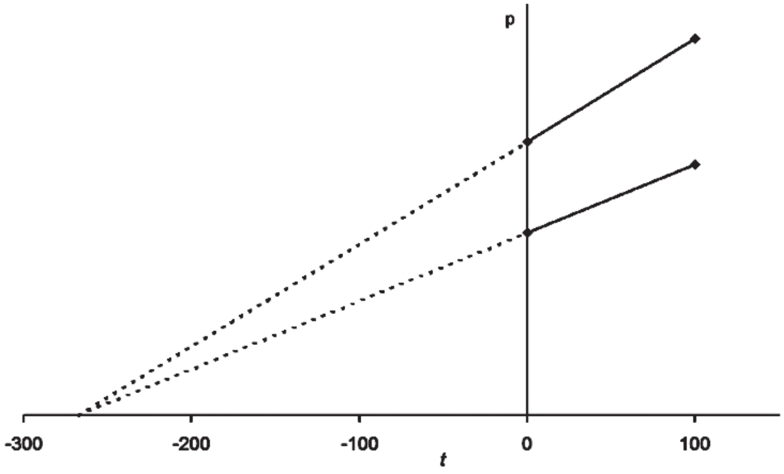


Figure 1.3: Pressure vs temperature plot according to Gay-Lussac's law

1.4 Avogadro's Law

Different volumes of any gas can vary in volume even if the temperature and pressure are constant. The relationship between volume and mass of a gas is derived from Avogadro's Law. Avogadro's Hypothesis or Avogadro's Law was first proposed in 1812. The law states:

"Equal volumes of all gases at the same temperature and pressure contain equal numbers of particles."

According to this statement, if different types of gases are confined in same volume (V) at same temperature (TK) and pressure (P atm) then they will contain same number of molecules. The characteristic masses of these gases will be different but they must contain the same number of molecules.

Standard temperature and pressure (STP) is defined as 0oC (273.15K) and 1 atm pressure. At this condition, if the number is equal to $N_A = 6.023 \times 10^{23}$, then the amount of substance in the characteristic mass (m) is one mole and M is the molar mass. Also, M is N_A times the mass of the individual molecule, m, or M = NA.m. At STP, 1 mole of all gas occupies 22.4 Liter volume. This is the molar volume of the gases at STP.

1.5 The Equation of State and The Ideal Gas Law

The overall state of a gas is expressed by pressure, temperature, volume and mass. Pressure, temperature and volume are interrelated. The mathematical equation that expresses the state of a gas is called the equation of state of a gas. We can interpret the previously discussed gaseous formulas as follows.

Let *n* be the number of gram-molecules in a certain amount of gas, pressure is P, volume V and temperature T.

According to Boyle's law, $V \alpha 1/P$ when n and T are constant.

According to Charles' law, $V \alpha T$ when n and P are constant.

According to Avogadro's law, $V \alpha n$ when P and T are constant.

So overall we can write $V \alpha = \frac{nT}{P}$, or $V = \frac{nRT}{P}$

$$PV = nRT \qquad (6)$$

Equation 6 is known as the Ideal Gas Law or equation of state for an ideal gas. For one mole of gas equation 6 is written as PV=RT. The constant R does not depend on the chemical nature of the gas. One gram molecule of any gas will have the same volume at any given temperature and pressure. This is why R is called the universal gas constant, because the value of R will be the same for all gases.From equation 6 we can write, $R = \frac{PV}{nT}$. As pressure is defined as force per area of measurement, the gas equation can also be written as

$$R = \frac{\frac{\text{force}}{\text{area}} \times \text{volume}}{\text{amoumt} \times \text{temperature}}$$

Area and volume are $(\text{length})^2$ and $(\text{length})^3$ respectively. So

$$R = \frac{\frac{\text{forece}}{(\text{length})^2} \times (\text{length})^2}{\text{amount} \times \text{temperature}} = \frac{\text{force} \times \text{length}}{\text{amount} \times \text{tempareture}}$$

Since force × length = work

$$R = \frac{\text{work}}{\text{amount} \times \text{tempareture}}$$

Repeated experiments have shown that at standard temperature (273 K) and pressure (1 atm or 101325 N/m^2), one mole (n = 1) of gas occupies 22.4 L volume. So R = 0.082 $L.atm.mol^{-1}.K^{-1}$. In SI units, P = 101325 N/m^2 (Pa for pascal) instead of 1 atm. The volume is 0.0224 m3. The numerical value and units for R is 8.314 J. $mol^{-1}.K^{-1}$. In calorie unit, R = 1.987 cal. $mol^{-1}.K^{-1}$.

Example 1.1: One mole of an ideal gas occupies 12 L at 25 °C. What is the pressure of the gas?

Solution:

The required relation between the data aned the unknown is the udeal gas law. Converting to SI we have

$T\text{-}273.15 + 25 = 298$ K and $V = 12 \text{ L} \times 10^{-3} \text{ m}^3/\text{L} = 0.012 \text{ m}^3$.

Then,

$$p = \frac{nRT}{V} = \frac{1\,\mathrm{mol}(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}{0.012\,\mathrm{m^{-3}}} = 2.06\times10^{5}\,\mathrm{J/m^{3}}$$

$= 20.06 \times 10^5$ Pa = 206 kPa.

If the pressure is needed in atm, then p = 206 kPa (1 atm/101 kPa) = 2.04 atm.

Example 1.2: Determine the volume of occupied by 2.34 grams of carbon dioxide gas at STP.

Solution:

Rearranging PV = nRT to V = nRT / P

V = [(2.34 g / 44.0 g $\mathrm{mol^{-1}}$) (0.08206 L atm $\mathrm{mol^{-1}\ K^{-1}}$) (273.0 K)] / 1.00 atm

V = 1.19 L

Example 1.3: A sample of argon gas at STP occupies 56.2 liters. Determine the number of moles of argon and the mass of argon in the sample.

Solution:

Rearranging PV = nRT to n = PV / RT

n = [(1.00 atm) (56.2 L)] / [(0.08206 L atm $\mathrm{mol^{-1}\ K^{-1}}$) (273.0 K)]

n = 2.50866 mol

Multiplying the moles by the atomic weight of Ar to get the grams: 2.50866 mol x 39.948 g/mol = 100. g

Example 1.4: 5.600 g of solid CO_2 is put in an empty sealed 4.00 L container at a temperature of 300 K. When all the solid CO_2 becomes gas, what will be the pressure in the container?

Solution: Number of moles of CO2: 5.600 g / 44.009 g/mol = 0.1272467 mol

PV = nRT

(P) (4.00 L) = (0.1272467 mol) (0.08206 L atm $\mathrm{mol^{-1}\ K^{-1}}$) (300 K)

P = 0.7831 atm

1.6 Dalton's Law of Partial Pressure

If a container contains a mixture of two or more gases, the total pressure of the gas mixture depends on the amount of each gas. The pressure of each gas is expressed in partial pressure.

The pressure exerted by a gas at a given temperature when a single component of a gas mixture is allowed to occupy the entire volume alone is called the partial pressure of the gas present in the mixture.

The total pressure of a mixture of two or more non-reacting gases at a given temperature is equal to the sum of the partial pressures of the component gases present in the mixture.

This is Dalton's partial pressure formula. Consider a container of volume V at a certain temperature (T). There are three different gases in the mixtures with n1, n? and n? moles. If the total pressure of the gas mixture is Ptotal and the partial pressures of the component gases are respectively P_1, P_2, and P_3, then $P_{total} = P_1+P_2+ P_3$. For "*i*" number of components in the mixture

$$P_{total} = \sum_i P_i \qquad (7)$$

The partial pressure of each of the ideal gas present in the mixture is given by

$$P_i = \frac{nRT}{V} \qquad (8)$$

From the partial pressure of a certain gas and the total pressure of a certain mixture, the mole ratio, called Xi, of a gas can be found. The mole ratio describes what fraction of the mixture is a specific gas. For example, if oxygen exerts 4 atm of pressure in a mixture and the total pressure of the system is 10 atm, the mole ratio would be 4/10 or 0.4. The mole ratio applies to pressure, volume, and moles as seen by the equation below. This also means that 0.4 moles of the mixture is made up of gas i.

$$X_i = \frac{P_i}{P_{total}} = \frac{n_i}{n_{total}} \qquad (9)$$

Dalton's Law of Partial Pressures is often used to determine the pressure in a closed container containing both gas and water. In such a system, the total pressure is the sum of the pressures exerted by the gas and the evaporated water. The gas present in the container consists of the collected sample along with water vapor. According to Dalton's law, the pressure of the collected gas can be determined by subtracting the pressure of water vapor from the total pressure.

An important point to note is that real gases are gases that do not behave ideally. Real gases behave ideally when the gases are at low pressure and high temperature. Therefore, at high pressures and low temperatures, Dalton's law is not applicable since the gases are more likely to react and change the pressure of the system.

Example 1.5: A gas is collected over water at 25°C, and the total pressure in the container is 760 mmHg. The vapor pressure of water at 25°C is 23.8 mmHg. Calculate the pressure of the dry gas.

Solution: According to Dalton's Law of Partial Pressures:

$P_{total}=P_{gas} + P_{water}$

Rearranging to solve for

$P_{gas} = P_{total} — P_{water}$

Substituting the values:

Pgas = 760 mmHg – 23.8 mmHg = 736.2 mmHg

The pressure of the dry gas is 736.2 mmHg.

Example 1.6: 24.0 L of nitrogen gas at 2 atm and 12.0 L of oxygen gas at 2 atm are added to a 10 L container at 273 K. Find the partial pressure of nitrogen and oxygen and then find the total pressure.

Solution:

Find the number of moles of oxygen and nitrogen using PV = nRT which is n = PV/RT

1. oxygen : ((1 atm) (12L))/(0.08206 atm L mol^{-1} K^{-1}) (273 K) = 0.536 moles oxygen
2. nitrogen : ((1 atm) (24.0L))/(0.08206 atm L mol^{-1} K^{-1}) (273 K) = 1.07 moles of Nitrogen
3. add to get n_{tot} : $.536mol_{oxygen}$ + 1.07 $mol_{Nitrogen}$ = 1.61 moles total

Use PV = nRT or P = (nRT)/V to find the total pressure

1. Plot = ((1.61 moltotal) (0.08206 atm L mol-1 K-1) (273 K))/(10.0 L) = 3.61 atm

$P_A/P_{tot} = n_A/N_{tot}$ can be rearranged to $P_A = (P_{tot})\ (n_A/N_{tot})$ to find the partial pressures

1. $P_{oxygen} = (3.61\ atm_{total})\ (.536\ mol_{oxygen}/1.61\ mol_{total}) = 1.20\ atm_{oxygen}$
2. $P_{nitrogen} = 3.61\ atm_{total} - 1.20\ atm_{oxygen} = 2.41\ atm_{nitrogen}$

1.7 Graham's Law of Diffusion

Diffusion is the gradual mixing of gases caused by the movement of their individual particles, even without external agitation like stirring. This process leads to the formation of a uniformly mixed gas. Diffusion also occurs in liquids and liquid solutions, and to a lesser extent, in solids and solid solutions. A related phenomenon, effusion, refers to the movement of gas molecules through a tiny opening, such as a pinhole in a balloon, into a vacuum.

The phenomenon of effusion had been known for thousands of years, but it was not until the early 19th century that quantitative experiments related the rate of effusion to molecular properties. Graham's law of effusion (also called Graham's law of diffusion) was formulated by Scottish physical chemist Thomas Graham in 1848.

The rate of effusion of a gaseous substance is inversely proportional to the square root of its molar mass at a particular temperature and pressure.

If the molar mass (molecular weight) of two gases are M_1 and M_2, then the ratio of their rate of effusion (or diffusion) will be given by

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{M_2}{M_1}}$$

Since at a particular temperature and pressure the molar volume of the gases will be same, so we can also write

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{M_2}{M_1}} = \sqrt{\frac{p_2}{p_1}} \qquad (10)$$

Here,p_1 and p_2 are the densities of the two gases. According to this law, if the molecular weight of one gas is four times that of another, it would diffuse through a porous plug or escape through a small pinhole in a vessel at half the rate of the other (heavier gases diffuse more slowly). Graham's law provides a basis for separating isotopes by diffusion-a method that came to play a crucial role in the development of the atomic bomb. Graham's law is most accurate for molecular effusion which involves the movement of one gas at a time through a hole. It is only approximate for diffusion of one gas in another or in air, as these processes involve the movement of more than one gas

Example 1.7: During World War II, scientists working on the first atomic bomb were faced with the challenge of finding a way to obtain large amounts of ^{235}U. Naturally occurring uranium is only 0.720% ^{235}U, whereas most of the rest (99.275%) is ^{238}U, which is not fissionable (i.e., it will not break apart to release nuclear energy) and also actually poisons the fission process. Because both isotopes of uranium have the same reactivity, they cannot be separated chemically. Instead, a process of gaseous effusion was developed using the volatile compound UF_6 (boiling point = 56°C).

Calculate the ratio of the rates of effusion of $^{235}UF_6$ and $^{238}UF_6$ for a single step in which UF_6 is allowed to pass through a porous barrier. (The atomic mass of ^{235}U is 235.04, and the atomic mass of ^{238}U is 238.05.)

If n identical successive separation steps are used, the overall separation is given by the separation in a single step (in this case, the ratio of effusion rates) raised to the n-th power. How many effusion steps are needed to obtain 99.0% pure $^{235}UF_6$?

Solution :

The first step is to calculate the molar mass of UF_6 containing ^{235}U and ^{238}U. Luckily for the success of the separation method, fluorine consists of a single isotope of atomic mass 18.998.

The molar mass of $^{235}UF_6$ is 234.04 + (6)(18.998) = 349.03 g/mol

The molar mass of $^{238}UF_6$ is 238.05 + (6)(18.998) = 352.04 g/mol

The difference is only 3.01 g/mol (less than 1%). The ratio of the effusion rates can be calculated from Graham's law

$$\frac{\text{rate}^{235}UF_6}{\text{rate}^{238}UF_6} = \sqrt{\frac{352.04\,g/mol}{349.03\,g/mol}} = 1.0043$$

Thus passing UF_6 containing a mixture of the two isotopes through a single porous barrier gives an enrichment of 1.0043, so after one step the isotopic content is (0.720%)(1.0043) = 0.723% $^{235}UF_6$.

1.8 The Barometric Equation

In the discussion of ideal gases, it is assumed that the gas pressure is equal everywhere in the container. This concept only applies if there is no other force acting on the gas. Density decreases with height due to gravitational force in the atmosphere. Consider a columnar atmosphere whose cross-section is one square unit.

Imagine a slice of gas of thickness dx within this column (Fig. 1.4) and a pressure difference dP between the top and bottom.

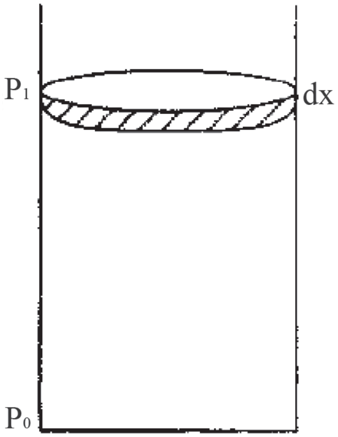


Figure 1.4: Change of pressure in a columnar atmosphere

$$-dP = \rho g dx$$

Where ρ is the density of the gas and *g* is the acceleration due to gravity. Here we will assume that the atmosphere behaves like a ideal gas and the temperature is same everywhere inside the column. Since PV=P $\frac{M}{P}$ =RT, so

$$-dP = \frac{PM}{RT} g dx$$

$$-\frac{dP}{P} = \frac{M}{RT} gdx$$

$$-\int_{P_0}^{P_1} \frac{dP}{P} = \frac{Mg}{RT} \int_{o}^{x} dx$$

$$\frac{P_1}{P_0} e^{-\frac{Mgx}{RT}}$$

$$P_1 = P_0 e^{-\frac{Mgs}{RT}} \qquad (11)$$

Equation 11 is known as the barometric equation.

1.9 Summary

In this unit we learned about Boyle's law, Charles' law, Gay-Lusak's law, Avogadro's law, ideal gas equation, Dalton's partial pressure law, Graham's gas diffusion law, and barometric equation are discussed in this unit respectively. These empirical observations paved the way for further understanding of the behavior of gases. We will discuss the explanation behind these empirical observations in the next unit.

1.10 Self-Assessment Questions

(1) At what conditions an ideal gas has pressure of 1.01325×10^5 Nm and density 1 moles/dm^3?

(2) Molar volume of helium at 100 times atmospheric pressure and 0°C (0.01107 times the volume at 0°C and one atmospheric pressure. Determine the radius of the helium atom. Assume helium is used as an ideal gas.

(3) 5 gm C-H is placed in a bulb of volume 1 dm'. If the bulb is pressurized to 10 times atmospheric pressure, the bulb breaks. At what temperature will the pressure of the gas be equal to this pressure?

(5) 110 gm of hydrogen and 64 gm of oxygen in 10 decim. The container is kept at a temperature of 47.3 K. What is the total pressure of the mixture?

(6) Calculate the relative importance of carbon dioxide and weight from the known relative importance of carbon dioxide 0.58: 0.342.

(7) Determine the partial pressures of oxygen and nitrogen in air at a pressure of 1.01325 × 10° Nm at 0°C. Air is 78% nitrogen by volume and 2. Share oxygen.

(8) Draw the graph of P vs 1°C and TK and calculate the value of the gradient from this graph.

Unit 2 ❒ Kinetic Theory of Gases - I

Structure

2.1 Objectives

2.2 Introduction

2.3 Kinetic model of gas - postulates;

2.4 Velocity of gas molecules

2.5 Concept of Pressure and Temperature from Kinetic Theory

2.6 The Maxwell Boltzmann Distribution

2.7 Maxwell Kinetic Energy Distribution

2.8 Summary

2.9 Self-Assessment Questions

2.1 Objectives

After completing this unit, learners will be able to:

- Explain the postulates of the kinetic model of gases and their significance in describing gas behaviour.
- Understand the concept of molecular velocity and its role in determining macroscopic gas properties.
- Derive expressions for pressure and temperature using the kinetic theory of gases.
- Establish the relationship between kinetic theory and gas laws, deriving key gas laws from fundamental principles.
- Analyse the nature of velocity distribution among gas molecules and interpret Maxwell's distribution of speeds in one, two, and three dimensions.
- Understand the distribution of kinetic energy in different dimensions and its implications for molecular motion.
- Calculate average speed, root mean square (RMS) speed, and the most probable speed of gas molecules from Maxwell's distribution.

2.2 Introduction

The kinetic theory of gases provides a microscopic perspective on gas behaviour by describing the motion of individual molecules. It is based on a set of fundamental postulates that relate molecular motion to macroscopic properties such as pressure and temperature. By considering the velocity of gas molecules and their distribution, this theory explains the origin of gas laws and offers a deeper understanding of thermodynamic principles.

Maxwell's distribution of molecular speeds further refines this model by describing how gas molecules move with varying velocities in one, two, and three dimensions. The distribution of kinetic energy among these molecules plays a crucial role in predicting average, root mean square (RMS), and most probable speeds, which are essential for understanding molecular collisions, diffusion, and reaction rates. This unit explores these foundational concepts, bridging the gap between molecular dynamics and observable gas properties.

2.3 Kinetic Model of gas - postulates

The kinetic theory, like other theories, is based on some simple postulates or assumptions. These postulates may be summarised as follows:

1. Gases are composed of minute discrete particles, now called molecules. In any one gas, all the particles are of the same size and mass.
2. The molecules of a gas are in a state of ceaseless chaotic motion in all possible directions with very high velocities. They incessantly collide with each other and with the walls of the container. Between two successive collisions, a molecule moves in a straight line.
3. The molecules exert no appreciable attraction on each other and are supposed to be perfectly elastic. Hence no energy is lost from their collisions.
4. The dimensions of the molecules are negligible. The actual volume occu-pied by the molecules is negligible compared to the volume of the gas. The mole-cules are regarded as point masses.
5. The average force per unit-area that the molecules exert in their impacts on the walls is the pressure. The larger the number of impacts, the greater will be the pressure.

6. The absolute temperature of a gas is a measure of the average kinetic energy of the molecules of the gas. The average kinetic energy is proportional to the absolute temperature of the gas.

2.4 Velocity of Gas Molecules

At any instant, the randomly moving particles in a gas possess different velocities, some high and others low velocities. Due to incessant collisions, the velocity of any given molecule must always be constantly changing both in direction and in magnitude. To visualize the state of their motion, some sort of mean value for the velocities of the molecules has to be conceived.

Suppose there are *N* molecules present in a given quantity of a gas. Out of these *N* molecules, let us say, there are

n_1 molecules with velocity c_1 and kinetic energy e_1

n_2 molecules with velocity c_2 and kinetic energy e_2,

n_3 molecules with velocity c_3 and kinetic energy e_3 etc.

Then $N=n_1+n_2+n_3+...$

The total translational kinetic energy (*E*) is given by

$$E = n_1 \in_1 + n_2 \in_2 + n_3 \in_3 + ...$$

The arithmetic mean of the velocities of the molecules, called *average velocity,* c_{av}, is given by

$$C_{av} = \frac{n_1c_1 + n_2c_2 + n_3c_3}{N} = \frac{\sum n_ic_i}{N} \qquad (2.1)$$

The sum of the squares of the velocities would be

$$n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + ... = N\overline{c^2} \qquad (2.2)$$

where $\overline{c^2}$ is the mean of the squares of all the velocities , $\overline{c^2}$ is called mean square velocity

$$\overline{c^2} = \frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + ...}{N} \qquad (2.3)$$

Taking the root,

$$c_{rms} = \sqrt{\frac{n_1c_1^2 + n_2c_2^2 + n_3c_3^2 + \ldots}{N}} \qquad (2.4)$$

c_{rms} is called the root mean square velocity (r. m .s. velocity).

2.5 Concept of Pressure and Temperature from Kinetic Theory

We know gas exerts pressure. How this pressure is developed and how much is that?

For analysis, we take a gas in a cylindrical box, at one end of which there is a frictionless piston, which can move along either direction. The molecules inside are in ceaseless erratic motion and continuously bombard on the piston. Each time the piston receives a certain momentum for each collision, it picks up speed. Let there be vacuum outside.

Receiving a certain amount of momentum from each collision, the piston starts moving out of the box. In order to keep it from moving out, we must therefore hold the piston with a certain force F. The magnitude of the Force applied normally per unit area of the piston which is just sufficient to keep the piston at its position is defined as the pressure (P) of the gas.

The tactics of the calculation involve three steps:

1. The calculation of the change in momentum that occurs when one molecule strike a wall.
2. The calculation of the total number of collisions with a wall of given area in a given interval.
3. The conversion of the total change in momentum to a force per unit area

Calculation

How much momentum transferred normally per second on the wall by bombarding molecules?

i) Let us fix the reference frame so that the x-axis of the coordinate system is perpendicular to the piston.

ii) Cx is the velocity component of a molecule along the +ve X- axis collides with the wall on the right and is deflected back along its path, its momentum changes from mCx before collision to –mCx after the collision (when it is travelling in the opposite direction).

iii) The momentum therefore changes by 2mCx on each collision (the y and z component are unchanged) .

iv) The number of molecules that collide with the wall in the time interval 1 sec or in a time interval Δ t, travels a distance Cx.1 or Cx.Δ t along x axis and if the wall has area A, then all the particles in a volume A×Cx.1 or A×Cx. Δ t is $\left(\frac{nV_A}{V}\right)$ACx.$\Delta$ t.

v) On average, at any instant half the particles are moving to the right, and half moving to the left. Therefore the average number of collisions with the wall during the interval Δ t is $\frac{1}{2}nN_A AC_x \frac{\Delta t}{V}$.

The total momentum change in that interval is the product of this number and the change is = $\frac{nN_A AC_x \Delta t}{2V} \times 2mC_x = \frac{nN_A mAC_x^2 \Delta t}{}$

The product of the molecular mass m and Avogadro's constant molar mass M of the molecules, so Momentum change $= \frac{nMC_x^2 A\Delta t}{V}$

vi) Force is the rate of change of momentum divided by the interval Δ t during which it occurs;

Rate of change of momentum $= \frac{nMC_x^2 A}{V}$

Force per unit area is Pressure $= \frac{nMC_x^2}{V}$

vii) Let there be unit volume, n_1 molecules with x-component velocity C_{x1}, n_2 molecules with x-component velocity Cx2, Since not all the molecules travel with the same velocity, so the

$$< C_x^2 >= \frac{n_1 C_{x1}^2 + n_2 C_{x2}^2 + ...}{n_1 + n_2 + ...}$$

So, the pressure equation P= 2m $(nC_{x1}^2 + n_2 C_{x2}^2 + ...)$, including average of C_x^2 is given by

$$< C_x^2 >= \frac{\sum n_i C_{xi}^2}{n}$$

$$P = \frac{nM < C_x^2 >}{V}$$

Molecules are moving about y direction with mean squared velocity, $< C_y^2 >$ and also up and down in z direction with $< C_z^2 >$. Due to isotropic movement, $< C_x^2 >=< C_y^2 >=< C_z^2 >$

And if $< C^2 > + < C_x^2 > + < C_y^2 > + < C_z^2 >= 3 < C_x^2 >$

$$< C_x^2 >= \frac{1}{3} < C^2 >$$

$$P = \frac{1}{3V} nM < C^2 >= \frac{1}{3}\frac{nM}{V} C_{rms}^2, = \frac{1}{3}\rho C_{rms}^2$$

Concept of Temperature from Kinetic Theory of gas

From the basic KTG equation

$$P = \frac{1}{3}\frac{mN}{V} C_{rms}^2$$

$$P = \frac{2}{3} N \frac{1}{2} m C_{rms}^2 = \frac{2}{3} N < \varepsilon >$$

where $< \varepsilon >= \frac{1}{2} m C_{rms}^2$ is the average kinetic energy

Now comparing with the ideal gas law $PV = Nk_BT$ where k_B is the Boltzmann constant and T is the absolute temperature.

$$\frac{2}{3}N < \varepsilon >= Nk_BT$$

$$< \varepsilon >= \frac{3}{2}k_BT$$

$$T = \frac{2}{3}\frac{< \varepsilon >}{k_B}$$

The average molecular kinetic energy is proportional to the ideal gas law's absolute temperature. Temperature is the manifestation of average kinetic energy.

Derivation of empirical gas laws from basic equation of KTG

1. Boyle's Law

From the basic equation of KTG, pressure is given by $P = \frac{1}{3}\frac{mN}{V}C_{rms}^2$

This equation can be rearranged as $P = \frac{2N}{3V}\frac{1}{2}mC_{rms}^2 = \frac{2N}{3V} < \varepsilon >$

As the temperature is a measure of average kinetic energy, when temperature is kept constant, average kinetic energy is also constant. For fixed amount of gas and fixed temperature volume of the gas is inversely proportional to applied pressure i.e. $V \alpha \frac{1}{P}$

2. Charles' law

From basic equation of KTG, pressure is given by

$$P = \frac{1}{3}\frac{mNc_{rms}^2}{V} = \frac{2N}{3V}\frac{1}{2}mc_{rms}^2 = \frac{2N}{3V} < \varepsilon >$$

$$\text{Or } V = \frac{2N}{3P} < \varepsilon >$$

For fixed amount of gas and pressure, Volume Temperature.

2.6 The Maxwell Boltzmann Distribution

Plotting the number of molecules within narrow velocity ranges yields a slightly asymmetric curve called the velocity distribution, with its peak representing the most probable velocity. This curve, known as the Maxwell-Boltzmann distribution, was formulated by James Clerk Maxwell (1860) and later refined by Ludwig Boltzmann, who advanced statistical mechanics and strongly advocated atomic theory.

The kinetic molecular theory describes the motion of an ideal gas molecule under specific conditions. However, for a macroscopic sample, tracking the velocity of each molecule at every instant is impractical. Instead, the Maxwell-Boltzmann distribution provides the probability of molecules having velocities between v and v+dv. Assuming the independence of velocity components in different directions-such that motion along one axis does not influence the others-the Maxwell-Boltzmann distribution is expressed as:

$$f(\mathrm{v_x}) = \left(\frac{\mathrm{m}}{2\pi \mathrm{k_B T}}\right)^{\frac{1}{2}} \mathrm{e}^{-\frac{\mathrm{mv}^2}{2\mathrm{k_B T}}} \qquad (2.5)$$

However, in real gases, molecules exhibit both a distribution of speeds and a random orientation of motion. Applying vector magnitude properties, it follows that:

$$(\mathrm{v})^2 = (\mathrm{v_x})^2 + (\mathrm{v_y})^2 + (\mathrm{v_z})^2$$

Since the direction of travel is random, the velocity can have any component in x, y, or z directions with equal probability. As such, the average value of the x, y, or z components of velocity should be the same. And so

$$(\mathrm{v})^2 = 3(\mathrm{v_x})^2$$

In his 1860 paper, *Illustrations of the Dynamical Theory of Gases*, Maxwell proposed a speed distribution consistent with observed gas properties, such as viscosity. He derived this expression by transforming from Cartesian coordinates (x,y,z) to spherical polar coordinates (v, θ, ϕ), where v represents speed, while and $\phi\theta$ define direction. In this new coordinate system, the infinitesimal volume element becomes:

$$dxdydz = v^2 \sin\theta dv d\theta d\varphi$$

Applying this transformation of coordinates Maxwell's distribution

$$f(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2k_B T}} \tag{2.6}$$

Velocity distributions depend on temperature and mass

At higher temperatures, a greater fraction of molecules acquire more kinetic energy, causing the Maxwell-Boltzmann distribution to broaden. Figure 2.1 illustrates this temperature dependence: at lower temperatures, molecules have less energy, resulting in lower speeds and a narrower distribution. As temperature increases, the distribution flattens, reflecting higher molecular speeds.

The left end of each plot remains anchored at zero velocity, as some molecules are always at rest. With increasing temperature, the curves extend further, as more high-velocity states become accessible. However, the area under each curve remains constant, corresponding to the fixed number of molecules.

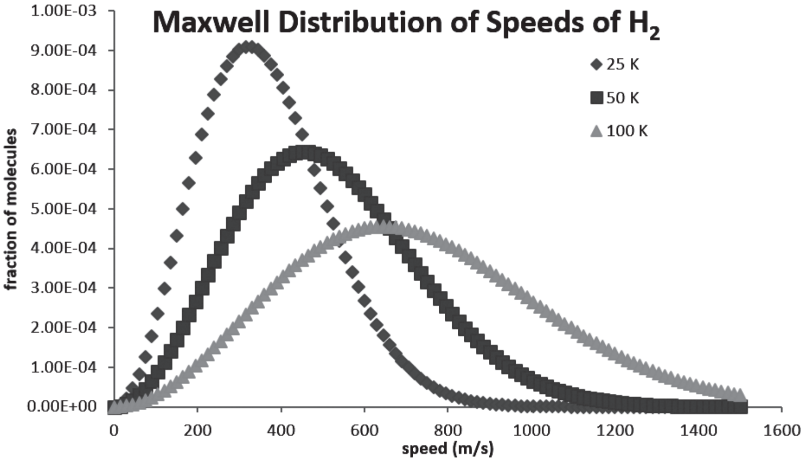


Figure 2.1: Maxwell Distribution of speeds for hydrogen molecules at differing temperatures.

Since all molecules have the same kinetic energy at a given temperature, a greater fraction will have higher velocities as molecular mass mmm decreases. Figure 2.2 illustrates how the Maxwell-Boltzmann distribution depends on molecular mass: heavier molecules move more slowly on average and exhibit a narrower speed distribution, whereas lighter molecules have a broader distribution with higher speeds

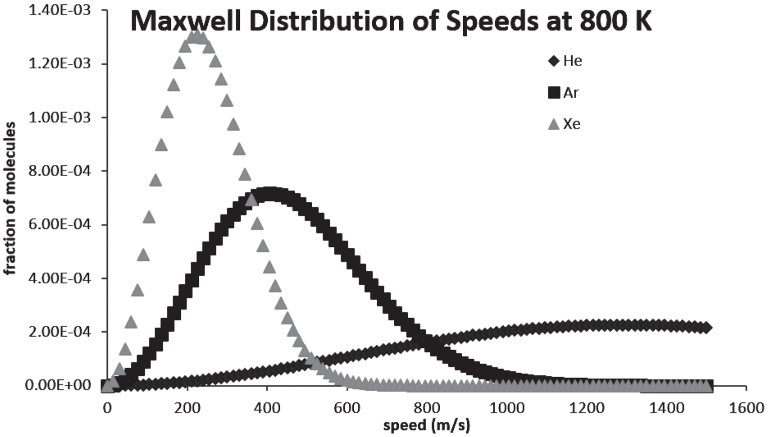


Figure 2.2: Maxwell Distribution of speeds at 800 K for different gasses of differing molecular masses.

Usually, we are more interested in the speeds of molecules rather than their component velocities. The Maxwell-Boltzmann distribution for the speed follows immediately from the distribution of the velocity vector, above. Note that the speed of an individual gas particle is

The most probable speed is the maximum value on the distribution plot (Figure 2.3). This is established by finding the velocity when the derivative of Equation 2.6 is zero

$$\frac{df(v)}{dv} = 0$$

$$\frac{d}{dv}\left[4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)\right] = 0$$

Applying the product rule

$$\left[2v\exp\left(-\frac{mv}{2k_BT}\right)+V^2\left(\frac{m}{k_BT}\right)\exp\left(-\frac{mv^2}{2k_BT}\right)\right]=0$$

Factoring Out Common Terms

$$\exp\left(-\frac{mv^2}{2k_BT}\right)v\left[2-\frac{mv^2}{k_BT}\right]=0$$

Solving for Most Probable Velocity

$$2-\frac{mv^2}{k_BT}-0$$

Most Probable Velocity Expression

$$V_{mp}=\sqrt{\frac{2k_BT}{m}}=\sqrt{\frac{2RT}{M}} \qquad (2.7)$$

Where R is the gas constant, T is the absolute temperature and M is the molar mass of the gas

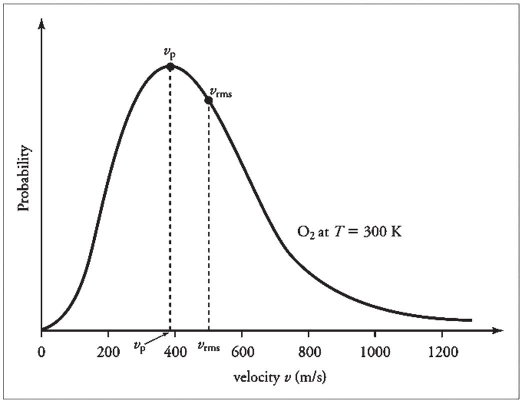


Figure 2.3: The Maxwell-Boltzmann distribution is shifted to higher speeds and is broadened at higher temperatures.

The average speed is the sum of the speeds of all the molecules divided by the number of molecules

$$v_{avg} - \int_0^\infty v f(v) dv$$

Substituting f(v)

$$vavg = \int_0^\infty v.4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)dv$$

$$v_{avg} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_0^\infty v^3 \exp\left(-\frac{mv^2}{2k_B T}\right)dv$$

Using the standard integral formula:

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}$$

Here, n = 1 and a = $m/(2k_BT)$

Evaluating the Integral

$$v_{avg} = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \times \frac{1}{2}\left(\frac{k_B T}{m}\right)^2 \frac{\sqrt{\pi}}{4}$$

Simplifying

$$v_{avg} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \qquad (2.8)$$

The root-mean-square speed is square root of the average speed-squared.

$$v_{rms} = \sqrt{\frac{\int_0^\infty v^2 f(v) dv}{\int_0^\infty f(v) dv}}$$

Since f(v) is already normalized, denominator is 1

$$\mathrm{vrms} = \sqrt{\int_0^\infty v^2 f(v)dv}$$

Substituting f(v)

$$V_{rms} = \sqrt{\int_0^\infty v^2 .4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 \exp\left(-\frac{mv^2}{2k_B T}\right)dv}$$

Simplifying

$$v_{rms}\sqrt{4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^4 \exp\left(-\frac{mv^2}{2k_B T}\right)dv}$$

Using the standard integral formula:

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{(2n-1)}{2^{n+1} a^{n+1/2}}\sqrt{\pi}$$

Here, n = 2 and $a=m(2k_BT)$

Evaluating the Integral

$$v_{rms} = \sqrt{4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} \times \frac{3}{4}\left(\frac{k_B T}{m}\right)^{5/2}\sqrt{\pi}}$$

Simplifying

$$v_{rms} = \sqrt{\frac{3k_B T}{m}}$$

Final Expression

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}} \qquad (2.9)$$

Where R is the gas constant, T is the absolute temperature and M is the molar mass of the gas

It always follows that for gases that follow the Maxwell-Boltzmann distribution

$$v_{mp} < v_{avg} < v_{rms}$$

2.7 Maxwell Kinetic Energy Distribution

The kinetic energy of a molecule is given by

$$E = \frac{1}{2}mv^2$$

To transform the distribution from velocity v to kinetic energy E, we use the relation

$$dE = m\, v\, dv$$

Thus, substituting $v = \sqrt{2E/m}$ and $dv = \frac{dE}{mv}$

$$f(E)dE = f(v)(dE/dv)\, dE$$

From the one-dimensional velocity distribution, the kinetic energy distribution is

$$f(E) = \frac{1}{\sqrt{\pi k_B T}}\frac{1}{\sqrt{E}}\exp\left(-\frac{E}{k_B T}\right) \qquad (2.10)$$

Using the three-dimensional speed distribution and substituting

$$f(E) = \frac{2}{\sqrt{\pi}}\frac{1}{(k_B T)^{3/2}}\sqrt{E}\exp\left(-\frac{E}{k_B T}\right) \qquad (2.11)$$

For a gas in D dimensions, the kinetic energy distribution is

$$f(E) = \frac{1}{\Gamma(D/2)}\frac{E^{(D/2)-1}}{(k_B T)^{D/2}}\exp\left(-\frac{E}{k_B T}\right) \qquad (2.12)$$

where $\Gamma(x)$ is the Gamma function. Here we should note that-

- Unlike velocity distribution kinetic energy distribution is independent of mass of the molecules and it is a function of temperature only.
- When ε is very small, f (ε) varies with $\frac{1}{\sqrt{\in}}$ When ? is much greater compared to the thermal energy <$k_B T$> , f (ε) decreases exponentially . As it does not passes through a maximum, there is nothing so called most probable energy.
- When temperature tends to infinity the distribution will be along the horizontal axis that will be along the ε - axis. If the temperature is zero kelvin, then the distribution curve will be along the vertical axis that is along the P(ε) - axis.

Average energy of gas molecules

Definition of Average Energy

$$\langle E\rangle = \int_0^\infty E\, f(E) dE$$

Substituting f(E)

$$\langle E\rangle = \int_0^\infty E.\frac{2}{\sqrt{\pi}}\frac{1}{(k_B T)^{3/2}}\sqrt{E}\exp\left(-\frac{E}{k_B T}\right)dE$$

Simplifying

$$\langle E\rangle = \frac{2}{\sqrt{\pi}(k_B T)^{3/2}}\int_0^\infty E^{3/2}\exp\left(-\frac{E}{k_B T}\right)dE$$

Using the standard Gamma function result

$$\int_0^\infty x^n e^{-ax} dx = \frac{\Gamma(n+1)}{a^{n+1}}$$

Here, n = 3/2 and a=1/(k_BT)

Evaluating the Integral

$$\langle E\rangle = \frac{2}{\sqrt{\pi}\left(k_B T\right)^{3/2}}\times\frac{\Gamma(5/2)}{(1/k_B T)^{5/2}}$$

Using $\Gamma(5/2) = \frac{3}{4}\sqrt{\pi}$

$$\langle E \rangle = \frac{2}{\sqrt{\pi}(k_B T)^{3/2}} \times \frac{3}{4}\sqrt{\pi}\left(k_B T\right)^{5/2}$$

Simplifying

$$\langle E \rangle = \frac{3}{2} k_B T \qquad (2.13)$$

This result aligns with the classical equipartition theorem, which states that each degree of freedom contributes $\frac{1}{2}k_B T$ to the average energy.

2.8 Summary

This unit explores the kinetic model of gases, describing their behavior based on molecular motion. The postulates of kinetic theory provide a microscopic explanation for macroscopic gas properties, assuming that gas molecules are in continuous random motion and obey Newtonian mechanics.

The velocity of gas molecules is analyzed to understand molecular motion at different conditions. The concepts of pressure and temperature are derived from kinetic theory, linking them to molecular collisions and energy. The derivation of gas laws from kinetic theory establishes a fundamental connection between microscopic molecular motion and macroscopic gas behaviour.

The Maxwell-Boltzmann distribution describes the statistical spread of molecular speeds in one, two, and three dimensions. The kinetic energy distribution is also explored in different dimensions, leading to the calculation of important velocity parameters.

2.9 Self-Assessment Questions

1. Kinetic Model of Gases: State the postulates of the kinetic theory of gases. How does it explain the macroscopic properties of gases?

2. Molecular Velocities: Define and derive expressions for average velocity, root mean square velocity, and most probable velocity of gas molecules.
3. Kinetic Interpretation of Temperature: Show that the average kinetic energy of gas molecules is directly proportional to the absolute temperature.
4. Concept of Pressure: Derive an expression for the pressure of an ideal gas using the kinetic theory of gases.
5. Gas Laws from Kinetic Theory: Explain how Boyle's law and Charles' law can be derived from the kinetic theory of gases.
6. Maxwell's Distribution of Speeds: Describe Maxwell's distribution of molecular speeds and explain its significance in kinetic theory.
7. Speed Distributions in Different Dimensions: Discuss how molecular velocity distribution differs in one, two, and three dimensions.
8. Kinetic Energy Distribution: Derive the expression for kinetic energy distribution in one, two, and three dimensions.
9. Effect of Temperature on Velocity Distribution: Explain how the Maxwell-Boltzmann speed distribution changes with increasing temperature.
10. Gas Laws and Kinetic Energy: How does the kinetic theory explain Avogadro's law and the ideal gas equation?
11. Numerical Problem: Calculate the root mean square speed of oxygen molecules at 300 K. (Given: Molar mass of O_2 = 32 g/mol, R = 8.314 J mol^{-1} K^{-1})
12. Numerical Problem: The most probable speed of nitrogen molecules at 400 K is 500 m/s. Calculate its root mean square and average speed.
13. Numerical Problem: If the root mean square speed of a gas at 273 K is 500 m/s, what will be its speed at 546 K?
14. Numerical Problem: At what temperature will the most probable speed of hydrogen molecules be 1500 m/s? (Given: Molar mass of H_2 = 2 g/mol)

Unit 3 ❐ Kinetic Theory of Gases - II

Structure

3.1 Objectives

3.2 Introduction

3.3 Collision of Gas Molecules

3.4 Collision diameter

3.5 Collision number

3.6 Collision Number

3.7 Frequency of binary collisions

3.8 Mean Free Path

3.9 Calculation of number of molecules having energy ? ?,

3.10 Degrees of Freedom

3.11 Principle of equipartition of energy

3.12 Heat Capacity of gases

3.13 Summary

3.14 Self-Assessment Questions

3.1 Objectives

After completing this unit, learners will be able to:

- Understand the concept of molecular collisions in gases and their significance in kinetic theory.
- Define and determine collision diameter, collision number, and mean free path of gas molecules.
- Analyse the frequency of binary collisions for both similar and different molecules.
- Explain the concept of wall collisions and derive expressions for the rate of effusion of gases.
- Calculate the number of gas molecules possessing energy greater than or equal to a given threshold (ε).

- Apply the principle of equipartition of energy to determine the distribution of energy among gas molecules.
- Evaluate the heat capacity of gases using kinetic theory and the equipartition theorem.

3.2 Introduction

The behaviour of gases at the molecular level is governed by collisions between gas molecules and their interactions with container walls. These collisions play a crucial role in determining macroscopic properties such as pressure, diffusion, and thermal conductivity. Key parameters such as collision diameter, collision number, and mean free path provide insight into the frequency and nature of these interactions.

Binary collisions, whether between identical or different molecules, influence transport phenomena in gases, while wall collisions help explain effusion and gas flow through small openings. The statistical distribution of molecular energies allows for the calculation of the fraction of molecules possessing energy above a given threshold, which is particularly important in reaction kinetics and thermodynamic studies.

Additionally, the principle of equipartition of energy provides a fundamental framework for understanding how energy is distributed among different degrees of freedom in gas molecules. This principle helps in determining the heat capacity of gases, linking microscopic molecular motion to macroscopic thermodynamic properties. This unit explores these concepts, offering a deeper understanding of gas dynamics and energy distribution.

3.3 Collision of Gas Molecules

Due to the random erratic motion, the molecules of a gas suffer continuous collisions among themselves and with the walls of the container. We count the number of collisions among the molecules. A molecular collision may be a two body (i.e. binary; two molecule collide) or many body. But since the probability that the centres of three or more molecules comes at a particular point in space at a particular instant is very small, we consider only the binary collisions. The calculation of the binary molecular collisions is important because: It helps calculating the rate of chemical reactions in the gas phase. It helps calculating the mean free path of the molecules in a gas.

3.4 Collision diameter

The kinetic Theory of gases treats molecules as point masses. When two such molecules approach each other, a point is reached at which the mutual repulsion between the molecules becomes so strong that it causes reversal of the direction of their motion. The distance between the centers of the two molecules at the point of their closest approach is known as collision diameter. It is represented by sigma (σ). Evidently, a gaseous molecule can be regarded as a rigid (or hard) sphere of radius σ. The volume $\frac{4}{3}\pi\sigma^3$ is known as the effective volume of the molecule.

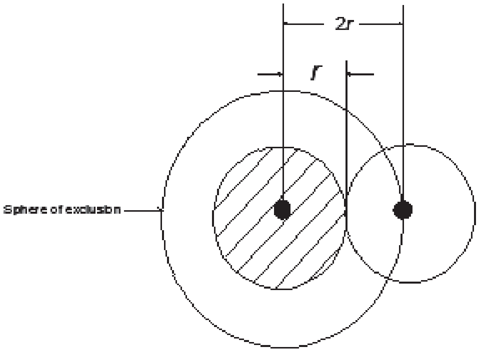


Fig. (a) Actual Collision

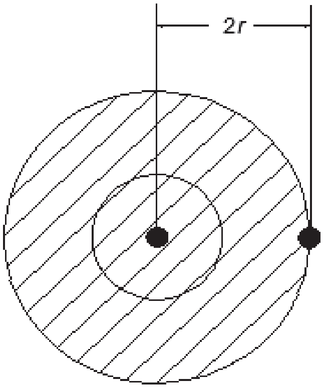


Fig. (b) Sphere of exclusion

If the distance between the centres of two molecules is less than σ, there would be a collision between them. Thus, collision is an event in which the centres of two identical can be easily visualised that when two molecules come within a distance σ from each other.

3.5 Collision Number

The model of gaseous molecules as hard, non-interacting spheres of diameter σ can satisfactorily account for gaseous properties such as the transport properties (viscosity, diffusion, thermal conductivity), The mean free path and the number of collisions the molecules undergo. It can easily be visualised that when two molecules collide, the effective area of the target is $\pi\sigma^2$. The quantity $\pi\sigma^2$ is called the collision cross-section of the molecule into which the centre of another molecule cannot penetrate.

3.6 Collision Number

In a gas the number of molecules with which a single molecule will collide per unit time is given by $\sqrt{2}\pi\sigma^2 < c > \rho$ where ρ is the number density i.e number of molecules per unit volume of the gas. This expression gives the number of collisions suffered by a single molecule per unit time per unit volume of the gas. This is known as the collision number.

$$Z_1 = \sqrt{2}\pi\sigma^2 < c > \rho$$

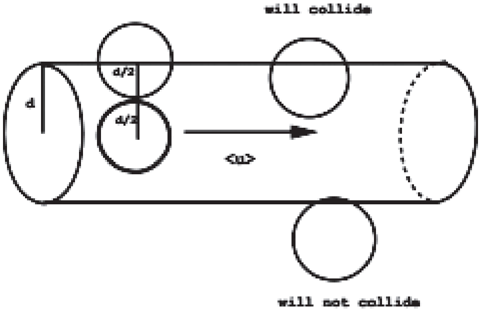
The total number of molecules colliding per unit time per unit volume of the gas is, therefore, given by $\sqrt{2}\pi\sigma^2 < c > \rho^2$. Since each collision involves two molecule, the number of collisions of like molecular occurring per unit volume of the gas is given by

$$Z_{11} = \frac{1}{2}\left(\sqrt{2}\pi\sigma^2 < c > \rho\right)$$

$$Z_{11} = \frac{1}{\sqrt{2}}\pi\sigma^2 < c > \rho^2 \qquad = \frac{1}{\sqrt{2}}\pi\sigma^2 < c > \frac{(P)^2}{(kT)^2}$$ = Units of collision number is s^{-1}

3.7 Frequency of binary collisions

The number Z_{11} in the above equation gives collision frequencyof the gas. Thus collision frequency is thenumber of molecular collisions occur ring per unit time per unit volume of the gas.



The number of collisions of molecules of type 1 with type 2 given by $Z_{12} = \frac{1}{\sqrt{2}} \pi\sigma^2 < c > \rho_1\rho_2$ where ρ_1 and ρ_2 are the number of densities of the molecules 1 and 2 respectively. The number density ρ is equal to $\frac{P}{kT}$,

For ideal gas PV=nRT n is number of mole, $PV = \frac{N}{N_A} RT = N\frac{R}{N_A} T = Nk_B T$

$P = \frac{NkT}{V}$ hence $\rho = \frac{N}{V}$. Thus $P = \rho kT$ and $\rho = \frac{P}{kT}$

$$Z_1 = \sqrt{2}\pi\sigma^2 < c > \rho = \sqrt{2}\pi\sigma^2 < c > \frac{P}{kT} \text{ collision number.}$$

Since the number of collision is counted twice, the number of binary collision between different molecules of two different gases A and B per unit volume per sec is given by

$$Z_{11} = \frac{1}{2}\sqrt{2}\pi\sigma^2 < c > \rho^2$$

$$Z_{11} = \frac{\pi\rho^2 < c > P^2}{\sqrt{2(kT)}^2} \text{ units of collision frequency } s^{-1}m^{-3}.$$

Frequency of Binary collision between Molecules of Different gases

Let us consider a mixture of two different gases containing respectively n_A and n_B number of molecules per unit volume at temperature T and pressure P. Molecular masses m_A and m_B. Molecular diameter σ_A, σ_B. As collision between the molecules of A and B gases may occur at any angle, the average angle of collision considered as 90°. If average velocities $\langle c_A \rangle, \langle c_B \rangle$ then for 90° collision the average relative velocity of A with respect to B is given by.

$$< c_{rel} >= \sqrt{\langle c_A \rangle^2 + \langle c_B \rangle^2} = \sqrt{\frac{8kT}{\pi}\left(\frac{1}{m_a} + \frac{1}{m_B}\right)} = \sqrt{\frac{8kT}{\pi\mu}}$$

Where $\frac{1}{\mu}=\frac{1}{m_A}+\frac{1}{m_B}\mu m=\frac{m_1 m_2}{m_1+m_2}=\frac{M_A M_B}{N_A^2}\times\frac{N_A}{M_A+M_B}=\frac{M_A M_B}{N_A(M_A+M_B)}$ and is called reduced mass of the two colliding molecules.

To find out the number of collisions of $(\sigma_A+\sigma_B)/2$ from the centre of the given A molecule with B molecules per sec.instead of considering both the types of molecules are moving. All the B molecules are stationary and A molecules are moving, it isequivalent to consider that B molecules are stationary and a molecules are moving with velocity crel,av.

Hence all the B molecules present in the cylinder of radius $(\sigma_A+\sigma_B)/2$ and length $\text{Crel, av} = <\text{Crel}>$ suffer collisions with the A molecule passing along the axis of the cylinder in a sec. Therefore, the number of collisions suffered by one A molecule per sec with B molecules.

$$=\pi\left(\frac{\sigma_A+\sigma_B}{2}\right)\left\langle C_{rel}\right\rangle n_B$$

$$=\pi\left(\frac{\sigma_A+\sigma_B}{2}\right)^2\sqrt{\frac{8kT}{\pi\mu}}n_B=\pi(\sigma_A+\sigma_B)^2\frac{1}{4}\sqrt{\frac{8kT}{\pi\mu}}n_B$$

$$=(\sigma_A+\sigma_B)^2\sqrt{\frac{8\pi^2 kT}{16\pi\mu}}n_B$$

$$=(\sigma_A+\sigma_B)^2\sqrt{\frac{\pi kT}{2\mu}}n_B$$

So the total number of collisions between A and B molecules per unit volume per sec

$$=(\sigma_A+\sigma_B)^2\sqrt{\frac{\pi kT}{2\mu}}n_B n_A$$

Since the number of collision is counted twice , the number of binary collision between different molecules of two different gases A and B per unit volume per sec is given by

$$Z_{AB} = \frac{1}{2}\left(\sigma_A + \sigma_B\right)^2 \sqrt{\frac{\pi kT}{2\mu}} n_B N_A$$

$$Z_{AB}\,(\text{w,r,t to radius}) = N_A N_B (r_A + r_B)^2 \pi \sqrt{\frac{8kT}{\pi\mu_{AB}}} = N_A N_B\,(r_A + r_B)^2 \sqrt{\frac{8\pi kT}{\mu_{AB}}}$$

Variables that affect Collisional Frequency

Temperature: As is evident from the collisional frequency equation, when temperature increases, the collisional frequency increases.

Density: From a conceptual point, if the density is increased, the number of molecules per volume is also increased. If everything else remains constant, a single reactant comes in contact with more atoms in a denser system. Thus if density is increased, the collisional frequency must also increase.

Size of Reactants: Increasing the size of the reactants increases the collisional frequency. This is directly due to increasing the radius of the reactants as this increases the collisional cross section. This in turn increases the collisional cylinder. Because radius term is squared, if the radius of one of the reactants is doubled, the collisional frequency is quadrupled. If the radii of both reactants are doubled, the collisional frequency is increased by a factor of 16.

3.8 Mean Free Path

The mean free path is defined as the distance a particle will travel, on average, before experiencing a collision event. This is defined as the product of the speed of a particle and the time between collisions.

λ is defined as the mean distance travelled by a gas molecule between two successive collisions.

$$\lambda = \frac{<c>}{Z_1} = \frac{<c>}{\left(\sqrt{2}\right)\pi\sigma^2 <c> P/kT} = \frac{kT}{\left(\sqrt{2}\right)\pi\sigma^2 P}$$

Following are the features of mean free path:

- Mean free path is inversely proportional to the macroscopic collision cross section.
- Since the unit of macroscopic collision cross section is the reciprocal of the unit of length, the unit of mean free path is the unit of length.
- Mean free path does not depend upon the molecular speed.
- Mean free path increases as pressure is decreased.

Example 3.1 A cylinder containing hydrogen at 400 K, 1 atm is placed in an evacuated chamber. If a hole of area 0.03mm2 is made in the cylinder. Calculate the number of molecules leaking through the hole per second. Take the average velocity of the molecules as 0.725 of the rms speed

PV=NKT

$$n = \frac{N}{V} = \frac{P}{KT} = \frac{1.01325 \times 10^{5}}{1.38 \times 10^{-23} \times 400}$$

$$1.83 \times 10^{25}\,\text{moleculed} / \text{m}^{3}$$

$$V_{rmc} = \left[\frac{3KT}{m}\right]^{1/2}$$

$$= \left[\frac{3 \times \left(1.38 \times 10^{-23}\right) \times 400}{3.32 \times 10^{-27}}\right]^{\frac{1}{2}}$$

$$= 2233.3\,{}^{m}\!/_{s}$$

$$\bar{v} = 0.725 \times 2233.3 = 1619.14\,{}^{m}\!/_{s}$$

Rate of flux of molecules per unit area

$$= \frac{1}{4} n \bar{v}$$

$$= \frac{1}{4} \times 41.83 \times 10^{25} \times 1619.14$$

$$= 2.96 \times 10^{28} \text{ molecules}/\text{m}^3\text{s}$$

Rate of hydrogen leakage through the hole

$$= 2.96 \times 10^{28} \times 0.03 \times 10^{-6}$$

$$= 8.88 \times 10^{20} \text{ molecules}/\text{s}$$

3.9 Calculation of number of molecules having energy $\geq \varepsilon$

$$f(\varepsilon') = \frac{N(\varepsilon')}{N} = \int_{\varepsilon'}^{\infty} f(\varepsilon)d\varepsilon = \left(\frac{1}{\pi k_B T}\right)\frac{1}{2}\int_{\varepsilon'}^{\infty} \varepsilon^{-\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

Let $\varepsilon = k_B T x^2$, then $d\varepsilon = 2k_B T\ x dx$. When $\varepsilon = \varepsilon'$, $x = \sqrt{\frac{\varepsilon'}{k_B T}}$ and as $\varepsilon \to \infty$ then $\to \infty$

Therefore $$\frac{N(\varepsilon')}{N} = \left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} e^{-x^2} \times 2k_B T \ \ x \ \ dx$$

$$\frac{N(\varepsilon')}{N} = \frac{2}{\sqrt{\pi}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} dx = \operatorname{erfc}\left(\sqrt{\frac{\varepsilon'}{k_B T}}\right)$$

In a special case when $\varepsilon' >> k_B T, \operatorname{erfc}\left(\sqrt{\frac{\varepsilon'}{k_B T}}\right) \to 0$ and hence $\frac{N(\varepsilon')}{N} \to 0$

With the increase in temperature average kinetic energy increases and hence fraction of molecules having kinetic energy $\varepsilon \geq \varepsilon'$ increases. This is significant when we consider rate of a gas phase reaction. For a reactant molecule to be transformed into a product it has to cross the activation energy barrier. Hence the rate of reaction should be proportional to that fraction of reactant molecules which has energy $\varepsilon \geq E_{act}$ Eact, the activation energy. Consequently the rate of reaction increases with increase in pressure

Fraction of molecules having Kinetic energy $\Phi \geq \Phi'$ in two dimensions

$$f(\varepsilon') = \frac{N(\varepsilon')}{N} = \int_{\varepsilon'}^{\infty} f(\varepsilon)d\varepsilon$$

$$= \left(\frac{1}{k_B T}\right)\int_{\varepsilon'}^{\infty} e - \frac{\varepsilon}{k_B T} d\varepsilon$$

$$\frac{N(\varepsilon')}{N} = \frac{1}{k_B T}\left[\frac{e - \frac{\varepsilon}{k_B T}}{-\frac{1}{k_B T}}\right]_{\varepsilon' = }^{\infty} e - \frac{\varepsilon'}{k_B T}$$

Fraction of molecules having Kinetic energy $\Phi \geq \Phi'$ in three dimensions

$$f\left(\varepsilon'\right) = \frac{N(\varepsilon')}{N} = \int_{\varepsilon'}^{\infty} f(\varepsilon')d\varepsilon$$

$$= 2\pi\left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}}\int_{\varepsilon'}^{\infty} \varepsilon^{\frac{1}{2}} e^{-\frac{\varepsilon}{k_B T}} d\varepsilon$$

Let $\varepsilon = k_B T x^2$, then $d\varepsilon = 2k_B T x dx$. When $\varepsilon = \varepsilon', x = \sqrt{\frac{\varepsilon'}{k_B T}}$ and as $\varepsilon \to \infty$, Therefore

$$f(\varepsilon') = \frac{N(\varepsilon')}{N} = 2\pi\left(\frac{1}{\pi k_B T}\right)^{\frac{3}{2}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} \left(k_B T x^2\right)^{\frac{1}{2}} \quad e^{-x2} \times 2k_B T \; xdx$$

$$= 2\pi\left(\frac{1}{\pi k_B T}\right)^{\frac{1}{2}} \left(k_B T\right)^{\frac{3}{2}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} \left(2^{x2}\right) \; e^{-x2} \; dx$$

$$= \frac{2}{\sqrt{\pi}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} (2^{x2}) \; e^{-x2} dx$$

$$= -\frac{2}{\sqrt{\pi}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} xd\left(e^{-x^2}\right) \quad \text{[Integrating by parts]}$$

$$= -\frac{2}{\sqrt{\pi}}\left[\left(xe^{-x^2}\right)^{\infty} \sqrt{\frac{\varepsilon'}{k_B T}} - \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} \frac{dx}{d(e^{-x^2})} e^{-x2} d(e^{-x2})\right]$$

$$= \frac{2}{\sqrt{\pi}}\left[-\sqrt{\frac{\varepsilon'}{k_B T} e - \frac{\varepsilon'}{k_B T}} - \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} e^{-x^2} dx\right]$$

$$= 2\sqrt{\frac{\varepsilon'}{\pi k_B T}} e^{-\frac{\varepsilon'}{k_B T}} + \frac{2}{\sqrt{\pi}} \int_{\sqrt{\frac{\varepsilon'}{k_B T}}}^{\infty} e^{-x^2} dx$$

$$= 2\sqrt{\frac{\varepsilon'}{\pi k_B T}}e^{-\frac{\varepsilon'}{k_B T}} + \mathrm{erfc}\left(\sqrt{\frac{\varepsilon'}{k_B T}}\right)$$

In a special case when $\varepsilon / >> K_B T$, then the second term involving co-error function becomes zero and we get $\{\mathrm{erfc}\left(\sqrt{\frac{\varepsilon'}{k_B T}}\right) \to 0\}$

$$\frac{N(\varepsilon')}{\pi k_B T} = 2\sqrt{\frac{\varepsilon'}{\pi k_B T}}e^{-\frac{\varepsilon'}{k_B T}}$$

The Gamma Function

The Gamma function introduced by Euler in the 1700s is the gamma function, and is defined by integral

$$\Gamma(n) = \int_0^\infty e^{-x} x^{n-1} dx \quad n > 0$$

Note that the integral is a function x and n, and the resulting integral is a function of n.

If $n \geq 2$, we can integrate $\Gamma(n)$ by parts : using e^{-x} dxdv and x^{n-1} as u

$$\left|\int udv = uv - \int vdu\right|$$

$$\Gamma(n) = [-x^{n-1\, e^{-x}}]_0^\infty + (n-1)\int_0^\infty x^{n-2} e^{-x} dx$$

$$\Gamma(n) = 0 + (n-1)\int_0^\infty x^{n-2} e^{-x} dx$$

$$\Gamma(n) = (n-1)\Gamma(n-1)$$

We can now write $\Gamma(n-1) = (n-2)\overline{)(n-2)}$ and so on, finally

$$\Gamma(n) = (n-1)(n-2).....\Gamma(1)$$

$$\Gamma(n) = (n-1)! \qquad \therefore \Gamma(1) = \int_0^\infty e^{-x}dx = 1$$

Up to this point the equation $\Gamma(1) = \int_0^\infty e^{-x}dx = 1$ is restricted to integer values of $n \geq 2$; but we can also define factorials for other values of n. For n = 1, $\Gamma(1) = 1 = 0!$, which is interesting.

For other values of n (non-integers). For n = $\frac{1}{2}\int_0^\infty e^{-x}x^{-\frac{1}{2}}dx$

Let x = u^2, then $x^{-1/2}$ dx =2 du

$$\Gamma\left(\frac{1}{2}\right) = 2\int_0^\infty e^{-u^2}du = \sqrt{\pi}$$

3.10 Degrees of Freedom

Degrees of freedom of a molecule may be defined as number of independent parameters which must be specified to describe the state or position of the molecule completely. Formula =3N, N is the number of atoms.

For a monoatomic gas, there will be 3 degrees of freedom, all of which are translational

For a diatomic molecule, gas, there will be six degrees of freedom. Out of these three will be translational, two will be rotational and one will be vibrational.

For a triatomic molecule , there will be nine degrees of freedom, of which three will be translational. That means there will be six degrees of freedom for the vibrational and rotational modes. Linear (CO_2) , there are two rotational degrees of freedom , four vibrational degrees of freedom. For Nonlinear tri-atomic molecule(H_2O) there will be three rotational and three vibrational degrees of freedom

In general, the number of vibrational degrees of freedom of a molecule containing N atoms.

(i) A linear molecule has (3N-5) vibrational degrees of freedom

(ii) A non-linear molecule has (3N-6) vibrational degrees of freedom

3.11 Principle of equipartition of energy

The theorem of equipartition of energy states that molecules in thermal equilibrium have the same average energy associated with each independent degree of freedom of their motion and that the energy is

$\frac{1}{2}kT$ per molecule

$\frac{1}{2}RT$ per Mole

k = Blotzmann's constant

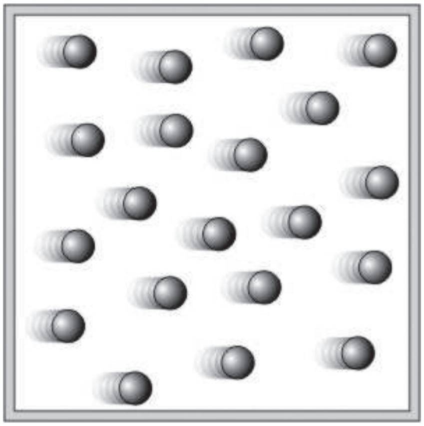
R = Gas constant

$\frac{3}{2}kT$

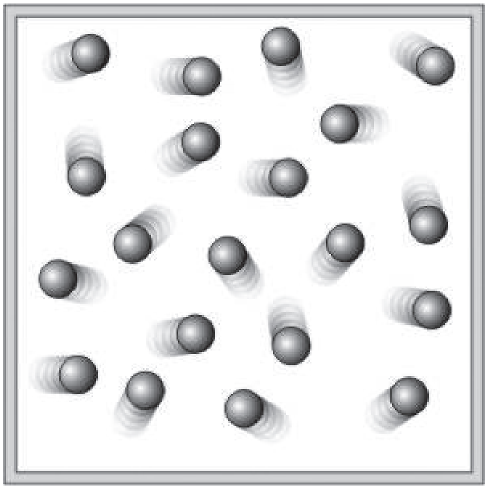
$\frac{3}{2}RT$

For three translational degrees of freedom, such as in an ideal monoatomic gas.

To give a rather contrived example, consider a container in which we have placed a number of ping-pong balls. Initially the balls are stationary. Imagine we now throw some energy randomly into our box, which will be shared out amongst the ping-pong balls in some way such that they begin to move about. While you might not realise it, intuitively you know what this motion will look like. For example, you would be very surprised if the particle motion looked like this:



You would probably predict something more like this:



i.e. completely random motion of the ping-pong balls. This is exactly the same result as predicted by the equipartition theorem - the energy is shared out evenly amongst the x, y, and z translational degrees of freedom.

The equipartition theorem can go further than simply predicting that the available energy will be shared evenly amongst the accessible modes of motion, and can make quantitative predictions about how much energy will appear in each degree of freedom. Specifically, it states that each quadratic degree of freedom will, on average, possess an energy ½kT. A 'quadratic degree of freedom' is one for which the energy depends on the square of some property. Consider the kinetic and potential energies associated with translational, rotational and vibrational energy.

Law of equipartition of energy: Statement

According to the law of equipartition of energy, for any dynamic system in thermal equilibrium, the total energy for the system is equally divided among the degree of freedom.

The kinetic energy of a single molecule along the x-axis, the y-axis and the z-axis is given as

$\frac{1}{2}mv_{x^2}$, along the x-axis

$\frac{1}{2}mv_{y^2}$, along the y-axis

$\frac{1}{2}mv_{z^2}$, along the z-axis

When the gas is at thermal equilibrium, the average kinetic energy is denoted as

$\left(\frac{1}{2}mv_{x^2}\right)$, along the x-axis

$\left(\frac{1}{2}mv_{y^2}\right)$, along the y-axis

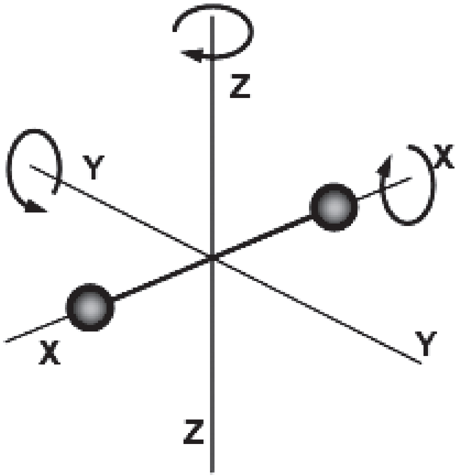
$\left(\frac{1}{2}mv_{z^2}\right)$, along the z-axis

According to the kinetic theory of gases, the average kinetic energy of a molecule is given by, $\frac{1}{2}mv_{rms^2} = \frac{3}{2}k_BT$ where V_{rms} is the root mean square velocity of the molecules, k_b is the Boltzmann constant and T is the temperature of the gas.

The mono-atomic gas has three degrees of freedom, so the average kinetic energy per degree of freedom is given by $KE_x = \frac{1}{2}k_BT$

If a molecule is free to move in space, it needs three coordinates to specify its location, thus, it possesses three translational degrees of freedom. Similarly, if it is constrained to move in a plane, it possesses two translational degrees of freedom and if it is a straight line, it possesses one translational degree of freedom. In case of a tri-atomic molecule, the degree of freedom is 6. And the kinetic energy of the per molecule of the gas is given as,

$$6 \times N \times \frac{1}{2}k_BT = 3 \times \frac{R}{N}Nk_BT = 3RT$$



Molecules of a mono-atomic gas like argon and helium has only one translational degree of freedom. The kinetic energy per molecule of the gas is given by

$$3\times N\times\frac{1}{2}k_BT = 3\times\frac{R}{N}Nk_BT = \frac{3}{2}RT$$

The diatomic gases such as O_2 and N_2 which have three translational degrees of freedom can rotate only about their centre of mass. Since, they have only two independent axis of rotation, as the third rotation is negligible, due to its 2-D structure. Thus, only two rotational degrees of freedom are considered. The molecule thus has two rotational degrees of freedom, each of which contributes a term to the total energy consisting of transnational energy t and rotational energy.

3.12 Heat Capacity of a Gas

Following the equipartition principle, the mean total energy of a molecule having *f* degrees of freedom is: $\varepsilon = \frac{f}{2}kT$ and the total energy of *N* molecules is

$$U = N\bar{\varepsilon} = \frac{f}{2}NKT = \frac{f}{2}n\bar{R}T$$

or, the molal internal energy, $u = \frac{f}{2}\overline{R}T$ and molal specific heat at constant volume

$$C_v = \left[\frac{\partial u}{\partial T}\right]_v = \frac{f}{2}\overline{R}$$

For an ideal gas

$$C_p - C_v = \overline{R}$$

$$C_p = \frac{f}{2}\overline{R} + \overline{R} = \frac{f+2}{1}\overline{R}$$

and

$$\gamma = C_p / C_v = \frac{f+2}{f}$$

It is to be noted that cv.cp and ? are all the constant and independent temperature. For a monatomic gas which has only transnational kinetic energy, f = 3. Thus,

$$u = \frac{3}{2}\overline{R}T,\ C_v = \frac{3}{2}\overline{R}, C_p = \frac{5}{2}\overline{R} \text{ and } \gamma = \frac{5}{3} = 1.67$$

A diatomic molecule is commonly pictured as having the dumbbell structure . Its moment of inertia about y and z axes is very much greater than that about x axis, and the latter is neglected.

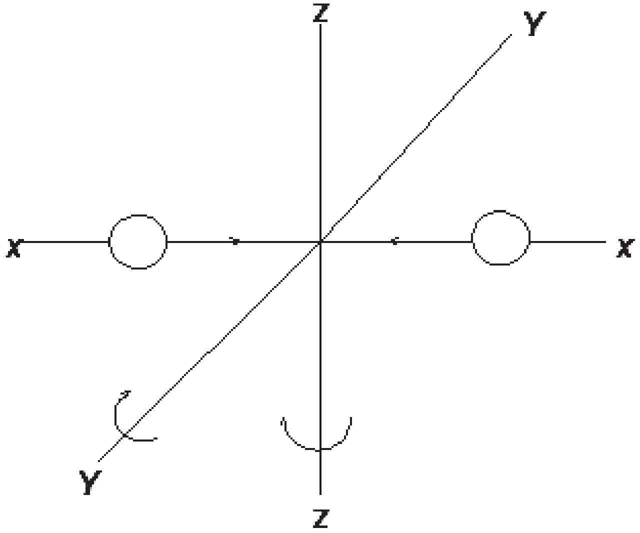


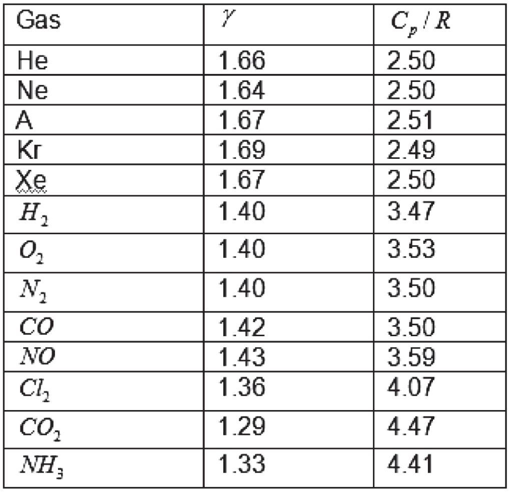
Fig. A diatomic molecule and its rotational and vibrational degree of freedom

The molecule has thus two rotational degrees of freedom. Since the atoms can also vibrate along the line joining them, the molecule has two vibrational degrees of freedom, one for kinetic energy and the other for potential energy, because the vibrational energy is partly kinetic and partly potential. A diatomic molecule is thus expected to have seven degrees of freedom (3 for translation, 2 for rotation and 2 for vibration). Thus,

$$f = 7, C_v = \frac{7}{2}\overline{R} \text{ and } \gamma = \frac{9}{7} = 1.29$$

These values do not tally with experimental results (ref: Table 4.5).

Table Experimentally measured values of C_p and γ of different gases at room temperature



Gas	γ	C_p/R
He	1.66	2.50
Ne	1.64	2.50
A	1.67	2.51
Kr	1.69	2.49
Xe	1.67	2.50
H_2	1.40	3.47
O_2	1.40	3.53
N_2	1.40	3.50
CO	1.42	3.50
NO	1.43	3.59
Cl_2	1.36	4.07
CO_2	1.29	4.47
NH_3	1.33	4.41

Much better agreement is achieved if f = 5. Then,

$$u = \frac{5}{2}\overline{R}, C_v = \frac{5}{2}\overline{R}, C_p = \frac{7}{2}\overline{R}, \text{and}\, \gamma = \frac{7}{5} = 1.40$$

This implies that at room temperature, the diatomic molecules possess either rotational or vibrational energy, but not both. At higher temperature, however, both of these modes become active. At very low temperature, c_v approaches $\frac{3}{2}\overline{R}$, suggesting that only translational motion is present. Minimum degree of freedom for a single molecule is f = 3, thus $\gamma = 1 + 2/3 = 1.67$. For heavy molecules the degree of freedom is large thus 2/f in the expression of ? approaches to 0 value. Hence γ must be between 1 and 1.67.

Molecular basis of Specific heats

Specific heat of a substance is defined as the quantity of heat required to raise the temperature of one gram of the substance through one degree kelvin.

Molar heat at constant volume- Heat energy required to raise the temperature of one mole of a gas through 1°C keeping the volume of the gas constant, is called heat capacity at constant volume.

Molar heat at constant pressure- Heat energy required to raise the temperature of one mole of a gas through 1°C keeping the pressure of the gas constant, is called heat capacity at constant pressure.

3.13 Summary

This unit explores the fundamental concepts of molecular collisions in gases, essential for understanding gas behavior at the microscopic level. It covers the collision diameter, which defines the effective size of gas molecules during collisions, and the collision number, representing the average number of collisions a molecule undergoes per unit time. The concept of mean free path is introduced to describe the average distance a molecule travels between successive collisions.

The unit also discusses the frequency of binary collisions, both for identical and different gas molecules, and explains wall collisions that determine gas pressure. The rate of effusion is analyzed based on molecular movement through small openings. The probability of molecules possessing energy greater than or equal to a given threshold $(\geq \varepsilon)$ is examined using the Maxwell-Boltzmann distribution.

Finally, the principle of equipartition of energy is introduced, which states that energy is equally distributed among all degrees of freedom in a system. This principle is applied to derive the heat capacities of gases, helping to explain the differences in heat capacity between monatomic, diatomic, and polyatomic gases.

3.14 Self-Assessment Questions

1. Define collision diameter and explain its significance in gas kinetics.
2. What is the mean free path of a gas molecule? Derive an expression for its calculation.
3. Differentiate between collision number and collision frequency in the kinetic theory of gases.
4. Derive an expression for the frequency of binary collisions between similar molecules.
5. How does the collision frequency change when considering collisions between dissimilar molecules?
6. Explain the concept of wall collisions and derive an expression for the rate at which molecules collide with the walls of a container.
7. What is effusion? State and derive the Graham's Law of Effusion.

8. Derive an expression for the rate of effusion of a gas through a small hole.
9. Explain the role of the Maxwell-Boltzmann distribution in determining the fraction of molecules with energy greater than or equal to a given value $(\geq \varepsilon)$.
10. Calculate the number of molecules having energy greater than ? in a gas sample using the Maxwell-Boltzmann distribution function.
11. Explain the Principle of Equipartition of Energy and how it applies to an ideal gas.
12. Derive expressions for the heat capacities (C_v and C_p) of a monatomic gas using the equipartition theorem.
13. How do the heat capacities of diatomic and polyatomic gases differ from those of monatomic gases? Explain using the equipartition theorem.
14. Discuss the effect of temperature on the degrees of freedom and heat capacities of gases.
15. A sample of oxygen gas (O_2) at a certain temperature has a mean free path of 8×10^{-8} m. If the molecular diameter of O_2 is 3×10^{-10}m, calculate the number density of the gas molecules.

Unit 4 ❐ Real Gases-I

Structure

4.1 Objectives

4.2 Introduction

4.3 Deviations from Ideal Behavior;

4.4 Causes of Deviation From Ideal Behaviour

4.5 van der Waals equation

4.6 Other Equation of States

4.7 Summary

4.8 Self-Assessment Questions

4.1 Objectives

After completing this unit, learners will be able to:

- Understand the limitations of the ideal gas law and the causes of deviations from ideal behaviour.
- Analyse Andrew's and Amagat's experimental plots to study the behaviour of real gases.
- Derive the van der Waals equation and explain its significance in describing real gas behavior.
- Interpret the features of the van der Waals equation and its corrections for intermolecular forces and molecular volume.
- Apply the van der Waals equation to explain real gas properties, including liquefaction and critical phenomena.
- Explore other equations of state that extend or modify the van der Waals model for real gases.

4.2 Introduction

The ideal gas law provides a simple mathematical relationship between pressure, volume, and temperature, but real gases often deviate from this behaviour under certain conditions.

These deviations arise due to intermolecular forces and the finite volume occupied by gas molecules, which the ideal gas model does not consider. Understanding these deviations is crucial for accurately describing gas behaviour in real-world applications, such as in high-pressure systems and low-temperature environments.

Experimental studies, including Andrew's and Amagat's plots, provide insights into the compressibility and phase transitions of gases, revealing their departure from ideality. To account for these deviations, van der Waals introduced a modified equation of state that incorporates corrections for molecular interactions and volume exclusion. This equation not only explains real gas behaviour but also provides a framework for understanding critical phenomena and gas liquefaction.

Beyond the van der Waals equation, several other equations of state have been developed to describe gas behaviour more precisely under extreme conditions. This unit explores the causes and nature of deviations from ideality, along with theoretical models that help bridge the gap between ideal and real gas behavior.

4.3 Deviation from Ideal Behaviour

In the nineteenth century, Andrews, Amagat, Regnault and others made extensive studies of the behaviour of many gases like H_2, O_2, CO_2, N_2, CH_4, etc. It was observed that these gases follow the kinetic equation, $PV = \frac{1}{3}mnc^2$ (and hence $PV = nRT$), only approximately. An ideal gas has therefore been defined as one which would strictly obey the kinetic gas equation ($PV = \frac{1}{3}mnc^2$) and thus conform to all the postulates of the theory. The gases, which we actually deal with, are hence non-ideal or real gases.

At a constant temperature, for a given mass of gas, the product PV should ideally remain constant, regardless of pressure. This implies that a plot of PV against P should yield a straight line parallel to the pressure axis. Amagat conducted extensive studies on this relationship for various gases at different constant temperatures.

Experimental PV-P curves, as illustrated in Figures 4.1, reveal deviations from this expected behaviour. At very low pressures (below 1 atm), the plots exhibit linearity but are not perfectly parallel to the pressure axis (Figure 4.1). At higher pressures, where variations are more pronounced, the PV-isotherms follow a distinct trend (Figure 4.1). Initially, the PV value decreases, reaches a minimum, and then increases, forming a characteristic U-shaped curve as pressure rises. This observed behaviour indicates a significant departure from ideal gas behaviour, highlighting the influence of intermolecular interactions at different pressure ranges. The curves in Fig. 4.1 reveal that at low pressures, the gases are more com-pressable than the ideal gases. At high pressures, the gases become less compressible than the ideal gases.

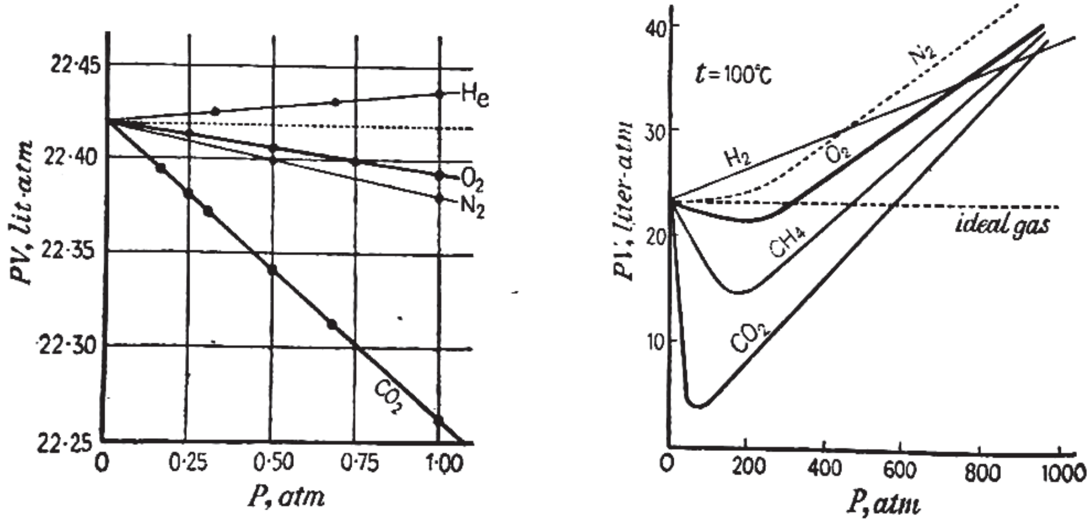


Figure 4.1: Plot of PV vs P plots for different gases at low pressure (left panel) and high pressure (right panel)

Variation of P with V: From the Boyle's law, the plot of pressure against volume (P-V plot) at a constant temperature should be a rectangular hyperbola. The historically famous experiments of Andrews on the study of P-V relations with carbon dioxide gas revealed considerable departure from the Boyle's law. The P-V curves were found to be as those represented in Figure 4.2. At higher temperatures, the isotherms look similar to those for ideal gases, though not strictly rectangular hyperbolas. At lower temperatures, the curves seem to consist of three parts, as at 13.1°C it is formed of PQ, QR and RS. We shall discuss these Andrew's curves in detail later. These show that real gases deviate from ideal behaviour.

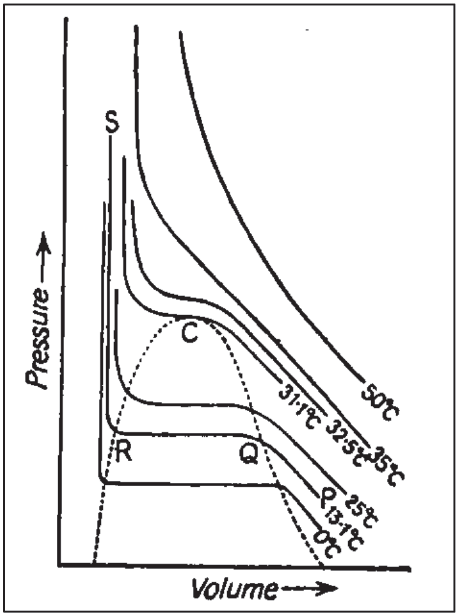


Figure 4.2: P-V plots for CO_2

On the kinetic theory Avogadro's law was based. At a constant temperature and pressure, one mole of any gas must have the same volume. Experimental values for the volume of a mole of different gases show that the volume is not constant. That is, PV = nRT is only approximately true.

4.4 Causes of Deviation from Ideal Behaviour

Now that the ideal gas laws have been shown to be only approximations, it is evident that some postulates of the kinetic theory are inadequate and require modification. The deviations from ideal behaviour arise primarily from two factors that were either overlooked or simplified in the theory:

The molecules were assumed to be perfectly elastic, and the existence of intermolecular attractive forces was neglected.

The molecules were considered as point masses with no volume, whereas, in reality, they occupy a finite volume.

The presence of intermolecular attractive forces is evident from the fact that gases condense into liquids upon cooling, where molecular cohesion becomes significant. This cohesion plays a crucial role in the liquefaction of gases, implying that attractive forces also exist in the gas phase. Further experimental evidence comes from the Joule-Thomson effect. When a stream of gas is passed through a porous plug made of cotton or earthenware, a temperature drop is observed. This cooling occurs because the outgoing gas molecules must overcome the attractive forces exerted by the molecules left behind, requiring them to perform work. The energy expended in overcoming these forces results in a temperature decrease. In an ideal gas, where intermolecular attractions are absent, no such cooling would be expected.

A portion of the total volume (V) of a gas is actually occupied by the molecules themselves. While this volume may be negligible at very low pressures, where V is large, it becomes more significant at ordinary pressures. In fact, under typical conditions, the space occupied by gas molecules accounts for approximately 0.1% of the total volume, making it non-negligible.

Additionally, intermolecular attractions reduce the frequency of molecular collisions with the container walls. If there were no such attractive forces, each molecule would collide with the walls more frequently. Consequently, the observed pressure (P) is lower than the pressure (P_0) the gas would exert if it were ideal and unaffected by intermolecular forces. If this reduction in pressure is denoted by P', then the ideal pressure is given by $P_0=P+P'$.

4.5 van der Waals Equation

The equation is named after Dutch physicist Johannes Diderik van der Waals, who first derived it in 1873 as part of his doctoral thesis. He won the 1910 Nobel Prize in Physics. van der Waals introduced two corrections for the pressure and volume term.

Pressure Correction, P'

In the interior of a gas, *a molecule is surrounded by other molecules on all sides*, experiencing equal attractive forces in all directions. As a result, there is no net force acting on the molecule. However, *when a molecule approaches the container wall, the distribution of surrounding molecules becomes asymmetrical*. Since there are more molecules in the bulk of the gas than in the direction of the wall (Fig. 4.3), the molecule experiences a stronger inward attraction from the gas molecules than from the relatively empty space near the wall.

This inward attraction slows down the molecule's motion towards the wall, reducing the number of collisions it makes with the surface per second. Since pressure depends on the frequency of molecular impacts on the walls, this reduction in collisions leads to a lower observed pressure than what would be expected for an ideal gas, where no intermolecular forces exist.

Thus, *the measured pressure of a real gas is lower than the pressure it would exert if intermolecular attractions were absent*. If one mole of gas occupies a volume V at an observed pressure P and temperature T, this deviation from ideal behaviour must be accounted for in the pressure correction.

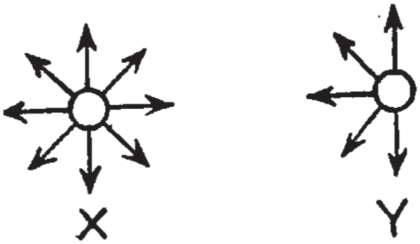


Figure 4.3: Forces on molecules of a gas

The attractive force exerted on a single molecule would obviously depend upon the number of molecules present in the bulk, hence on density (d) of the gas. Again, the number of molecules which would collide with the wall in unit time would also depend upon the density. Hence the total attractive force (P') which pulls the striking molecules backwards is proportional to the square of the density.

$$P' \alpha d^2 \alpha \frac{1}{v^2}$$

$$P' = \frac{a}{v^2} \qquad (4.1)$$

Here **a** is a constant. The quantity $\frac{a}{v^2}$ is the additional amount of pressure (P') to be added to the observed pressure P. This is usually called the internal pressure or cohesive pressure.

The ideal pressure should then be $P + P' = P + \frac{a}{v^2}$

Volume Correction, V':

In deriving the ideal gas equation, gas molecules were treated as point masses, implying that the entire volume V is available for their movement. However, in real gases, molecules have a finite size, reducing the actual space available for their motion.

Assuming gas molecules are spherical with radius r and diameter $\sigma = 2r$, the volume occupied by a single molecule is given by $b_1 = \frac{4}{3}\pi r^3$. When two molecules approach each other, the minimum distance between their centers is equal to ?, meaning they cannot come any closer. This effectively accounts for the repulsive forces that prevent molecules from overlapping.

As illustrated in Fig. 4.4, the presence of repulsive forces creates an excluded volume around each molecule. The space unavailable to a pair of colliding molecules is represented by a dashed circle with a diameter of 2δ. This excluded volume for the interacting pair is given by $\frac{4}{3}\pi(\sigma)^3$.

Then excluded volume for each molecules is $\beta = \frac{2}{3}\pi(\sigma)^3 = 4b_1$

For a mole of the gas, such excluded volume will be, $4N_0\, b_1$=b (say), which is a constant. The volume correction v' is thus b, which is equal to *four times the actual volume of the bodies of the molecules*. The observed volume should therefore be reduced by this amount (b) in computing the pressure of the gas. The volume V should be replaced by (V-b).

The equation of state, corrected for the two factors, takes the form,

$$\left(P + \frac{a}{v^2}\right)(v - b) = RT \qquad (4.2)$$

This is the van der Waals equation for 1 mole of gas. For n moles of gas

$$\left(P+\frac{n^2a}{v^2}\right)(V-nb)=nRT \qquad (4.3)$$

'a' and 'b' are called van der Waals constants; these are different for different gases. 'a' is expressed in atm-litre²-mole^{-2} and 'b' in litre-mole^{-1}. The values of a and b of some gases are given here.

Table : van der Waals constants [*a* in litre^2-atm mole^{-3}, *b* in litre-mole^{-1}]

Gas	H_2	O_2	N_2	CO_2	NH_3	CH_4	A	He
a	0.244	1.36	1.39	3.59	4.17	2.25	1.35	0.034
b	0.027	0.032	0.039	0.043	0.037	0.073	0.032	0.024

At extremely low pressures and very high temperatures, the volume will be very large, so that the terms (a/V^2) and b are relatively very small. Under such conditions real gases would behave ideally

Limitations of van der Waals equation

The van der Waals equation is an improvement over the ideal gas law as it accounts for intermolecular attractions and the finite volume of gas molecules. However, it has several limitations, including:

1. The van der Waals equation introduces two correction terms. These corrections are empirical and do not perfectly describe all real gases, especially at high pressures and low temperatures.
2. The equation does not accurately describe the behavior of gases near the critical temperature and pressure. It fails to predict the exact shape of the isotherms in this region, leading to deviations from experimental data.
3. The equation assumes that all gas molecules have the same size and experience the same intermolecular forces. In reality, different gases exhibit varying molecular interactions, which are not fully accounted for by a single set of aaa and bbb values.
4. At very high pressures, the equation does not accurately predict gas behavior because molecular interactions become complex and multi-body effects arise. The volume correction term assumes rigid, non-overlapping spheres, which is an oversimplification.

5. While the van der Waals equation predicts phase transitions, it does not provide an exact liquid-gas coexistence curve. The predicted values for critical constants often deviate from experimental values.
6. The equation does not consider anisotropic (non-spherical) molecular shapes or polarity, which affect intermolecular forces and real gas behavior. Gases like NH_3, H_2O, and CO_2 exhibit strong dipole or hydrogen bonding effects, leading to deviations from the equation's predictions.

Despite these limitations, the van der Waals equation provides valuable insight into real gas behavior and serves as the foundation for more refined equations of state, such as the Redlich-Kwong, Peng-Robinson, and virial equations.

Example 4.1: Calculate the pressure exerted by 1 mole of CO_2 gas at 300 K occupying a volume of 0.5 L. Given van der Waals constants for CO_2: $a = 3.59$ L² atm/mol², $b = 0.0427$ L/mol. Use $R = 0.0821$ L atm/mol K.

Solution: The van der Waals equation is: $\left(P+\frac{a}{v^2}\right)(v-b) = RT$

Substituting the given values:

$(P+14.36)\ (0.4573)=24.63$

$P+14.36=53.86$

$P = 39.5$ atm.

Example 4.2: Determine the molar volume of 1 mole of nitrogen gas (N_2) at 273 K and 10 atm. Given van der Waals constants for N_2: $a = 1.39$ L² atm/mol², $b = 0.0391$ L/mol. Use $R = 0.0821$ L atm/mol K.

Solution: The van der Waals equation is:

4.6 Other Equation of States

Many equations of state have been proposed over time, all seeking to address the same two limitations of the van der Waals equation: the simplified representations of intermolecular forces and the finite volume of molecules. A few notable examples are given here.

Dieterici equation: $P(V-b) = RTe^{\frac{-a}{RTV}}$

Berthelot equation: $\left(P+\frac{a}{TV^2}\right)(V-b)=RT$

Clausius equation: $\left(P+\frac{a}{T(V+C)^2}\right)(V-b)=RT$

Virial Equation: $PV=RT\left(1+\frac{B}{V}+\frac{C}{v^2}+..\right)B,C$ etc. are second, third virial coefficient etc.

4.7 Summary

This unit explores the deviations of real gases from ideal behavior and the underlying causes of these deviations. The limitations of the ideal gas equation arise due to intermolecular forces and the finite volume of gas molecules. Experimental observations, such as Andrew's and Amagat's plots, illustrate these deviations across different conditions of pressure and temperature.

To account for real gas behavior, van der Waals' equation is introduced, incorporating corrections for molecular attractions and volume. The derivation, key features, and applications of this equation are discussed, along with its ability to explain phase transitions and critical phenomena. Additionally, other equations of state, which further refine the description of real gases, are briefly introduced to highlight improvements over the van der Waals model. This unit provides a fundamental understanding of real gas behavior, bridging the gap between idealized assumptions and experimental observations.

4.8 Self-Assessment Questions

1. Why do real gases deviate from ideal behaviour? Explain the primary factors responsible for these deviations.
2. Describe Andrew's and Amagat's plots. How do these experimental curves provide evidence for the deviation of real gases from ideal gas behavior?

3. Derive van der Waals' equation for real gases, explaining the significance of the correction terms for pressure and volume.
4. Discuss the physical significance of van der Waals' constants a and b. How do they vary for different gases?
5. What are the limitations of van der Waals' equation? Why does it fail to accurately predict real gas behaviour under all conditions?
6. Compare and contrast the van der Waals equation with the ideal gas equation. Under what conditions does a real gas behave like an ideal gas?
7. Discuss other equations of state used to describe real gas behavior.
8. Carbon dioxide CO_2 gas (1 mole) is confined in a 5 L container at 300 K. Given that van der Waals constants for CO_2 $a = 3.59\ L^2\ atm/mol^2$, $b = 0.0427$ L/mol Calculate the pressure exerted by the gas using the van der Waals equation and compare it with the ideal gas law.

Unit 5 ❐ Real Gases-II

Structure

5.1 Objectives

5.2 Introduction

5.3 Compressibility factor, Z,

5.4 Boyle temperature

5.5 Critical States

5.6 Continuity of States

5.7 Critical Constants in terms of van der Waals Constants

5.8 Law of corresponding states

5.9 Intermolecular forces.

5.10 Summary

5.11 Self-Assessment Questions

5.1 Objectives

After completing this unit, learners will be able to:

- Define the compressibility factor (Z) and analyze its variation with pressure and temperature for different gases.
  Understand the concept of Boyle temperature and its significance in gas behaviour.
- Explain the critical state of a substance and the continuity of states in the context of phase transitions.
- Express critical constants in terms of van der Waals parameters and their relevance in describing real gases.
- Apply the law of corresponding states to compare the behaviour of different gases under similar reduced conditions.
- Understand the virial equation of state and its role in correcting deviations from ideal gas behaviour.

- Explore intermolecular forces, including Debye, Keesom, and London interactions, and their impact on gas properties.
- Gain an elementary understanding of the Lennard-Jones potential and its significance in modelling molecular interactions.

5.2 Introduction

Building upon the understanding of real gas behavior and deviations from ideality, this unit explores advanced concepts that further refine our description of gases under varying conditions. The compressibility factor (Z) serves as a key parameter in quantifying deviations from ideal gas behavior, with its variation providing valuable insights into the influence of pressure and temperature on different gases. The Boyle temperature marks the point where a gas behaves most ideally over a range of pressures, highlighting the interplay between intermolecular forces and thermal motion.

At extreme conditions, gases reach their critical state, a point beyond which distinct liquid and gas phases cease to exist. The continuity of states concept explains how gases and liquids transition smoothly under varying conditions. Critical constants, expressed in terms of van der Waals parameters, provide a quantitative understanding of this transition and are central to the law of corresponding states, which unifies the behavior of different gases under similar reduced conditions.

To account for real gas behavior more accurately, the virial equation of state introduces higher-order corrections beyond the van der Waals model. These corrections are closely linked to intermolecular interactions, which play a fundamental role in determining gas properties. Attractive and repulsive forces such as Debye (induced dipole), Keesom (dipole-dipole), and London (dispersion) interactions significantly influence gas behavior, as does the Lennard-Jones potential, which provides a theoretical framework for modelling molecular interactions.

This unit deepens our understanding of real gases by integrating thermodynamic, mathematical, and molecular perspectives, bridging the gap between theoretical models and experimental observations.

5.3 Compressibility factor, Z

Real gases do not obey the kinetic gas equation. Let us assume that, for real gases

$$PV = z.nRT$$

$$z = nRT/PV \qquad (5.1)$$

where z is a factor which accounts for and covers the departure of real gases from ideal behaviour, 'z' is called the compressibility factor. Since deviations from ideality vary under different conditions, the compressibility factor zzz changes accordingly. To illustrate the degree of non-ideality, z is plotted against pressure at various temperatures. Figure 5.1 and 5.2 displays the z-P isotherms for nitrogen, which follow the same general form as those of other gases, though their specific values differ.

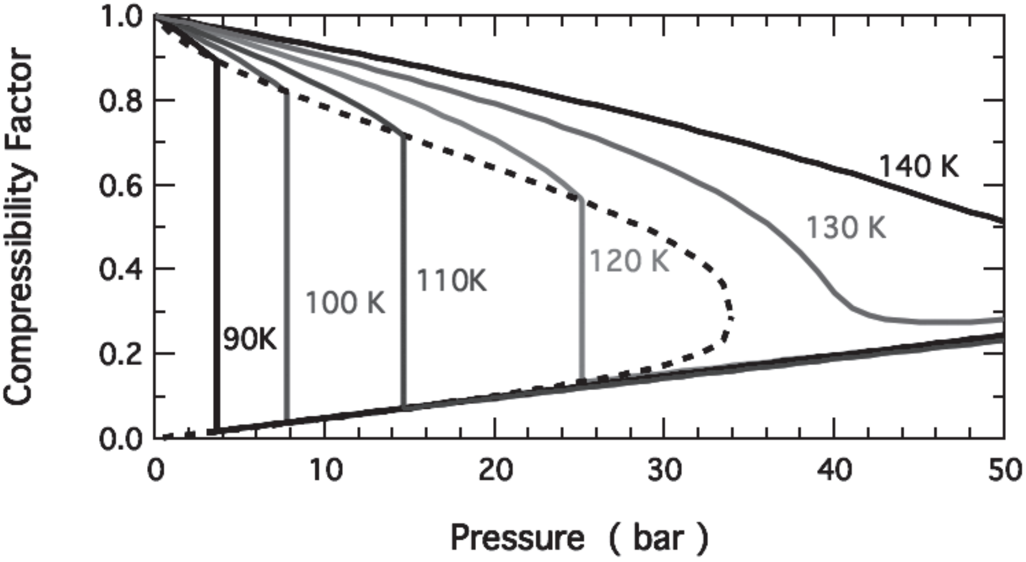


Figure 5.1: The pressure dependence of the compressibility factor for N_2 at low temperature.

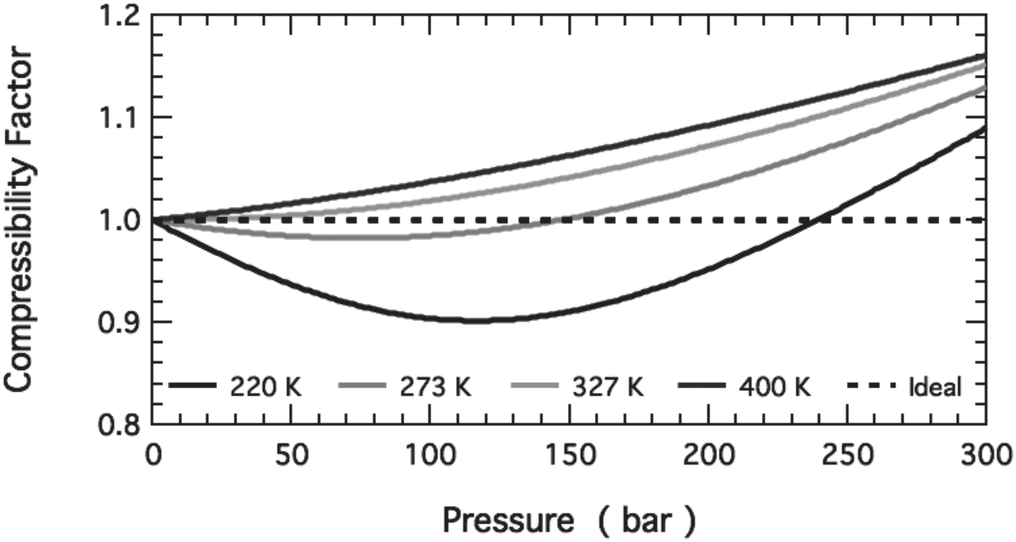


Figure 5.2: The pressure dependence of the compressibility factor for N_2 at high temperatures.

For an ideal gas at all pressures and temperatures, PV = nRT hence, z = 1. The z—P isotherms of all gases tend to unit value of z at extremely low pressures, Hence all gases tend to behave ideally at very low pressures. When PV < nRT, z is less than 1.0, hence z—p curve slopes downward at low ranges of pressure, showing the gas is more compressible than theoretically expected. When PV > nRT, z is greater than 1.0, indicating that the gas is less compressible than ideal gases. This is found in higher ranges of pressure. The curves also indicate that z depends both on pressure and temperature

The accuracy of the equation PV=nRT can be assessed by comparing the actual molar volume (Vm) of a gas to that of an ideal gas under the same temperature and pressure.

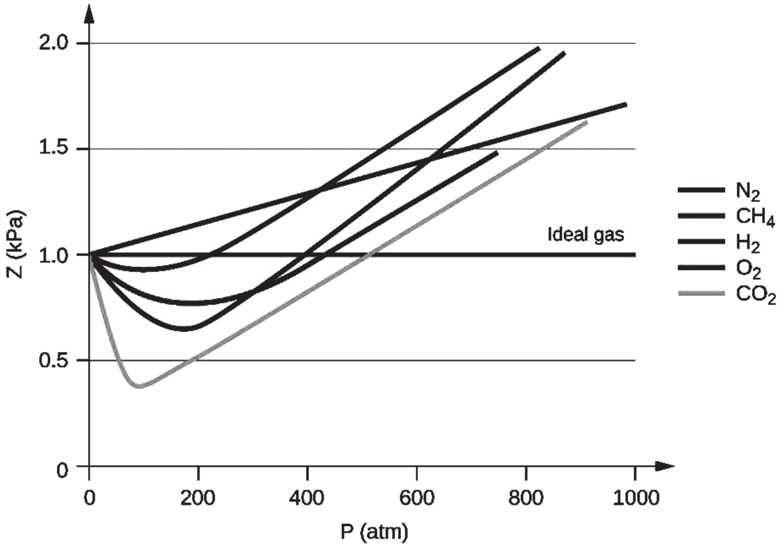


Figure 5.3: Compressibility factor (Z) vs. pressure curve for different gases.

For all of these gases, Z is practically equal to one at very low pressure. Real gases behave almost perfectly at low pressures (up to 10 atm). As the pressure rises, H_2 exhibits a steady increase in Z (from Z=1). As a result, the H_2 curve is higher than the ideal gas curve at all pressures. For N_2 and CO_2, Z decreases at first (Z<1) and finally increases with increasing pressure (Z>1). Because CO_2 is the most easily liquefied gas, it has the greatest drop in the curve.

Ideal gas particles have negligible volume and no intermolecular forces. Real gases approximate this behaviour at low pressures and high temperatures. However, at high pressures, reduced intermolecular spacing makes molecular volume significant, reducing compressibility and deviating from Boyle's law. Additionally, intermolecular attractions become more noticeable, lowering pressure at constant volume or reducing volume at constant pressure. These effects are more pronounced at low temperatures, where lower kinetic energy makes it harder for molecules to overcome attractive forces.

5.4 Boyle Temperature

Figure 5.4 illustrates the PV-P isotherms for carbon dioxide, which are representative of other gases. As the temperature increases, deviations from Boyle's law diminish, and the compressibility dips become shallower. The minima of these curves form a parabolic trajectory and approach the PV-axis at higher temperatures.

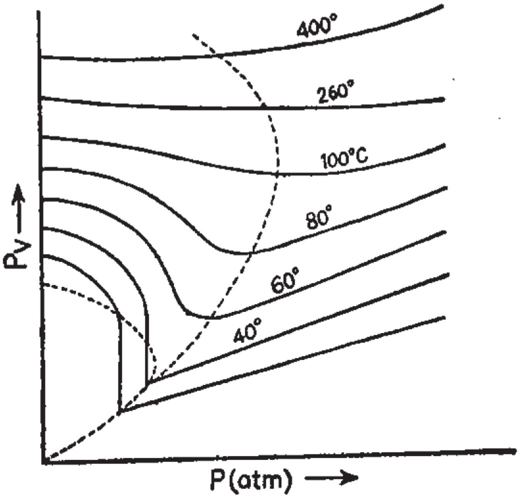


Figure 5.4: PV-P isotherm for CO_2

For each gas, there exists a characteristic temperature at which the PV-P curve remains nearly parallel to the P-axis over a broad pressure range. At this temperature, P remains nearly constant, meaning the gas closely follows Boyle's law within this range. This temperature is called the Boyle temperature (T_B).

Observing the compressibility factor (z) versus pressure plots, we find that for nitrogen at approximately 59°C, zzz remains close to unity from 0 atm to 80 atm, indicating near-ideal behavior. This temperature is the Boyle temperature of nitrogen.

The real gas equation can be expressed using the virial expansion

$$z = \frac{PV}{RT} = 1 + B(T)P + C(T)P^2 + ...$$

Where Z is the compressibility factor; B(T) is the second virial coefficient, which accounts for intermolecular interaction, C(T) is the third virial coefficient, and so on. At the Boyle temperature (T_B), the gas obeys Boyle's law over a range of pressures, meaning

$$\left(\frac{\partial z}{\partial P}\right)_{T=T_B}=0 \quad \text{at} \quad P\to 0 \tag{5.2}$$

Substituting the virial expansion

$$\frac{\partial}{\partial P}\left[1+B(T)\,P+C(T)P^2+...\right]=0$$

Evaluating at P=0, we get

$$B(T_B)=0$$

Thus, the Boyle temperature is the temperature at which the second virial coefficient B(T) vanishes

For van der Waals gases, the second virial coefficient is given by:

$$B(T)=b-\frac{a}{RT}$$

Setting $B(T_B)=0$, we solve for TB

$$T_B=\frac{a}{RB}$$

a and b are the van der Waals constants representing intermolecular attraction and finite molecular volume, respectively. R is the universal gas constant. Thus, the Boyle temperature depends on the intermolecular interactions of the gas.

5.5 Critical States

Gases are liquefied by lowering the temperature and increasing the pressure. As temperature is lowered the kinetic energy of the molecules decreases, the slow moving molecules come closer and they condense due to attraction. The increase of pressure has also the same effect. The influence of temperature is however more important. For every gas there is a temperature above which liquefaction is impossible whatever the pressure may be.

The limiting temperature above which liquefaction of a gas is impossible is called its *critical temperature* (Tc). Above the critical temperature the liquid state of the gas cannot exist. The *critical pressure* (Pc) is the minimum pressure required to liquefy the gas at the critical temperature, Tc. The volume occupied by a mole of the substance at the critical temperature and critical pressure is called its critical volume (Vc).

The idea of the critical state may be best explained from the classical experiments of Andrews (1869) on his investigations with carbon dioxide. He studied the P-V relations of this gas at different constant temperatures. He found that no liquefaction of carbon dioxide occurred above 31.1°C. Below this temperature, liquid carbon dioxide was formed under definite pressures. The critical temperature of carbon dioxide was thus 31.1°C

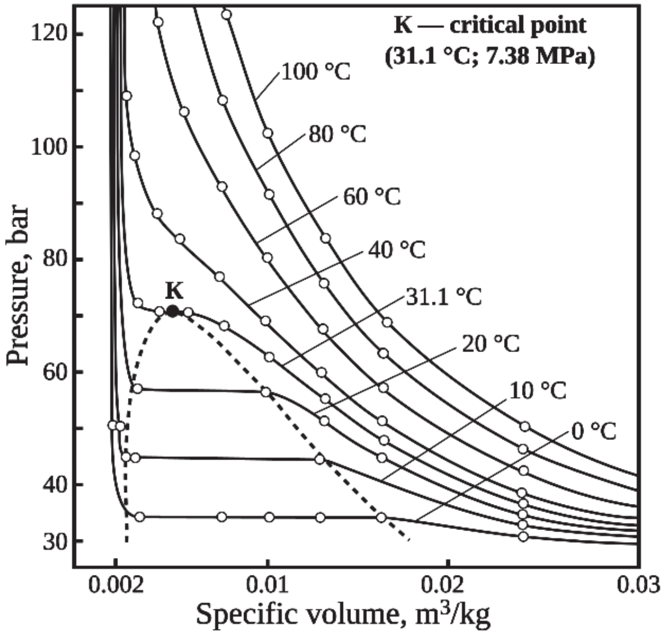


Figure 5.5: Carbon dioxide isotherms.

5.6 Continuity of States

An examination of the P-v isothermal at a temperature below the critical temperature may lead one to believe that since there are breaks and non-uniformity in the curve, the transformation of the gas into liquid would be a discontinuous one. But this is not so.

Consider the isotherm ABCD at T ° (< Tc). It is obvious that the substance is in the gaseous state at P and in the liquid state at S

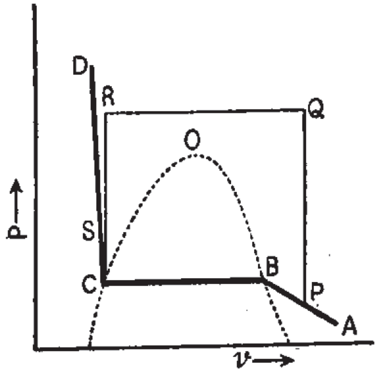


Figure 5.6: Continuity of States

Suppose the gas at P is raised in temperature at constant volume along PQ. From the point Q , the gas is gradually cooled at constant pressure along QR. The volume will be reduced considerably. On reaching R , the gas is again cooled at constant volume until the point S is reached. Nowhere in this process would liquid appear. At S, the system is a highly compressed gas. But we know from the isotherm that the system is in liquid state at the point S . Hence there is hardly any distinction between the liquid and the gaseous state. There is no line of demarcation or abrupt change between the two phases. This is known as the *continuity of state*. The transition of one state into another is practically imperceptible.

5.7 Critical Constants in terms of van der Waals Constants

The critical constants (Pc,Vc,Tc) of a gas are the values of pressure, volume, and temperature at the critical point, where the distinction between the liquid and gaseous phases disappears. These constants can be expressed in terms of the van der Waals constants (a and b), which account for intermolecular forces and molecular volume.

The van der Waals equation for a real gas is

$$\left(P+\frac{a}{V_m^2}\right)(V_m-b)=RT$$

Where P = pressure, Vm = molar volume, T = temperature, a and b = van der Waals constants, R = universal gas constant.

At the critical point, the isothermal compressibility vanishes

$$\left(\frac{\partial P}{\partial V_m}\right)_{T=T_c}=0$$

$$\left(\frac{\partial^2 P}{\partial V_m^2}\right)_{T=T_c}=0$$

1st Derivative Condition: Differentiating the van der Waals equation with respect to Vm

$$\frac{\partial}{\partial V_m}\left[\frac{RT}{V_m-b}-\frac{a}{V_m^2}\right]=0$$

Rearranging

$$T_c=\frac{8a}{27Rb} \qquad (5.3)$$

Differentiating again,

$$\frac{2RT}{(V_m-b)^3}-\frac{6a}{V_m^4}=0$$

Substituting Tc and solving for Vc

$$V_c = 3b \qquad (5.4)$$

Substituting Vc into the original van der Waals equation to find Pc

$$P_c=\frac{a}{27b^2} \qquad (5.5)$$

5.8 Law of corresponding states

The Law of Corresponding States states that all gases, when compared at the same reduced temperature, reduced pressure, and reduced volume, exhibit similar behavior regardless of their chemical identity. This principle allows for the generalization of thermodynamic properties across different gases.

The reduced variables are defined as

Reduced Pressure: $P_r = \frac{P}{P_c}$

Reduced Volume: $V_r = \frac{V}{V_c}$

Reduced Temperature: $T_r = \frac{T}{T_c}$

Using the van der Waals equation,

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT$$

we can express it in terms of reduced variables as:

$$\left(Pr + \frac{3}{V_r^2}\right)(3V_r - 1) = 8T_r \qquad (5.6)$$

This equation is universal, meaning that all substances (gases and vapours) obey this same equation in terms of their reduced variables.

5.9 Intermolecular forces

Intermolecular forces are attractive or repulsive forces between molecules that govern the physical properties of substances, such as boiling points, melting points, and solubility. These forces are weaker than chemical bonds but significant in determining the behavior of gases, liquids, and solids.

Types of Intermolecular Interactions

Debye Forces (Induced Dipole-Permanent Dipole Interaction)

These arise when a polar molecule (permanent dipole) induces a temporary dipole in a non-polar molecule due to electrostatic attraction. The strength of this interaction depends on the polarisability of the non-polar molecule and the dipole moment of the polar molecule. Example: Interaction between HCl (polar) and Ar (non-polar).

$$V_{\text{Debye}} = -\frac{\mu_2 \alpha}{4\pi\varepsilon_0 r^6} \qquad (5.7)$$

where: μ = dipole moment of the polar molecule, α = polarisability of the non-polar molecule, r = intermolecular distance, $\varepsilon 0$ = permittivity of free space.

Keesom Forces (Dipole-Dipole Interaction)

These forces occur between two permanent dipoles due to electrostatic attraction and repulsion. The strength of this interaction depends on the orientation and thermal motion of the molecules. Example: Interaction between HCl molecules.

$$V_{\text{Keesom}} = -\frac{\mu_1^2 \mu_2^2}{(4\pi\varepsilon_0)^2 k_B T r^6} \qquad (5.8)$$

where: $\mu 1, \mu 2$ = dipole moments of interacting molecules, kB = Boltzmann constant, T = temperature, r = intermolecular distance.

London Dispersion Forces (Induced Dipole-Induced Dipole Interaction)

Present in all molecules (polar and non-polar). Arises due to temporary dipoles created by electron movement. Weakest among van der Waals forces but significant in non-polar molecules like noble gases and hydrocarbons.

$$V_{\text{London}} = -\frac{3}{4}\frac{\alpha_1 \alpha_2 I_1 I_2}{(I_1 + I_2)(4\pi\varepsilon_0 r^6)} \qquad (5.9)$$

Where $\alpha 1, \alpha 2$ = polarisabilities of interacting molecules, I_1,I_2 = ionisation energies of the molecules.

Lennard-Jones Potential

It Describes the balance between attractive (van der Waals) and repulsive (Pauli repulsion) forces. Given by the Lennard-Jones 12-6 potential equation:

$$V(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (5.10)$$

where: ε = depth of the potential well (strength of attraction), σ = distance at which V(r)=0V(r) = 0V(r)=0, r = intermolecular distance.

5.10 Summary

This unit explores key concepts related to real gas behavior and intermolecular interactions. The compressibility factor (Z) quantifies deviations from ideal gas behavior, helping to assess non-ideality under varying conditions. Boyle temperature is the characteristic temperature at which a real gas obeys Boyle's law over a considerable pressure range. The concept of critical states defines the conditions at which gas and liquid phases become indistinguishable, while the continuity of states explains how phase transitions occur without abrupt changes under certain conditions. The critical constants (critical temperature, pressure, and volume) are expressed in terms of van der Waals constants, linking molecular interactions to macroscopic properties. The law of corresponding states states that all substances exhibit similar behavior when compared at their reduced state variables. Finally, intermolecular forces such as van der Waals interactions and the Lennard-Jones potential describe the fundamental attractive and repulsive forces governing gas behavior, influencing properties like compressibility and phase transitions.

5.11 Self-Assessment Questions

1. What is the compressibility factor Z, and how is it defined mathematically?
2. How does the value of Z indicate whether a gas behaves ideally or deviates from ideal behavior?
3. What is the Boyle temperature, and why is it significant in understanding real gas behavior?

4. How can the Boyle temperature be determined from a Z vs. P plot?
5. Define the critical temperature, critical pressure, and critical volume of a substance.
6. What happens to a substance at its critical point, and why is it important in phase transitions?
7. What is meant by the continuity of states, and how does it explain the transition between liquid and gas phases?
8. How does the concept of continuity of states challenge the traditional distinction between gases and liquids?
9. Express the critical temperature, pressure, and volume in terms of van der Waals constants aaa and bbb.
10. How do van der Waals constants account for intermolecular attractions and finite molecular volume?
11. State the law of corresponding states and explain its significance in the study of real gases.
12. What are reduced properties, and how are they used to compare different gases under similar conditions?
13. What are the three main types of van der Waals forces, and how do they differ?
14. Explain the Lennard-Jones potential and describe its significance in modeling intermolecular interactions.

Unit 6 ❐ The Liquid State: Surface tension

Structure

6.1 Objectives

6.2 Introduction

6.3 Surface tension and surface energy

6.4 Curved surfaces and Excess Pressure

6.5 Capillary action

6.6 Work of cohesion and adhesion

6.7 Surface Active Agents

6.8 Temperature dependence of surface tension

6.9 Methods of determination of surface tension

6.10 Summary

6.11 Self-Assessment Questions

6.1 Objectives

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

- Define and explain the concepts of surface tension and surface energy.
- Understand the molecular interpretation of surface tension and its role in various physical phenomena.
- Derive and explain the concept of excess pressure inside liquid droplets, bubbles, and capillaries.
- Describe contact angle and its significance in understanding wetting and adhesion properties.
- Explain the phenomenon of capillary action and derive the related equation.
- Differentiate between work of cohesion and work of adhesion and their applications.
- Understand the effect of curvature on vapour pressure and explain the Kelvin equation.
- Analyse the temperature dependence of surface tension and its practical implications.

- Discuss various experimental methods used for the determination of surface tension.

6.2 Introduction

Liquids exhibit unique properties at their surfaces due to the imbalance of intermolecular forces acting on surface molecules. This gives rise to surface tension, a fundamental property that influences various natural and industrial processes, such as the formation of droplets, capillary rise, and wetting behavior. Surface tension is closely related to surface energy, which quantifies the work required to create a new surface. The study of surface tension is crucial for understanding phenomena like excess pressure in droplets and bubbles, contact angle and wettability, and capillary action-all of which play significant roles in areas ranging from biology to engineering. This unit also explores the temperature dependence of surface tension and various experimental methods used to measure it, providing a deeper insight into liquid interfaces and their behavior.

6.3 Surface Tension and Surface Energy

Consider a liquid in contact with its vapour. A molecule within the bulk of the liquid experience equal attractive forces from all directions due to surrounding molecules, placing it in a uniform force field. However, a molecule at the surface is subject to a greater net attraction toward the liquid's interior, as the molecules in the vapour phase are more sparsely distributed (Fig. 6.1). This inward pull causes the liquid surface to contract naturally to minimize its area. The surface layer behaves like a stretched elastic membrane, creating a tendency for contraction. This phenomenon explains why small amounts of liquid, when left undisturbed-such as mercury droplets or raindrops-assume a spherical shape, as a sphere encloses the maximum volume with the least surface area.

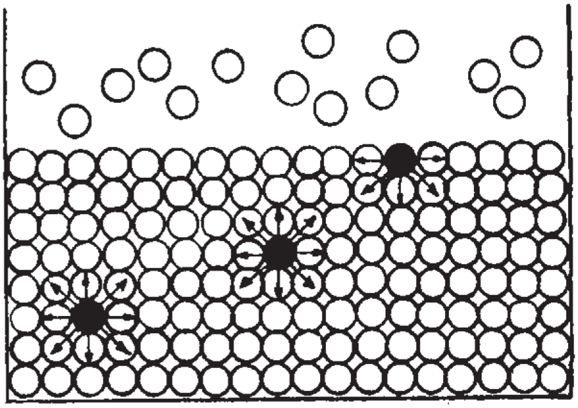


Figure 6.1: Forces on the molecules of a liquid

Now, since the surface is in a state of tension, an attempt to make a penetration along any line in the surface will require an application of force to pull apart the separate portions of the surface. This force is called the surface tension, denoted usually by the symbol γ.

The surface tension of a liquid is defined as the force acting at right angles to the surface along unit length of the surface.

Thus, the unit of surface tension is dyne per cm (or Newton per metre i.e., Nm^{-1} in the S.I. system). As a result of the inward pull on the molecules at the surface, the surface of the liquid tends to contract to the smallest possible area for a given volume of the liquid. It is for this reason that the drops of a liquid are spherical because for a given volume, a sphere has minimum surface area.

To increase the area of surface, some work has to be done against the inward pull. Consider a soap solution film contained in rectangular wire frame ABCD in which the side CD is movable (Fig. 6.2). In order to extend the surface area of the film, the movable wire has to be pulled from position CD to position EF. Thus, some work has to be done against surface tension.

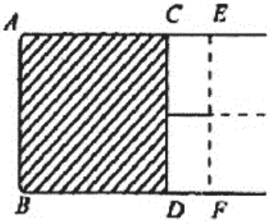


Figure 6.2: Concept of Surface Energy

The work required to be done to increase or extend the surface area by unit amount is called surface energy. The unit of surface energy is therefore joule per sq. metre in S.I. system.

In terms of dimensions, Surface energy = work per sq. cm. = (Force × length) per sq. cm = $\frac{\text{Newtown} \times \text{m}}{\text{m}^2}$ =Newton.m^{-1}. These units are the same as those of surface tension. Thus the surface energy is the same thing as surface tension

6.4 Curved surfaces and Excess Pressure

The tendency of a liquid to minimize its surface area often leads to the formation of a curved surface. A bubble is a thin liquid film enclosing vapour, and sometimes air, while a cavity is a vapour-filled void within a liquid. What are commonly referred to as "bubbles" in liquids are, in fact, cavities. True bubbles have two surfaces-one on each side of the enclosing film-whereas cavities possess only a single surface. Although the fundamental principles governing both are similar, the analysis of bubbles requires an additional factor of 2 to account for their doubled surface area.

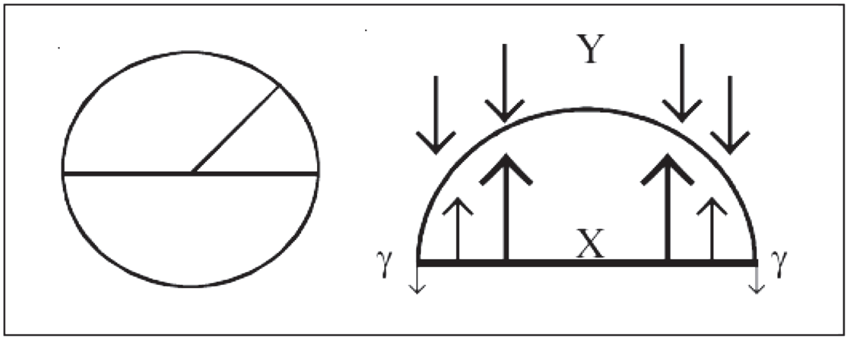


Figure 6.3: Excess Surface Pressure

A droplet is a small volume of liquid at equilibrium surrounded by its vapour (and possibly also air). The pressure on the concave side of an interface, P_{in}, is always greater than the pressure on the convex side, P_{out}. This relation is expressed by the Laplace equation.

(6.1)

r is the radius of curvature of the surface and γ is the surface tension. The Laplace equation indicates that the pressure difference across a curved surface approaches zero as the radius of curvature becomes infinite, which corresponds to a flat surface. Smaller cavities have smaller radii of curvature, resulting in a significant pressure difference across their surface. For example, a cavity (often mistaken for a bubble) with a radius of 0.10 mm in champagne creates a pressure difference of 1.5 kPa, sufficient to support a 15 cm column of water.

6.5 Capillary action

The rise of liquids in narrow tubes, known as capillary action, is a direct consequence of surface tension. When a glass capillary tube is immersed in a liquid that adheres to its walls, such as water, the liquid spreads into a thin film to minimize its energy. As this film advances up the inner surface, it causes the liquid inside the tube to form a curved meniscus. This curvature results in a pressure beneath the meniscus that is lower than the atmospheric pressure by approximately 2?/r, where r is the tube's radius, assuming a hemispherical surface. Outside the tube, just beneath the flat liquid surface, the pressure remains at P (atmospheric pressure). However, inside the tube, under the curved meniscus, the pressure is reduced to P - 2?/r. This pressure difference drives the liquid upward until hydrostatic equilibrium is established, ensuring equal pressures at the same depth.

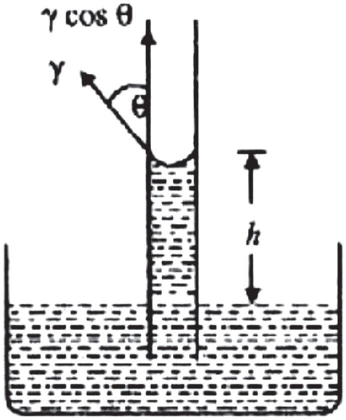


Figure 6.4: Capillary Action

To calculate the height to which the liquid rises, we note that the pressure exerted by a column of liquid of mass density ρ and height h is

$$P = \rho gh$$

This hydrostatic pressure matches the pressure difference $2\gamma/r$ at equilibrium. Therefore, the height of the column at equilibrium is obtained by equating $2\gamma/r$ and ρgh, which gives

$$h = \frac{2\gamma}{\rho gr} \qquad (6.2)$$

This simple expression provides a reasonably accurate way of measuring the surface tension of liquids. When the adhesive forces between the liquid and the capillary wall are weaker than the cohesive forces within the liquid, as in the case of mercury in glass, the liquid pulls away from the walls. This withdrawal creates a curved surface with the concave, high-pressure side facing downward. To maintain pressure equilibrium at the same depth throughout the liquid, the surface must lower to offset the increased pressure caused by its curvature. This adjustment leads to a capillary depression.

In many cases, the meniscus forms a nonzero angle with the wall, known as the contact angle (θ_c). To account for this, equation 17.40 should be modified by multiplying the right-hand side by cos θ_c. The contact angle arises from the balance of forces at the interface where the liquid meets the solid surface (Fig. 6.4). The equilibrium condition is determined by the interplay of surface tensions at the solid-gas (γsg), solid-liquid (γsl), and liquid-gas (γlg) interfaces, which represent the energy required to create a unit area of each interface. The vertical forces remain balanced when these tensions satisfy the appropriate equilibrium condition.

$$\gamma_{sg} = \gamma_{sl} + \gamma_{sg} \cos\theta_c$$

$$\cos\theta_c = \frac{\gamma_{sg} - \gamma_{sl}}{\gamma_{sg}} \qquad (6.3)$$

The liquid 'wets' (spreads over) the surface, corresponding to 0 < ?_c < 90°, The liquid does not wet the surface, corresponding to 90° < θ_c < 180°. For mercury in contact with glass, θ_c = 140°, indicating a relatively low work of adhesion of the mercury to glass on account of the strong cohesive forces within mercury.

6.6 Work of Cohesion and Adhesion

Adhesive Force

The force of adhesion, or adhesive force, refers to the attractive force that binds molecules of different substances together. This force plays a crucial role in various natural and industrial processes. For example, when a glass plate is dipped in water and then removed, a thin layer of water remains attached to the surface due to the adhesive force between water molecules and glass. Similarly, bricks are held together by mortar due to adhesive interactions, and electroplating relies on the adhesion of metal ions to a surface.

Adhesive forces also exist between gas molecules and the walls of the container in which they are enclosed. However, in the case of gases, these interactions are generally weak and do not significantly alter the net pressure of the gas inside the container. As a result, adhesive forces are usually neglected when analyzing the behaviour of gases.

Cohesive Force

The force of cohesion, or cohesive force, is the attractive force that holds molecules of the same substance together. This phenomenon, known as cohesion, is responsible for the structural integrity of solids and liquids. Cohesion arises due to intermolecular forces, which decrease rapidly as the distance between molecules increases. It is estimated that cohesive force varies inversely as the eighth power of the intermolecular distance, making it negligible when the separation is on the order of 10^{-7} cm.

In solids, cohesive forces are particularly strong, giving them a definite shape and rigidity. In liquids, cohesion is weaker, allowing molecules to move more freely, which gives liquids their fluid nature while still maintaining some structural integrity. However, in perfect gases, cohesive forces are practically nonexistent, allowing gas molecules to move independently without any significant intermolecular attraction.

Work of Adhesion:

Consider a column of unit cross-section of two immiscible layers of two liquids A and B. Let each of two liquids be separated by some hypothetical process producing two new interfaces each of unit cross-section, as shown in Fig. 6.5. Difference between the final and the initial free energies for this process

$$\Delta G = W_{AB} = \gamma_{\text{final}} - \gamma_{\text{initial}} = \gamma_A + \gamma_B - \gamma_{AB} \tag{6.4}$$

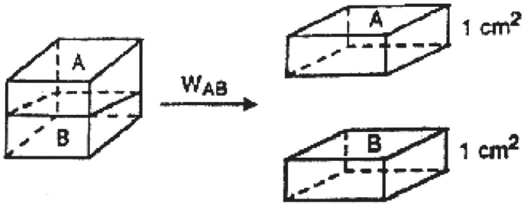


Figure 6.5: Adhesion and surface tension

W_{AB} is called work of adhesion. It is a measure of attraction between two different phases.

Work of Cohesion:

Consider a column of liquid of unit cross-section. It represents a volume element in an infinite volume of liquid. Suppose it is separated into two portions, each of unit cross-section, by some hypothetical process as shown in Fig. 6.6. For this process of producing two new interfaces of unit cross-section, change in free energy is given by

$$\Delta G = W_{AA} = 2\gamma_A \qquad (6.5)$$

This is work of cohesion, W_{AA} is the work required to pull a column of liquid apart. It is a measure of attraction between the molecules of two portions of the same kind of liquid.

6.7 Surface Active Agents

Certain substances, such as soaps, sulphonic acids, and organic compounds like methyl alcohol, ethyl alcohol, and acetone, have the ability to significantly reduce the surface tension of water, even when present in small amounts. These substances are known as surface active agents or surfactants. Their primary function is to alter the intermolecular forces at the interface between different phases, such as liquid-liquid or liquid-solid interactions.

One of the most common applications of surfactants is in detergents and cleaning agents. For example, when grease adheres to a fabric, water alone is ineffective in removing it because of its high surface tension, which prevents proper wetting of the greasy surface. However, when soap is added to water, it lowers the interfacial tension between water and grease. This allows the grease to disperse into the water in the form of micelles-small, spherical structures formed by soap molecules-making it easier to wash away the grease from the fabric.

Surfactants play a crucial role in numerous industries, including pharmaceuticals, cosmetics, food processing, and petroleum refining. They are also used in emulsification processes, foaming agents, and wetting agents, demonstrating their versatility in both industrial and everyday application

6.8 Temperature dependence of surface tension

Surface tension of liquids generally decreases with increase of temperature and becomes zero at the critical temperature. The decrease in surface tension with increase of temperature is obviously due to the fact that the kinetic energy of the molecules increases and therefore, the intermolecular attraction decreases. An important relationship between temperature and surface tension is as follows

$$\gamma\left(\frac{M}{D}\right)^{\frac{2}{3}} = k\left(t_c - t\right) \qquad (6.6)$$

where M = molecular mass of the liquid

D = density of the liquid at temperature t°C

t_c = critical temperature of the liquid

γ = surface tension (or surface energy) of the liquid at temperature t°C

k = a constant

6.9 Methods of determination of surface tension

We have already discussed about capillary rise. It is used for determining surface tension along with other methods.

Capillary Rise Method

A thoroughly cleaned capillary glass tube of uniform bore is kept partly immersed in the experimental liquid in a vertical position. The liquid rises in the tube and attains a particular height. The height h of the liquid from the surface of the bulk outside to the bottom of the meniscus is carefully measured with a travelling microscope. The radius r of the capillary tube is Ne predetermined by the usual method of inserting a weight.

The upper meniscus is concave and if θ_c be the angle of contact then, the vertical component of the surface tension (γ) will be y cos θ_c.. The radius of curvature of the concave meniscus may be taken to be the same as the radius of the capillary tube.

$$\gamma = \frac{\rho g r\left(h + \frac{1}{3}r\right)}{2\cos\theta_c}$$

Often $\theta_c \approx 0,$ hence

$$\gamma = \frac{\rho g r\left(h + \frac{1}{3}r\right)}{2}$$

Thus, the measurement of h and r with a knowledge of the density ρ will enable us to determine the surface tension. Since r is quite small, the expression used is

$$\gamma = \frac{\rho grh}{2} \qquad (6.7)$$

Determination of Surface Tension of a Liquid Using Stalagmometer

Drop weight method: This method is based upon the principle that the weight of drop falling slowly out of a capillary held vertically is directly proportional to its surface tension. Thus for two liquids, the drops of which fall almost at the same rate out of the same capillary

$$\frac{\gamma_1}{\gamma_2} = \frac{m_1}{m_2}$$

where γ_1 and m_1 are respectively the surface tension and weight of each drop of the first liquid and γ_2 and m_2 are the corresponding values for the second liquid. Thus knowing the surface tension of one of the liquids, that of the other can be determined. The apparatus used is called a stalagmometer and is shown in Fig. 6.6

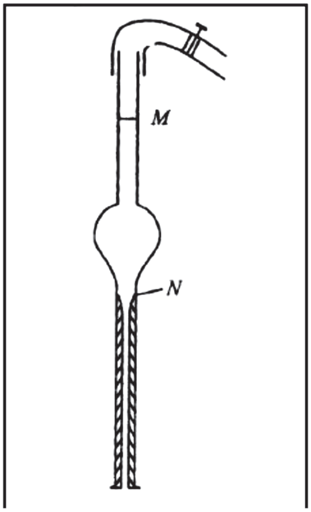


Figure 6.6: Stalagmometer

The procedure consists of the following steps :

(i) Stalagmometer is clamped vertically in a clamp stand and a rubber tube with a pinch cock is attached to the upper portion.

(ii) Distilled water is sucked into the apparatus and then the pressure adjusted with the help of pinch cock so that the rate of fall of drops is about 15-20 drops per minute.

(iii) 10 drops of water are allowed to fall into a clean weighing bottle which has already been weighed when empty. The weight of the weighing bottle alongwith the drops is taken.

(iv) The apparatus is now rinsed with acetone and then allowed to dry.

(v) Now, the experimental liquid is sucked into the stalgmometer, the rate of fall of drops adjusted as before and 10 drops of the liquid taken into the empty weighing bottle and the bottle weighed.

Calculation:

Suppose weight of empty bottle = w_1g

Weight of bottle + 10 drops of water = w_2 g

Weight of bottle +10 drops of liquid = w_3g

Weight of 10 drops of water = $(w_2 - w_1)$g

Weight of 10 drops of liquid = $(w_3 - w_1)$

If γ_w is surface tension of water, then the surface tension of the experimental liquid, γ_l is given by

$$\frac{\gamma_l}{\gamma_w} = \frac{w_3 - w_1}{w_2 - w_1} \qquad (6.8)$$

Knowing γ_w, γ_l can be calculated.

6.10 Summary

This unit explores the fundamental concepts of surface tension and surface energy, explaining their molecular origins and effects. The discussion includes excess pressure in curved liquid surfaces, the role of contact angle in wetting and adhesion, and the phenomenon of capillary rise. The difference between cohesive and adhesive forces is highlighted, along with their implications in surface interactions. The unit also examines how surface tension varies with temperature and how it influences vapour pressure over curved surfaces. Finally, different experimental techniques for measuring surface tension, such as the drop weight method and capillary rise method, are discussed. This knowledge is essential for understanding interfacial phenomena in both natural and applied sciences.

6.11 Self-Assessment Questions

1. Define surface tension and surface energy. How are they related?
2. Explain the molecular origin of surface tension and why it decreases with an increase in temperature.
3. What is excess pressure in a liquid droplet? Derive the expression for excess pressure inside a spherical liquid drop and a soap bubble.
4. Define contact angle and explain how it determines the wetting behavior of a liquid on a solid surface.
5. Differentiate between work of cohesion and work of adhesion with examples.
6. Explain capillary action and derive Jurin's law for capillary rise.
7. What is the effect of temperature on surface tension? How does it influence the shape of liquid droplets?
8. Describe two experimental methods used to determine surface tension.
9. Discuss the effect of curvature on vapour pressure and derive the Kelvin equation.
10. A soap bubble has a radius of 2 mm. If the surface tension of the soap solution is 0.072 N/m, calculate the excess pressure inside the bubble.
11. A liquid rises to a height of 5 cm in a capillary tube of 0.5 mm radius. If the contact angle is zero and the density of the liquid is 1000 kg/m^3, calculate the surface tension. (Take g = 9.81 m/s^2)
12. The surface tension of water at 25°C is 0.072 N/m. Calculate the work required to increase the surface area of a soap film by 50 cm^2.

13. A spherical water droplet of radius 1 mm evaporates completely. If the surface tension of water is 0.072 N/m, calculate the work done during the process.

14. A capillary tube of radius 0.3 mm is dipped in a liquid of density 800 kg/m³ and surface tension 0.05 N/m. Determine the height to which the liquid rises in the capillary.

Unit 7 ❐ The Liquid State: Viscosity

Structure

7.1 Objectives

7.2 Introduction

7.3 General features of fluid flow

7.4 Viscosity coefficient

7.5 Poiseuille's equation

7.6 Stoke's Law

7.7 Effect of Temperature and Pressure on Viscosity

7.8 Principle of Determination of Viscosity Coefficient

7.9 Summary

7.10 Self-Assessment Questions

7.1 Objectives

After completing this unit, learners will be able to:

- Distinguish between laminar and turbulent flow and describe their general characteristics in fluid dynamics.
- Understand Newton's equation for viscosity and its significance in defining the viscosity coefficient.
- Derive and apply Poiseuille's equation to describe the flow of liquids through narrow tubes.
- Explain Stoke's equation and its role in understanding the motion of spherical particles in a fluid.
- Analyse the effect of temperature and pressure on the viscosity of liquids and gases.
- Understand the principles and experimental methods used for determining the viscosity coefficient of fluids.

7.2 Introduction

Fluid flow plays a crucial role in various natural and industrial processes, from blood circulation in living organisms to the movement of liquids in pipelines. The study of fluid dynamics helps in understanding the behaviour of fluids under different conditions. One of the fundamental aspects of fluid flow is the distinction between laminar and turbulent flow, which influences the efficiency and stability of fluid transport.

Viscosity, a measure of a fluid's resistance to flow, is a key parameter in fluid mechanics. Newton's equation defines the viscosity coefficient, which characterizes the internal friction between fluid layers. Poiseuille's equation describes the flow of viscous liquids through narrow tubes, providing a mathematical foundation for applications in engineering and medicine. Additionally, Stoke's equation explains the motion of small spherical particles in a fluid, which is essential for understanding sedimentation and particle dynamics.

Temperature and pressure significantly affect the viscosity of both liquids and gases, influencing their flow properties in various environments. The accurate determination of viscosity coefficients is important for designing fluid systems, improving lubrication, and optimizing industrial processes. This unit explores these fundamental principles, offering a comprehensive understanding of fluid behaviour and viscosity.

7.3 General Features of Fluid Flow

Fluid flow, a subdiscipline of fluid mechanics, specifically addresses fluid dynamics, the study of fluids in motion. Fluids, encompassing both liquids and gases, exhibit flow behaviour when subjected to unbalanced forces. This motion persists as long as these forces remain unbalanced.

A common example illustrating fluid flow is the act of pouring water from a mug. The velocity profile of the water varies significantly throughout the process. At the lip of the mug, where the water is initially released, the velocity is at its maximum. As the water approaches the lip, its velocity decreases due to factors such as viscosity and the changing geometry of the flow path. Near the bottom of the mug, the water's velocity is minimal, approaching zero as it comes to rest.

The primary unbalanced force driving this flow is gravity. However, other forces also play a role. Viscosity, the fluid's resistance to flow, acts to slow the water down. Surface tension, particularly at the water-air interface, influences the shape and behavior of the water stream. Furthermore, pressure gradients within the fluid contribute to its acceleration and deceleration. The flow continues as long as a sufficient volume of water remains in the mug and the gravitational force, facilitated by the mug's tilt, overcomes resistive forces like viscosity.

Types of Fluid

1. Ideal fluid: A hypothetical fluid with no viscosity and incompressible, used for simplified fluid dynamics calculations; does not exist in reality.
2. Real fluid: Any fluid that exhibits viscosity and compressibility, encompassing all fluids found in nature (e.g., water, air, oil).
3. Newtonian fluid: A fluid where the shear stress is directly proportional to the rate of shear strain, with a constant viscosity (e.g., water, air).
4. Non-Newtonian fluid: A fluid where the shear stress is not directly proportional to the rate of shear strain, and viscosity can change with applied stress (e.g., ketchup, paint).
5. Ideal plastic fluid: A fluid that requires a certain amount of shear stress (yield stress) before it begins to flow, and then flows linearly with increasing shear stress. (ex: toothpaste, some thick muds).
6. Incompressible fluid: A fluid whose density remains constant regardless of pressure changes (e.g., liquids, especially water under typical conditions).
7. Compressible fluid: A fluid whose density changes significantly with pressure variations (e.g., gases, especially air).

Laminar Flow

Laminar flow is a type of fluid flow characterized by smooth, parallel layers of fluid. Laminar flow occurs when a fluid moves in parallel layers, with no disruption between the layers.

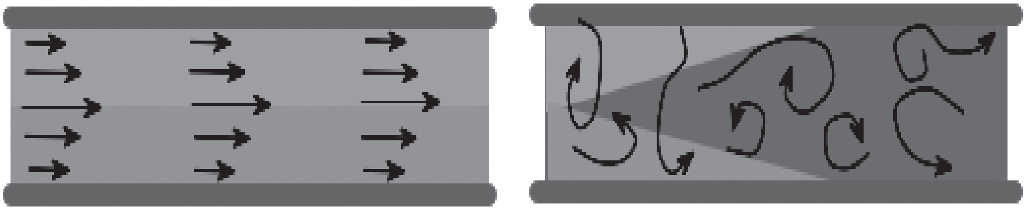


Figure 7.1: Laminar and turbulent flow

The key characteristics of laminar flow are

- Smooth, parallel layers of fluid motion.
- Minimal or no mixing between layers.
- Typically occurs at lower velocities.
- "Viscous forces dominate over inertial forces.

Laminar flow occurs in flow of viscous fluids (like honey or oil) at low speeds; flow in small-diameter pipes; blood flow in small blood vessels; laminar flow hoods used in clean rooms, and laboratories.

Turbulent Flow

Turbulent flow is a fluid motion characterized by chaotic and irregular changes in pressure and flow velocity. Turbulent flow is highly disorganized, with fluid particles moving in a seemingly random manner. It involves the formation of eddies (a circular movement of liquids), vortices, and swirls, which contribute to significant mixing within the fluid. Turbulent flow promotes a very high level of mixing within the fluid.

7.4 Viscosity and Viscosity coefficient

Viscosity in liquids arises from the internal friction caused by intermolecular forces. These forces, such as van der Waals forces and hydrogen bonding, create resistance to flow as layers of the liquid slide past each other. Specifically, molecules in a slower-moving layer exert attractive forces on molecules in a faster-moving layer, attempting to decelerate them. Conversely, faster-moving molecules pull on slower-moving ones, trying to accelerate them. This momentum exchange between layers results in a shear stress, a tangential force per unit area, that must be overcome to maintain a constant velocity gradient, or uniform flow.

This internal friction is temperature-dependent. As temperature increases, the kinetic energy of the molecules rises, weakening the intermolecular attractions and reducing viscosity. This is why liquids generally flow more easily when heated. The magnitude of viscosity is a measure of a liquid's resistance to deformation under shear stress, and it is a crucial property in various applications, from lubrication to fluid transport.

Definition of Coefficient of viscosity

The tangential force required to maintain uniform velocity will depend upon two factors

(i) Area of contact A between the two layers

(ii) Velocity gradient

Thus

$$F \infty A \frac{du}{dz}$$

$$F = \eta A \frac{du}{dz} \qquad (7.1)$$

Where ψ is known as the coefficient of viscosity. It is the tangential force that must be applied in order to maintain a velocity difference of unity between two parallel layers unit distance apart and having unit area of contact. SI unit of the coefficient of viscosity is $Nm^{-2}.s$. In CGS units, it has the unit of dyn $cm^{-2}s$ and is known as the poise unit. Equation 7.1 is known as the Newton equation of viscosity.

7.5 Poiseuille's equation

Assumptions:

1. The fluid is Newtonian i.e. the tangential stress is proportional to the velocity gradient.
2. The liquid in contact with the wall of the tube is at rest
3. No acceleration acts along the axis of the tube.
4. The pressure difference is solely utilised to just balance the viscous force

5. Pressure is same at all points along the radius i.e. , there is no radial flow of the liquid
6. The motion is stream-line and parallel to the axis of the tube.

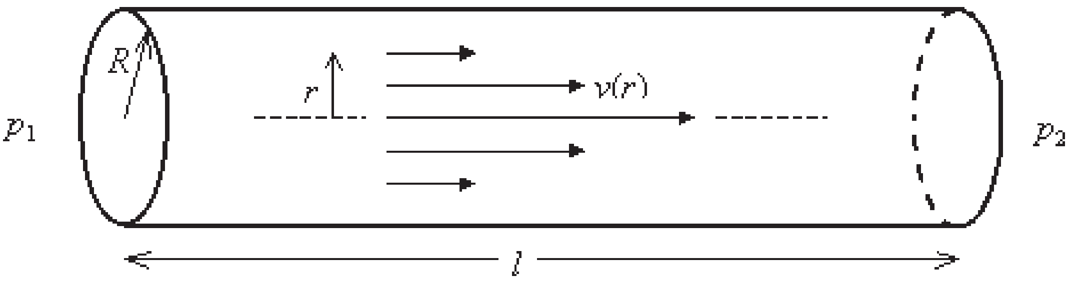


Figure 7.2: Flow of liquid through a pipe/tube

Let us consider steady flow of a liquid through a capillary of radius, r; length, l; under the pressure difference (P_1 - P_2).

Considering a thin liquid cylinder of thickness dz at a distance z from the axis of the tube which flows with velocity, v.

The volume of the liquid coming out due to the flow of the thin liquid cylinder

$$= \pi\left|(z+dz)^2 - z^2\right| v = 2\pi z.dz.v \text{ (neglecting } dz^2\text{)}$$

Therefore, the rate of the liquid through the capillary is,

$$\frac{dv}{dt} = \int_0^r 2\pi z.v.dz$$

The outer surface of the liquid cylinder of radius (z) is in contact with the slower moving layer and f_2 frictional force experienced opposite to the flow.

The inner surface is in contact with a faster moving layer feels frictional force, f_1, negative.

$$f_1 = -\eta.2\pi z.1\frac{dv}{dz} \text{ since } \frac{dv}{dz} \text{ is } (-ve) \text{ and } f_2 = (\eta.2\pi z.1\frac{dv}{dz})$$

Total frictional force (dragging force) $f = f_1 + f_2 = d(2.\pi z.\eta.1\frac{dv}{dz})$

The driving force for the liquid in the cylinder = $\pi\left|(z+dz)^2 - z^2\right|(p_1 - P_2)$

$= 2.\pi z.dz.(P_1 - P_2)$

For steady flow , driving force + dragging force = 0

$$\therefore 2.\pi z.dz(P_1 - P_2) + d(2.\pi z.\eta.1\frac{dv}{dz}) = 0$$

$$\text{Or, } d(2.\pi z.\eta.1\frac{dv}{dz}) = -2.\pi z.dz.(P_1 - P_2)$$

Integrating

$$2.\pi z.\eta.1\frac{dv}{dz} = -\pi(P_1 - P_2)z^2 + A$$

The equation is arranged

$$\text{Or, } dv = \frac{(P1 - P2)}{2\eta\ell}z.dz + \frac{A}{2\pi\eta\ell} \times \frac{1}{z}dz$$

Integrating again

$$\text{Or, } v = -\frac{1}{4}\frac{(P_1 - P_2)}{\eta\ell} \times z^2 + \frac{A}{2\pi\eta\ell} \times \ln z + B$$

When z =0 , v is maximum, in other words , finite. So, A must be zero otherwisev will be undefined.

$$\therefore v = -\frac{P_1 - P_2}{4\eta\ell} + B$$

Case 2.

When z= r and v =0 , $B = \frac{P_1 - P_2}{4\eta\ell} \times r^2$

The general expression of v becomes

$\therefore v = \frac{P_1 - P_2}{4\eta\ell} \times \left(r^2 - z^2\right)$. The plot of the equation represents parabolic for laminar flow through a capillary.

V is V_{maxm} at z =0

$\therefore v = \frac{P_1 - P_2}{4\eta\ell} \times (r^2)$, Pressure difference P_1 - P_2 = P

$$\therefore v_{max} = \frac{P}{4\eta\ell} \times \left(r^2\right)$$

Rate of flow through the capillary is $\frac{dv}{dt} = \int_0^r 2.\pi z. \times \frac{P_1 - P_2}{4\eta\ell} \times (r^2 - z^2) zdz$

$$= \frac{P_1 - P_2}{2\eta\ell} \times \left(\frac{r^4}{2} - \frac{r^4}{4}\right)$$

$$= \frac{P_1 - P_2}{8\eta\ell} \times r^4$$

$$\therefore \eta = \frac{P_1 - P_2}{8\ell\left(\frac{dv}{dt}\right)} \times (r^2) \qquad (7.2)$$

Equation 7.2 is known as the Poiseuille's equation.

7.6 Stoke's Law

When a heavy object is dropped in a liquid, it falls under gravitational pull. As the object's velocity increases, a force opposite to the object's motion begins to act due to the viscosity of the fluid. For adhesion, the liquid layer adjacent to the object moves with the object. But because the other fluid layers nearby are stationary, relative velocities are created between fluid layers near the object. As the object's velocity increases, so does this retarding force. If the force F and the weight of the object is mg, the total upward force on the object is mg - F. As F increases with increasing velocity, the equilibrium occurs when F = mg; The velocity of the object no longer increases. In this condition, the object starts falling with the same velocity (V_{term}). This velocity of the object in this medium is called the terminal velocity. The same happens with gases. But since the viscosity of the gas is very low, equilibrium is reached after a long distance.

Stokes' law quantifies the viscous drag force that resists the motion of a spherical object as it moves through a fluid. This force is directly proportional to the object's velocity, its radius, and the fluid's viscosity. Specifically, it states that the drag force, denoted as 'F', is directly proportional to several factors: the viscosity of the fluid, represented by 'η' (eta); the radius of the spherical object, 'r'; and the velocity of the sphere, 'v'.

$$F = 6\pi\eta rv \qquad (7.3)$$

In this equation, the constant '6?' arises from the geometric considerations of a sphere.

The conditions for validity for Stoke's law are - i) the fluid must be Newtonian (viscosity is constant), ii) the flow must be laminar (smooth, not turbulent), iii) the object must be spherical iv) the object must be small iv) the object must be moving at a slow velocity.

7.7 Effect of Temperature and Pressure on Viscosity

The Arrhenius equation, formulated in 1889, established a fundamental relationship between temperature and chemical reaction rates. This principle has been extended to describe the temperature dependence of a wide range of chemical and physical phenomena. Notably, *the decrease in viscosity observed in many liquids with increasing temperature* can be represented by an equation of the Arrhenius form

$$\eta = Ae^{\frac{Ea}{RT}} \qquad (7.4)$$

Where *A* is a constant known as the Arrhenius constant, Ea is the activation energy for flow, *R* is the ideal gas constant, and *T* is the temperature of the liquid using an absolute scale (almost always *K* - the units of Ea and *R* and *T* should be chosen so that the ratio is dimensionless, A will have the same dimensions as η, in our case cP). A plot of η vs. 1/T should be linear and have a slope equal to E_a /R if the liquid's viscosity exhibits Arrhenius-like behaviour.

The effect of pressure on the viscosity of liquids is generally less pronounced than the effect of temperature, but it's still a factor, especially at high pressure. In most liquids, increasing pressure leads to an increase in viscosity. This is because higher pressure forces the molecules closer together, increasing the intermolecular forces that resist flow. Essentially, the "crowding" of molecules makes it more difficult for them to move past each other. Liquids are already relatively incompressible, meaning their molecules are already quite close. However, very high pressures can still reduce the free volume between molecules. This reduction in free volume enhances the intermolecular forces, leading to greater resistance to flow.

Water is a notable exception. Due to its unique hydrogen bonding structure, the viscosity of water can initially decrease with increasing pressure in certain temperature ranges. However, at very high pressures, water's viscosity also increases. Also, there are non-Newtonian fluids that react differently to pressure

7.8 Principle of Determination of Viscosity Coefficient

Viscosity can be measured using a viscometer. The different types of viscometer are as follows:

1. Ostwald viscometer
2. Falling sphere viscometer
3. Falling piston viscometer
4. Oscillating piston viscometer
5. Vibrational viscometers
6. Rotational viscometers
7. Bubble viscometer

Ostwald viscometer is a commonly used viscometer, which consists of a U-shaped glass tube held vertically. For more accurate measurements it is held in a controlled temperature bath. It is also known as a glass capillary viscometer. A liquid is allowed to flow through its capillary tube between two etched marks and the time of flow of the liquid is measured using a stopwatch.

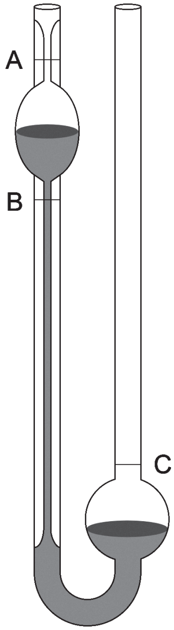


Figure 7.3: Ostwald's Viscometer

According to Poiseuille equation,

$$\eta = \frac{\pi r^4 Pt}{8VL} \qquad (7.5)$$

Where η is called the viscosity coefficient, t is the time of flow of liquid, *V* is the volume of the liquid, *P* is the hydrostatic pressure, and *L* is the distance travelled by the liquid during time *t*. In the honour of Hagen-Poiseuille the unit of viscosity is called the Poise (P). The official SI unit for absolute viscosity is kg/m s (or Pascal-seconds, Pa s).

In an Ostwald viscometer the measured distance the liquid travels, *L*, will be always a constant; the radius, *r* will always be a constant; and by procedure the volume of liquid, *V* will also be constant. Equation (7.5) can then be simplified to:

$$\eta = KPt$$

Where K is a constant and $K = \frac{\pi r^4}{8VL}$

The hydrostatic pressure is *P* proportional to the density of the fluid being measured. In our experiment we will be measuring the mass of equal volumes of liquid so that the viscosity will be proportional to the masses measured. Therefore, we have the relation:

$$\eta \ \alpha \ Kmt$$

Where K and t are defined above and m is the mass of the liquid.

For finding the viscosity of liquids it is important to calibrate the viscometer using a reference liquid. Water is a commonly used reference liquid. The viscosity of water at 30.0 °C is 0.8007 centipoise (cP). Knowing the values for the reference liquid and relation (3), we get:

$$\frac{\eta}{\eta_r} = \frac{mt}{m_r t_r} \qquad (7.6)$$

Where: η_r is viscosity coefficient of the reference sample (water), m_r is the mass of the reference sample, and t_r is the time flow of the reference sample. Note that *K* cancels out. The other variables are the viscosity coefficient, mass, and time flow of the sample respectively. With an Ostwald viscometer we can measure the time flow of a liquid (mass can be measured using standard laboratory procedures, e.g. a relative density bottle and a scale) and determine its viscosity by solving equation (7.6) for η.

$$\eta = mt\left(\frac{\eta_r}{m_r t_r}\right)$$

7.9 Summary

This unit explores fluid flow and viscosity, key concepts in fluid dynamics. It distinguishes between laminar and turbulent flow and introduces the viscosity coefficient, which measures a fluid's resistance to flow. Poiseuille's equation describes laminar flow through narrow tubes, while Stoke's Law explains the motion of small particles in a viscous medium. The effect of temperature and pressure on viscosity is also examined-liquid viscosity decreases with temperature, whereas gas viscosity increases. Finally, the determination of viscosity coefficient is discussed, covering experimental methods like capillary flow and falling sphere techniques, essential in various industries.

7.10 Self-Assessment Questions

1. Differentiate between laminar flow and turbulent flow with examples.
2. Define viscosity coefficient and explain its significance in fluid dynamics.
3. Derive Poiseuille's equation for the flow of a liquid through a capillary tube.
4. State and explain Stoke's Law. How is it applied in the determination of viscosity?
5. How does temperature affect the viscosity of liquids and gases? Explain with reasons.
6. Discuss the effect of pressure on the viscosity of gases and liquids.
7. Describe different experimental methods used for the determination of viscosity coefficient.
8. Explain the working principle of Ostwald's viscometer and describe the procedure for determining the viscosity of a liquid using this instrument.
9. Derive the equation for viscosity determination using Ostwald's viscometer, highlighting the relationship between viscosity, flow time, and density of the liquid.
10. A liquid flows between two parallel plates, where the upper plate moves with a velocity of 0.5 m/s, while the lower plate is stationary. The distance between the plates is 2 mm, and the viscosity of the liquid is 0.8 Pa·s. Calculate the shear stress acting on the liquid.
11. The viscosity of a liquid at 300 K is $2.5 \times 10?^{3}$ Pa·s, and at 350 K, it is $1.8 \times 10?^{3}$ Pa·s. Calculate the activation energy for viscous flow, assuming Arrhenius' equation
12. A liquid with viscosity 0.0015 Pa·s flows through a 2 mm diameter tube under a pressure difference of 2000 Pa. If the length of the tube is 50 cm, calculate the volume flow rate.
13. A capillary tube of radius 1 mm and length 25 cm carries a liquid with viscosity $1.2 \times 10?^{3}$ Pa·s. If the volume flow rate is 0.5 cm^3/s, determine the pressure difference between the two ends of the tube.
14. The flow times for a given liquid and water in an Ostwald's viscometer are 120 seconds and 90 seconds, respectively. The density of the liquid is 0.85 g/cm^3, and the density of water is 1.0 g/cm^3. If the viscosity of water is $1.0 \times 10?^{3}$ Pa·s, determine the viscosity of the liquid.

Module 2:
Chemical Thermodynamics - I

Unit 8 ❐ Basic Concepts and Zeroth Law of Thermodynamics

Structure

8.1 Objectives

8.2 Introduction

8.3 Thermodynamic terms

8.4 Thermodynamic processes

8.5 Mathematical background

8.6 Zeroth law of thermodynamics

8.7 Summary

8.8 Self-Assessment Questions

8.1 Objectives

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

- Differentiate between intensive and extensive variables.
  Classify systems as isolated, closed, or open based on their interactions with surroundings.
- Distinguish between cyclic, reversible, and irreversible processes.
- Understand the concept of exact and inexact differentials in thermodynamic equations.
- Apply partial derivatives, Euler's reciprocity rule, and the cyclic rule in thermodynamic relationships.
- Explore Thermodynamic Functions and Their Differentials
- Differentiate between state and path functions.
- Comprehend the Zeroth Law of Thermodynamics

8.2 Introduction

Chemical thermodynamics is the study of energy transformations that accompany physical and chemical processes. It explores the relationships between heat, work, and the properties of systems arising from the interactions of matter and energy. While matter is discrete and finite, energy is continuous and can manifest in various forms.

A helpful analogy is to consider space within a room. We can recognize the room's boundaries, defining a finite space. However, we can also perceive the room as existing within a larger, continuous space. Similarly, matter can be viewed as the 'boundaries' that contain and structure energy. Energy, like space, flows and transforms.

The fundamental principles of thermodynamics are remarkably robust. As Albert Einstein noted, *“Thermodynamics is the only physical theory of universal content which, within the framework of the applicability of its basic concepts, I am convinced will never be overthrown.”*

A familiar example illustrates these principles: In a hot environment, such as a summer day with an ambient temperature of 45^{o}C, a human body, normally at 36^{o}C, is susceptible to heat transfer. The temperature difference drives heat flow from the surroundings into the body. This heat transfer can lead to a rise in body temperature and, in extreme cases, heatstroke. To mitigate this, the body must expend energy to maintain its internal temperature, often aided by cooling mechanisms like sweating and the intake of water. This example highlights the concept of a system (the human body) interacting with its surroundings. The system's ability to maintain its internal state depends on its capacity to manage energy exchange with the environment.

8.3 Thermodynamic Terms

Before discussing the laws of thermodynamics, it is necessary to know some thermodynamic definitions, because these basic concepts will be used in the discussion of thermodynamics.

Extensive and intensive variables/ properties

Water at high temperature the state of system (here water) has different set of properties, i.e. steam. At normal temperature it is liquid. At lower temperature water is obtained as ice, having different set of properties. However, the state of macroscopic system can be identified from the macroscopic properties such as T, P, V, n, their values determine the properties of the state.

The wide variety of macroscopic properties can be divided into two categories - Extensive and Intensive properties.

(i) Extensive property - this property depends upon the mass of the system and is additive.

(ii) Intensive Property- this property is independent of mass and has the same magnitude throughout the homogeneous system when the system is under equilibrium condition otherwise.

How can a property be characterized as intensive and extensive? To Characterize the property as intensive or extensive at f*irst determine the magnitude of the property for the whole system and then determine the magnitude of the same property virtually imagining the half-portion of the system or for a portion of the system. If the magnitudes are found to be the same, the property is intensive*. Say Volume of something is V, cut the volume of something into half then the magnitude alters to V/2. So volume is an extensive property. Specific, molar idea when attached to heat, energy etc. the property represented are intensive.

Extensive property / Extensive property = Intensive property

Intensive property / Intensive property = Intensive property

To define the state of a pure substance values of all the intensive properties not required since all intensive properties are not independent. From P and T of a gas, ρ can be determined, $\rho = \frac{PM}{RT}$ i.e $\rho = f(P,T)$. Once ? is known viscosity coefficient of the gas can be determined.

Examples of Extensive Properties

Mass (m), Volume (V) , Total internal energy (U), Total enthalpy (H), Total entropy (S), Gibbs free energy (G), Helmholtz free energy (A or F), Heat capacity (C), Total number of moles (n)

Examples of Intensive Properties

Temperature (T), Pressure (P), Density ($\rho = m/V$), Specific volume (v = V/m), Specific internal energy (u = U/m or U/n), Specific enthalpy (h = H/m or H/n), Specific entropy (s = S/m or S/n), Specific Gibbs free energy (g = G/m or G/n), Specific Helmholtz free energy (a = A/m or A/n), Molar volume (Vm = V/n), Molar heat capacity ($C_m = C/n$), Refractive index (n), Surface tension (γ), Viscosity (η), Electrical conductivity (σ), Chemical potential (μ)

System: The part of the Universe which is considered for thermodynamic study is called a system.

Surroundings

The portion of the Universe which can interact with the system is called the surrounding.

Boundaries

The surfaces which separates the system from the surroundings are called the boundaries.

Two types of exchange can occur between the system and its surroundings:

a) Energy exchange (heat or work) and b) exchange of matter (movement of molecules across the boundary of the system and surroundings).

Based on the types of exchange, one can define

If the boundary does not allow heat (energy) exchange to take place it is called adiabatic boundary otherwise it is diathermal boundary.

Isolated System

A system that does not exchange mass or energy with its surroundings.

- Definition: A system that is completely insulated from its surroundings, meaning there is no transfer of heat, work, or matter.
- Example: A thermos flask containing hot coffee (ideal case). In reality, perfect isolation is difficult to achieve, but thermos flasks reduce heat exchange significantly.

Closed System

A system that exchanges energy but not mass with its surroundings.

- Definition: A system where heat and work can cross the boundary, but matter cannot.
- Example: A sealed pressure cooker on a stove. Heat enters, and the system does work on the steam inside, but mass (water/steam) does not leave or enter.

Open System

A system that exchanges both mass and energy with its surroundings.

- Definition: A system where both heat and matter can enter or leave.
- Example: A boiling pot of water without a lid. Steam escapes into the surroundings, and heat is continuously supplied.

Thermodynamic Equilibrium

A system is said to be in thermodynamic equilibrium when its thermodynamic variables remain constant over time, indicating that no spontaneous changes occur within the system. For a system to be in thermodynamic equilibrium, the following conditions must be satisfied:

- **Mechanical Equilibrium:** There are no unbalanced forces between the system and its surroundings, ensuring no macroscopic movement or pressure variations.
- **Thermal Equilibrium:** The temperature is uniform throughout the system and is equal to that of the surroundings, preventing any net heat flow.
- **Chemical Equilibrium:** The system has a uniform chemical composition, with no net chemical reactions or mass transfer occurring between different regions or with the surroundings.

8.4 Thermodynamic processes

A thermodynamic process refers to the change in the state of a system, involving variations in thermodynamic variables such as pressure (P), volume (V), and temperature (T). Depending on the conditions maintained during the change, thermodynamic processes can be classified as follows:

1. Isothermal Process (Temperature remains constant, T = 0)

The temperature of the system remains constant throughout the process, meaning there is heat exchange with the surroundings to maintain equilibrium. Since ?T = 0, the internal energy of an ideal gas remains unchanged, and any heat added to the system is entirely converted into work.

Examples:

- Slow expansion or compression of gas in a cylinder with a conducting wall in thermal contact with a heat reservoir.
- Melting of ice or boiling of water at constant temperature under atmospheric pressure.

- Slowly filling a balloon such that the air inside maintains thermal equilibrium with the surroundings.

2. Adiabatic Process (No heat exchange, $Q = 0$)

There is no transfer of heat between the system and surroundings. The change in internal energy is solely due to work done on or by the system. Adiabatic processes occur in perfectly insulated systems or when changes occur so rapidly that heat exchange does not have time to occur.

Examples:

- Sudden compression or expansion of a gas in an insulated cylinder (e.g., compressing air in a bicycle pump, where it heats up).
- Cloud formation - as air rises, it expands and cools adiabatically, leading to condensation.
- Explosion of a firecracker - the rapid expansion of gases after ignition occurs adiabatically.

3. Isobaric Process (Pressure remains constant, ?P = 0)

The pressure of the system remains unchanged while volume and temperature vary. Any heat added to the system does work in expanding the volume.

Examples:

- Boiling water in an open vessel - the pressure remains at atmospheric level while volume and temperature change.
- Heating air in a balloon - the gas expands at constant pressure, causing the balloon to inflate.
- A piston moving freely in a cylinder with heat supply - the gas expands or contracts while maintaining constant pressure.

4. Isochoric (Isovolumetric) Process (Volume remains constant, ?V = 0)

In this process, the volume of the system remains fixed, meaning no work is done ($W = 0$). Any heat supplied changes only the internal energy and temperature.

Examples:

- Heating gas in a sealed rigid container - since volume cannot change, all heat supplied increases internal energy and temperature.
- Heating a pressure cooker before the whistle blows - the volume of the gas inside remains fixed, leading to increased pressure.
- Explosion of a bomb in a closed chamber - rapid combustion increases pressure without any volume change.

5. Cyclic and Non-Cyclic Processes

- A cyclic process is one in which the system returns to its initial state after undergoing a series of transformations, meaning ?U = 0 over one complete cycle.
- A non-cyclic process is one in which the system does not return to its original state.

Examples:

- Cyclic Process: The Carnot cycle in heat engines, where a working substance undergoes isothermal and adiabatic processes and returns to its initial state.
- Non-Cyclic Process: Heating water from room temperature to 100°C and allowing it to evaporate-it does not return to the original liquid state on its own.

6. Reversible and Irreversible Processes

- A reversible process occurs infinitely slowly, maintaining equilibrium at every stage. It can be reversed without leaving any net change in the system or surroundings.
- An irreversible process occurs spontaneously and cannot be reversed without leaving changes in the system or surroundings. These processes often involve friction, turbulence, or rapid expansion.

Examples:

- Reversible Process:
  - Slow, quasistatic compression of an ideal gas where every intermediate step is at equilibrium.
- Irreversible Process:
  - Free expansion of gas into a vacuum - an irreversible expansion without external work.

- Rubbing hands together - the work done is converted into heat due to friction, and the process cannot be reversed.
- Spontaneous mixing of two gases - once mixed, they do not separate back spontaneously.

8.5 Mathematical Background

Total Differential and Partial Derivatives in Thermodynamics

In the equation of state P=P(T, V, n), pressure P is a function of temperature T, volume V, and the number of moles n. The partial derivative of P with respect to V at constant T and n is given by:

$$\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

This term describes how pressure varies with volume while keeping temperature and the number of moles constant.

Similarly, the partial derivative of P with respect to T at constant V and n is:

$$\left(\frac{\partial P}{\partial T}\right)_{V.n}$$

This represents how pressure changes with temperature while volume and the number of moles remain fixed.

Now, what happens if we change two or more independent variables simultaneously? For an infinitesimal change in V and T, the corresponding change in P is given by the total differential:

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial T}\right)_{V,n} dT \qquad (8.1)$$

This equation states that the total change in P is the sum of the contributions from the changes in V and T, each evaluated while keeping the other variable constant. If the changes are finite rather than infinitesimal, we integrate this expression to compute the total variation in P.

General Form of Total Differential

In a more general case, if a function u depends on multiple independent variables x1, x2, ..., xnx_1, x_2, ..., x_nx1, x2, ..., xn, its total differential is given by:

$$du = \left(\frac{\partial u}{\partial x_1}\right)_{X_2,\dots,X_n} dx_1 + \left(\frac{\partial u}{\partial x^2}\right)_{X_1,\dots,X_n} dx_2 + \dots + \left(\frac{\partial u}{\partial x_n}\right)_{X1,\dots,X_{n-1}} dx_n \qquad (8.2)$$

This general expression applies to various thermodynamic quantities and enables us to evaluate their changes when multiple variables are varied simultaneously.

Exact and Inexact Differentials

A total differential of a function $u(x_1, x_2, \dots, x_n)$ is given by:

$$du = \sum_{i=1}^{n} \left(\frac{\partial u}{\partial x_i}\right) dx_i \qquad (8.3)$$

If we are given a differential expression, we may ask:

1. Is it the total differential of some function?
2. If so, what is that function?

For example, the differential

$$dz = (9x^2 + 6xy + y^2)\, dx + (3x^2 + 2xy)\, dy$$

is the total differential of

$$z(x,y) = 3x^3 + 3yx^2 + xy^2$$

However, not all differentials are exact; for instance,

$$dz = xydx + x^2\, dy$$

is not the total differential of any function z(x,y) z (x,y) z (x,y).

Testing for Exactness

Given a differential of the form:

$$dz = f_1\,(x, y)\, dx + f_2\,(x, y)\, dy$$

it is exact if the mixed partial derivatives satisfy:

$$\left(\frac{\partial f_1}{\partial y}\right)_x = \left(\frac{\partial f_2}{\partial x}\right)_y$$

If this condition holds, the differential is exact; otherwise, it is inexact.

Example in Thermodynamics

Consider the differential:

$$dP = \frac{RT}{V-b}dT + \left|\frac{RT}{(V-b)^2} - \frac{a}{TV^2}\right|dV$$

To check if it is exact, we compare it with the total differential of P (T, V)

$$dP = \left(\frac{\partial P}{\partial T}\right)_v dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

From this, we identify:

$$\left(\frac{\partial P}{\partial T}\right)_v = \frac{RT}{V-b}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = \left[\frac{RT}{(V-b)^2} - \frac{a}{TV^2}\right]$$

Attempting to integrate and match these expressions shows that no function P(T,V) satisfies both conditions simultaneously, proving that this differential is inexact.

Thus, exact differentials correspond to state functions, while inexact differentials do not. This test is a fundamental tool in thermodynamics to determine whether a differential represents a physical state function.

Distinguishing between exact and inexact differentials is crucial in thermodynamics. State functions like internal energy (U), entropy (S), free energy (G), volume (V), pressure (P), and temperature (T) describe a system's state, independent of its history. For example, a gas at 298 K and 1 atm has well-defined properties, regardless of how it reached that state.

In contrast, work (w) and heat (q) are path functions-their values depend on the process taken between states. This distinction connects directly to differentials: state functions have exact differentials (dU, dS, dG, etc.), while path functions have inexact differentials (dw, dq). Integrating an exact differential depends only on the initial and final states, whereas integrating an inexact differential depends on the entire path.

This concept is essential for deriving thermodynamic equations. For example, the fundamental thermodynamic relationships:

$$dU = TdS - PdV$$

$$dH = TdS + VdP$$

$$dA = -SdT - PdV$$

$$dG = -SdT + VdP$$

Since (U,H,A,) and (G) are state functions, their differentials are exact, allowing the derivation of useful relationships. For instance, from the differential of (G)

$$dG = dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP$$

Comparing with ($dG = -SdT + VdP$), we conclude:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S, \left(\frac{\partial G}{\partial P}\right)_T = V$$

These relationships illustrate how changes in pressure or temperature affect free energy. Furthermore, since (dG) is exact, we derive a Maxwell relation:

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

This relation, along with others from the fundamental equations, provides practical ways to calculate entropy changes using measurable quantities like pressure and volume-critical for experimental thermodynamics.

The Euler Reciprocal Relation

Consider a state function z which is function of two independent variables x and y of the system i.e. $z = f(x, y)$. Since z is a state function, hence differential of z is an exact differential. The exact differential Prescription = (irrespective of order)

Fundamentally

$dz = M(x, y)dx + N(x, y)dy$ where $M(x, y) = (\frac{\partial z}{\partial x})_y$ and $N(x, y) = (\frac{\partial z}{\partial y})_x$

Taking mixed second derivatives, we have

$$\left(\frac{\partial M}{\partial T}\right)_x = \left(\frac{\partial^2 z}{\partial y \partial z}\right) \text{and} \left(\frac{\partial N}{\partial z}\right)_y = \left(\frac{\partial N}{\partial x}\right)_y = \left(\frac{\partial^2 z}{\partial x \partial y}\right)$$

Since $\frac{\partial^2 z}{\partial y \partial z} = \frac{\partial^2 z}{\partial x \partial y}$

$$\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y$$

The equation is called Euler reciprocal

Since z is a state function, then finite change, Δ z when the system passes from intial state A to final state B is given by $\Delta z = z_2 - z_1$. Also dz where cyclic integral means that the system is in the same state at the end of its path as it was in the beginning, i.e. it has traversed a closed path. Thus dz is an exact differential.

8.6 Zeroth law of thermodynamics

Although zeroth law of thermodynamics was formulated after first law of thermodynamics but was of primary importance thus called Zeroth law.

This law states that if two systems are in thermal equilibrium with a third system then they are in thermal equilibrium with each other i.e. if body A is in equilibrium with body C and body B is also in equilibrium with body C, then both the bodies are in equilibrium with each other. In other words if systems A and B are placed in contact with each other, then no exchange of heat will take place.

The use of thermometer is based on this principle. The thermometer behaves as the body C in above statement. Thus, in comparing the temperature of two systems A and B thermometer is allowed to come in equilibrium with the body A and then in equilibrium with body B by placing in contact with each other. Thus the readings of thermometer give comparative ideas of degree of hotness of the two bodies A and B. Because of small size of thermometer, an insignificant amount of energy exchange takes place during measurement of the temperature.

Change in property of fluid with degree of hotness helps in the measurement of temperature by thermometer. This property in a mercury thermometer involves change in length of the mercury column and in an air thermometer it involves change in volume (v) and pressure (P) of air enclosed within.

$$A\ (T_A) = C\ (T_C) = B\ (T_B)$$

$$f\ T_A = T_C = T_B \text{ then } T_A = T_B$$

8.7 Summary

This unit introduces fundamental thermodynamic concepts, including the classification of variables as intensive or extensive and systems as isolated, closed, or open. It covers different thermodynamic processes, distinguishing between cyclic, reversible, and irreversible processes. The mathematical framework necessary for thermodynamics, such as exact and inexact differentials, partial derivatives, Euler's reciprocity rule, and the cyclic rule, is explored. The unit also examines thermodynamic functions, differentiating state and path functions and their differentials. Finally, the Zeroth Law of Thermodynamics is discussed, establishing the foundation for the concept of temperature and thermal equilibrium.

8.8 Self-Assessment Questions

1. Define intensive and extensive thermodynamic variables and provide two examples of each.
2. Differentiate between isolated, closed, and open systems with suitable examples.
3. What are cyclic, reversible, and irreversible processes? How do they differ in thermodynamic analysis?
4. What is the difference between an exact differential and an inexact differential? Give an example from thermodynamics.

5. Write and explain Euler's reciprocity rule and the cyclic rule in thermodynamics.
6. Define state functions and path functions. Identify whether heat and work are state or path functions, with justification.
7. What are perfect and imperfect differentials in thermodynamics? How are they related to thermodynamic functions?
8. State the Zeroth Law of Thermodynamics and explain its significance in defining temperature.
9. Explain how the Zeroth Law of Thermodynamics leads to the concept of thermal equilibrium.
10. Consider a system undergoing a cyclic process. What is the net change in its internal energy, and why?
11. Why is the concept of partial derivatives important in thermodynamics? Provide an example where partial derivatives are used in thermodynamic equations.

Unit 9 ❐ First Law of Thermodynamics

Structure

9.1 Objectives
9.2 Introduction
9.3 Concept of internal energy and First law of thermodynamics
9.4 Work and Heat
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9.6 Heat Capacity
9.7 Work done in Reversible and Irreversible processes
9.8 Joule's experiment and its consequence
9.9 Summary
9.10 Self-Assessment Questions

9.1 Objectives

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

- Understand the First Law of Thermodynamics
- Explain the concept of internal energy (U) and its significance in thermodynamics.
- State and apply the First Law of Thermodynamics in different thermodynamic processes.
- Analyze Enthalpy and Heat Capacities
- Define enthalpy (H) and understand its relation to internal energy.
- Derive and explain the relation between heat capacities at constant pressure and constant volume.
- Perform Thermodynamic Calculations
- Calculate heat (q), work (w), internal energy change (?U), and enthalpy change (?H) for different gas expansion processes.
- Differentiate between reversible, irreversible, and free expansion of ideal and real (van der Waals) gases.

- Solve numerical problems involving isothermal and adiabatic processes for gas expansion and compression.
- Understand Joule's Experiment and Its Consequences
- Explain Joule's experiment and its implications for the relationship between internal energy and temperature.
- Discuss the significance of Joule's findings in thermodynamic systems.

9.2 Introduction

The First Law of Thermodynamics is a fundamental principle governing energy conservation in physical and chemical systems. This unit begins with the concept of internal energy (U) and its role in thermodynamic transformations. It introduces the First Law of Thermodynamics, which states that energy can neither be created nor destroyed, only transferred between a system and its surroundings as heat (q) and work (w). The unit explores enthalpy (H) as a thermodynamic function and establishes the relationship between heat capacities at constant pressure (Cp) and constant volume (Cv). Various gas expansion processes-reversible, irreversible, and free expansion-are analyzed for both ideal and real (van der Waals) gases under isothermal and adiabatic conditions. Finally, Joule's experiment is discussed, highlighting its impact on our understanding of internal energy and temperature dependence in thermodynamic systems. Through theoretical explanations and numerical applications, this unit provides a solid foundation for understanding energy transformations in gases.

9.3 Concept of internal energy and First law of thermodynamics

The First Law of Thermodynamics establishes the relationship between energy change, work, and heat in a system. Also known as the Law of Conservation of Energy, it states that energy can neither be created nor destroyed but can only be transformed from one form to another. This implies that any loss of energy in one form must be exactly compensated by a gain in another. Consequently, this law fundamentally prohibits the existence of a perpetual motion machine of the first kind-a hypothetical machine that could generate energy indefinitely without an external energy input. By defining the constraints on energy transformations, the First Law forms the foundation of thermodynamic principles and energy conservation in physical and chemical processes.

Internal Energy

A fundamental parameter in thermodynamics is internal energy (U), which represents the total energy within a system, regardless of how it is stored. It is the sum of all kinetic and potential energies associated with the microscopic components of the system, including molecular motion, intermolecular interactions, and electronic configurations.

Internal energy is a state function, meaning its value depends only on the system's current state (temperature, pressure, and volume) and not on the path taken to reach that state. Although the absolute value of U cannot be measured-since it includes various forms of energy, such as potential energy from molecular interactions, electronic energy, and even nuclear binding energy-its change (ΔU) during a process can be determined by analyzing energy exchanges with the surroundings. Thermodynamics focuses on this macroscopic viewpoint, where ?U depends on heat and work interactions. Internal energy can be expressed as a function of different thermodynamic variables, such as U = f(P, T), U = f(V, T), or U = f(P, V), fulfilling all criteria of a state function. Additionally, internal energy is an extensive property, meaning it scales with the size or amount of substance in the system.

Internal Energy and First Law

Consider a system undergoing changes in pressure and volume, where the initial state (A) and final state (B) are defined, as shown in Fig. 1. The internal energy of the system in these states is U_A and U_B, respectively, both of which are well-defined quantities. Consequently, the change in internal energy $(\Delta U = U_B - U_A)$ is also a definite quantity. Importantly, ΔU depends only on the initial and final states of the system and not on the specific path taken to transition between them.

To illustrate this, suppose the system moves from state A to state B via two different paths: Path I and Path II. If the energy change along Path I is ΔU and along Path II is ΔU, and if $\Delta U \neq \Delta U$, a contradiction arises. Consider a cyclic process where the system follows $A \rightarrow B$ via Path I and then returns to A via Path II. If $U > \Delta U$, then an excess energy equal to $\Delta U - \Delta U$ would be available after each complete cycle. Repeating this cycle indefinitely would continuously generate energy without any external input, effectively creating a perpetual motion machine of the first kind, which violates the First Law of Thermodynamics.

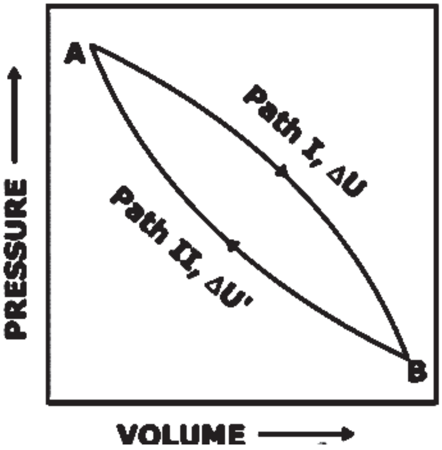


Figure 9.1: Change in internal energy

Since such a scenario is impossible, it follows that $\Delta U = \Delta U$, confirming that the internal energy change for a given process depends solely on the initial and final states, irrespective of the path taken. This property reinforces that internal energy (U) is a state function.

Energy changes in relation to work and heat changes

Let U_A and U_B represent the internal energies of a system in state A and state B, respectively, where the system undergoes a transition from A to B. During this process, the system absorbs heat (q) from the surroundings and performs work (w) (mechanical or electrical). Since heat absorption increases the system's energy while work done by the system results in energy expenditure, the change in internal energy ΔU is given by:

$$\Delta U = U_B - U_A = q - w$$

In general, if a system receives heat (q) from its surroundings and performs work (w), the change in internal energy is expressed as:

$$\Delta U = q + w$$

This equation represents the mathematical statement of the First Law of Thermodynamics, which expresses the conservation of energy in thermodynamic processes.

- When work is done on the system (e.g., during gas compression), w is taken as positive, meaning:

$$\Delta U = q + w$$

- When work is done by the system (e.g., during gas expansion), w is taken as negative, leading to:

$$\Delta U = q - w$$

For an infinitesimal change in a thermodynamic system, the differential form of the First Law is:

$$dU = dq + dw$$

Here, dq and dw are not exact differentials, as heat and work are path-dependent functions. Unlike state functions, the absolute heat content of a system is undefined; thus, dq represents only the small amount of heat exchanged, and dw represents the small amount of work done during the process.

When only mechanical work (i.e., expansion or compression work) is considered, the work done is given by:

$$dw = - PdV$$

Thus, the First Law simplifies to:

$$dU = dq - PdV$$

This equation describes how changes in internal energy relate to heat exchange and volume changes in a thermodynamic system.

9.4 Work and Heat

Work in Thermodynamics is defined as any quantity that flows across the boundary of a system during a change and is completely convertible into lifting of a weight in the surroundings.

Things to be noted in this definition of work are

1. Work appears only at the boundary
2. Work appears only during a change in state.
3. Work is manifested by an effect in the surroundings.

4. The quantity of work is equal to mgh , where m is the mass lifted, g is the acceleration due to gravity, h is the height through which the weight has been raised.
5. Work is algebraic quantity; it is positive if the mass is lifted (h is +), in which case we say that work has been produced in the surroundings or has flowed to the surroundings: it is negative if the mass is lowered (h is -).

Heat We explain the attainment of thermal equilibrium of two systems by asserting that a quantity of heat Q has flowed from the system of higher temperature to the system of lower temperature.

In thermodynamics heat is defined as a quantity that flows across the boundary of a system during a change in its state in virtue of a difference in temperature between the system and its surroundings and flows from a point of higher to a point of lower temperature.

1. Heat appears only at the boundary of the system
2. Heat appears only during a change in state.
3. Heat is manifested by an effect in the surroundings.
4. The quantity of heat is proportional to the mass of water in the surroundings that is increased by one degree in temperature starting at a specified temperature under a specified pressure.
5. Heat is an algebraic quantity; it is positive if a mass of water in the surroundings is cooled, in which case we say that the heat has flowed from the surroundings; it is negative if a mass of water in the surroundings is warmed, in which case we say that heat has flowed to the surroundings.

WORK and HEAT flow during transformation is based on observation of effects produced in the surroundings, not upon what happens within the system.

A example to understand distinction between work and heat.

Consider a system consisting of 10g of liquid water contained in an open beaker under constant pressure of 1 atm. Initially the water is at 25^{o}C, so that P =1 atm,T= 25^{o}C. The system is now immersed in the 100g of water at a high temperature, 90^{o}C. The system is kept in contact with this 100g of water until the temperature of the 100g has fallen to 89^{o}C, whereupon the system is removed. We say that 100 units of heat has flowed from the surroundings, since the 100g of water in the surroundings dropped 1°C in temperature. The final state of the system is described by p = 1atm, T = 35°C

Now consider the same system consisting of 10g of liquid water at P =1 atm,T= 25°C and immerse a stirring paddle driven by a falling mass. This can be adjusted in such a way that when mass m falls through height h once, the temperature of system rises to 35°C. The final state with P = 1 atm and T = 35°C. The change in state is same as in previous experiment. There was no heat flow but there was flow of work.

When we observe the system before and after the experiment, the change in state had been effected and nothing whatsoever can be said about the heat flow or work flow involved. Only conclusion that can be drawn is that the temperature of the system is higher afterward than before. This implies the energy of the system increased.

If we observe surrounding before and after, we find cooler bodies of water/or masses at lower elevations. These observations of surroundings leads in the easy deductions of the quantities heat and work.

9.5 Enthalpy

When fuel burns in a cylinder with a piston , the fuel produces carbon dioxide and water vapour, which occupy space than the original fuel and oxygen, and as a result the piston is driven out to accommodate the products. This expansion requires work. That is, when a fuel burns in a container that is free to expand , some of the energy is released in the combustion is used to do work. If the combustion is carried out in a container with rigid walls, the combustion releases the same amount of energy, but none of it is used to do work because no expansion can occur. More energy is available as heat at constant volume than at constant pressure process. To calculate the heat produced in the former case (constant pressure), we have to account for the energy that is used to make room for the carbon di oxide and water vapour and substract that from the total energy changes in energy. This is true even when there is no physical piston- reactions in test tube happen at constant pressure- the gaseous products makes room for themselves.

Mathematical Expression for Enthalpy

For finding an expression for enthalpy let us suppose that at constant P, when state of the system changes then the volume of system changes. Suppose the volume increases from

VA to VB , at constant pressure P. Then, the work done (w) by the system will be w = -P(V_B-V_A)

$$\text{Substituting } \Delta U = q + w$$

$$\Delta U = q - P(V_B - V_A)$$

$$U_B - U_A = q - P(V_B\text{-}V_A)$$

In Joule Thompson Experiment where adiabatically irreversible expansion process of real gas through fine orifices takes place , q=0. The above equation simplifies to

$$U_B + PV_B = U_A + PV_A$$

$$U_B \neq U_A ; V_B \neq V_A$$

The quantity U+PV = H (Enthalpy) of the system. H is the Total Energy stored in the system. Since U, P and V are state functions then U + PV must also be a state function. As U and PV have dimensions of energy, then H must also have dimensions of energy. The change in enthalpy is given by dH.

The analogy for Enthalpy can be thought as a Purse containing money within it. Money in the purse is used to purchase. If we lose the purse we lose money and the purse. The money is internal energy and the purse also has a price but in terms of space is the enthalpy.

$$dH = d\,(U+PV)$$

$$\text{First law of Thermodynamics} \quad dq = dU + PdV$$

$$dH = dU + PdV + VdP$$

$$dH = dq + VdP$$

Heat exchange at constant pressure

When the pressure of the system is constant, then the change in pressure will be zero i.e. dP = 0

$$\text{Therefore, } VdP = 0 \text{ and } dq = dqp$$

First law gives

$$(q)p = \Delta E + P\Delta V$$

$$= (E_2 - E_1) + P (V_2 - V_1)$$

$$= (E2 + PV2) - (E1 + PV1)$$

$$H = E + PV$$

$$\therefore dH = dE + PdV + VdP$$

$$dH = dq + VdP \quad \text{if } dP = 0 \text{ then } dH = (dq)_P$$

Heat absorbed in a process at constant pressure is equal to change in enthalpy if only work done is pressure - volume work

When the change is finite, then $\Delta H = qp$

$$\Delta H = H_B - H_A$$

Therefore, at constant pressure of the system, the heat exchange becomes equal to the change in enthalpy of the system. Whenever the system exchanges heat at constant pressure temperature of the system changes.

$$(UB - UA) + P(VB - VA) = q$$

Incorporating the above value of q in equation (8), we get

$$\Delta H = (UB - UA) + P(VB - VA) \text{ or } \Delta H = \Delta U + P\Delta V$$

where ΔV is the increase in volume of the system

So, some part of heat i.e. qp will be used to increase the internal energy and rest is used up for the change in volume. Hence, change in enthalpy results in change in internal energy as well as change in volume of the system. For solids and liquids the volume change is negligible, therefore, enthalpy and internal energy changes are practically same for them.

Relationship between ΔH and ΔU for an ideal gas

We know H = U + PV

$\Delta H = \Delta U + P\Delta V$

For an ideal gas, PV = nRT

$\Delta H = \Delta U + \Delta(nRT) = \Delta U + (\Delta n)RT$

Here, n is the change in the amount of the gas. If the temperature changes but the amount of gas is constant, then $\Delta H = \Delta U + nR\Delta T$

Characteristics of enthalpy

i) When the system is kept at constant pressure, then the enthalpy change becomes equal to the heat exchange by the system.

ii) It is a state function

iii) The expression of enthalpy is $H = U + PV$

iv) For solids and liquids, the enthalpy change (ΔH) is taken as equal to the change in the internal energy (ΔU).

v) The unit of enthalpy is same as that of unit of energy.

vi) When the system absorbs heat at a constant pressure, ΔH is positive and the process is known as an endothermic process.

vii) When the system loses heat to the surroundings at a constant pressure, ΔH is negative and the process is known as an exothermic process.

Enthalpy of vaporization

The change in enthalpy (ΔH) when 1 mole of liquid changes into vapour phase at a given temperature and pressure per mole of the liquid is known as enthalpy of vaporization. This enthalpy has positive sign when liquid changes into vapor and negative sign when vapor changes into liquid. Thus, we can say that during evaporation absorption of heat hence increase in enthalpy takes place. Similarly during condensation, evolution of heat hence decrease in enthalpy takes place. H_2O (l) ΔH_2O (g) H° (298 K) = 44.0 kJ

Enthalpy of Fusion

The change in enthalpy when 1 mole of solid state changes into liquid state or liquid state freezes to solid state is known as enthalpy of fusion. In the first case, enthalpy of the system increases. In the other case, the enthalpy of the system decreases.

The enthalpy of fusion for 1 mole of water at 0^oC is 6.02 kJ. We may express this result in the following way:

H_2O (s) $\rightarrow$ H_2O (l) $\Delta H_{fus} = 6.02$ kJ mol^{-1}

H_2O (l) $\rightarrow$ H_2O (s) $\Delta H = -\ 6.02$ kJ mol^{-1}

The heat of fusion of water is 6 kJ mol^{-1} ΔH (273K) = 6.0 kJ

9.6 Heat Capacity

Heat capacity of the system is defined as amount of heat required to raise the temperature of the system by 1°C from lower to the higher temperature divided by the temperature difference.

$$C = \frac{dq}{dT}$$

So, SI unit is JK^{-1}

Heat capacity at constant volume $C_V = \left(\frac{dq}{dT}\right)_v = \frac{dq_v}{dT} = \left(\frac{dE}{dT}\right)_v$

Heat capacity at constant pressure $C_P = \left(\frac{dq}{dT}\right)_P = \frac{dq_P}{dT} = \left(\frac{dH}{dT}\right)_P$

If the amount of substrate is 1g then it is called the specific heat capacity.

Specific Heat Capacity

It is defined as the heat needed to cause a unit rise in the temperature of a unit mass of a substance. It is denoted by s. It SI units of J K^{-1} kg^{-1}.

Molar Heat Capacity

It is defined as the heat needed to cause a unit rise in the temperature of one mole of a substance. It is denoted as C_m. Thus, molar heat capacity of the system between temperature T_1 and T_2 will be expressed as $C = \frac{q}{T_2 - T_1}$

Since the heat capacity is function of temperature, hence the true molar heat capacity is defined by the differential equation

Relation between Cp and Cv

When a gas is heated without making change in its volume then no internal work is done by the gas. Therefore, all the heat which is supplied to the gas is used in increasing internal energy. Thus if there is rise in temperature of one of mole of gas through 1 C, the increase in its internal energy itself gives the molar heat capacity at constant volume. However when heating of gas is done under constant pressure conditions there will be increase in the volume of the gas that is the gas will expand and do some external work. Therefore, some extra heat must be supplied so that gas can perform this external work. Hence, molar heat capacity of gas at constant pressure must be greater than that at constant volume, i.e. $C_P > C_V$. The difference between these two quantities gives the work done by one mole of the gas in expansion when heated through 1C at constant pressure. Thus, C_P - C_V = work done by one mole of the gas in expansion when heated through 1C at constant pressure.

$$C_P - C_V = \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$H = U + PV$$

$$\text{Or, } C_P - C_V = \left(\frac{\partial(U+PV)}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$\text{Or, } CP - CV = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$U = f(T,V) \text{ so, } dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Differentiating w.r.t T at constant P

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_V \left(\frac{\partial T}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

Using the above equation in CP - CV

$$C_P - C_V = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

This expression is not very useful as $\left(\frac{\partial U}{\partial V}\right)_T$ is not measurable quantity.

The absorbed heat is utilized in two portions

(i) Absorbed heat is utilized to perform mechanical work of expansion for per degree rise in temperature, the magnitude is $P\left(\frac{\partial V}{\partial T}\right)_P$. This portion is transferred to surrounding in the form of mechanical work.

(ii) the term $\left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$ is the amount of energy used up to increase the internal energy due to increase in volume per degree rise in temperature. [As magnet is moved or separated a distance apart the attractive energy is stored as potential energy].

(iii) The other portion of supplied heat is utilized to increase the kinetic energy associated with different modes of molecular motion and hence increase kinetic energy. At constant volume the (i) mechanical work and (ii) internal work to increase intermolecular separation do not happen. The total heat is utilized to increase the temperature.

C_P - C_V for different gases

(i) when system is ideal gas

The intermolecular force of attraction is absent for ideal gas, $\left(\frac{\partial U}{\partial V}\right)_T = 0$

$$C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = P\times\left(\frac{nR}{P}\right) = nR$$

$C_{P,m}$ - $C_{V,m}$ = R

(ii) when system is defined by equation P(V-b) = RT

The correction term for attractive force is not included in the equation.

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

$$\int_{initial,path}^{final} - P_{opp}\, dv$$

$C_{P,m} - C_{V,m} = R$

(iii) when the system is van der Waals gas in cylinder with piston,

$\left(\frac{\partial U}{\partial T}\right)_T = \frac{a}{V^2}$, for van der Waals gas

$\left(\frac{\partial U}{\partial T}\right)_P$ for van der Waals gas need to be calculated

Or, PV - Pb + $\frac{a}{V} - \frac{ab}{V^2}$ - = RTNeglecting the small term, $\frac{ab}{V^2}$

Or, PV - Pb + = RT

Differentiating w.r.t T at constant P

$P\left(\frac{\partial V}{\partial T}\right)_P = 0 = \frac{a}{V^2}\left(\frac{\partial V}{\partial T}\right)_P = R$ OR, $\left(\frac{\partial V}{\partial T}\right)_P = 0 = \frac{R}{P - \frac{a}{V^2}}$

CP - CV = $\left[P + \left(\frac{\partial V}{\partial T}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$ OR CP - CV = $\left(P + \frac{a}{V^2}\right)\frac{R}{P - \frac{a}{v^2}}$

Mathematical tricks

CP - CV = $\left(P + \frac{a}{V^2}\right)\frac{R}{P + \frac{a}{v^2} - \frac{2a}{V^2}}$

Or, CP - CV = $\left(P+\frac{a}{V^2}\right)\frac{R}{P+\frac{RT}{V^2}-\frac{2a}{V^2}}$

Or, CP - CV = $\left(P+\frac{a}{V^2}\right)\frac{R}{\frac{RT}{V-b}-\frac{2a}{V^2}}$

Or, CP - CV = $\left(P+\frac{a}{V^2}\right)\frac{R}{\frac{RT}{V-b}\left[1-\frac{2a}{V^2}\frac{(V-b)}{RT}\right]}$

Or, $\frac{\left(P+\frac{a}{V^2}\right)(V-b)}{RT}.R.\left[1-\frac{2a(V-b)}{RTV^2}\right]^{-1}=\frac{RT}{RT}.R.\left[1-\frac{2a(V-b)}{RTV^2}\right]^{-1}$

Or, $R[1+\frac{2aV}{RTV^2}]$ neglecting the higher terms

At ordinary pressure (V-b) = Vas V >> b

CP - CV = $R[1+\frac{2aV}{RTV^2}]$ = R + $\frac{2a}{TV}$, if V is replaced by ideal gas equation as an approximation

CP - CV = R + $\frac{2aP}{RT^2}$, thus (CP - CV) > R for van der Waals gas

(iv) In case of solids and liquids

Here, $\left(\frac{\partial V}{\partial T}\right)_P$ is positive but negligible, $\left(\frac{\partial U}{\partial V}\right)_T$ is also positive, CP is slightly greater than CV. For practical purpose CP CV for condensed phase.

(v) in case of water

CP - CV for water at 4^{o}C

The liquid water attains minimum molar volume at 4oC. So V =minimum at 4oC.

$$= \left(\frac{\partial U}{\partial V}\right)_P 0 \text{ at } 4\ {}^{o}\mathrm{C}$$

So, CP - CV = 0

CP = CV

Generalised form of CP - CV

We have obtained the relation

$$\text{CP - CV} = \left[P + \left(\frac{\partial U}{\partial V}\right)\right]_T \left(\frac{\partial v}{\partial T}\right)_P$$

Thermodynamic equation of state

$$= \left(\frac{\partial U}{\partial V}\right)_P \text{-P} + \left(\frac{\partial P}{\partial T}\right)_V T$$

[U, H are energy term equivalent PV, check dimension on $\frac{PV}{V}$ LHS]

$$\text{CP - CV} = [P + \{-P + T\left(\frac{\partial V}{\partial T}\right)_P \}] = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial P}{\partial T}\right)_P$$

$$\text{CP - CV} = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial P}{\partial T}\right)_P$$

CP - CV in terms of α and β

α = thermal expansion coefficient = $\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$

β = co-efficient of compressibility = - $\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\frac{\alpha}{\beta} = -\frac{(\frac{\partial V}{\partial T})_P}{\left(\frac{\partial V}{\partial T}\right)_T} = \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial V}\right)_T$$

Cyclic rule

For z = f(x,y)The relation is $\left(\frac{\partial x}{\partial y}\right)_z\left(\frac{\partial y}{\partial z}\right)_X\left(\frac{\partial z}{\partial x}\right)_Y = -1$

V = f(T,P)

cyclic rule

$$= \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V\left(\frac{\partial P}{\partial V}\right)_T = -1$$

$$= \left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial T}{\partial P}\right)_V = \frac{1}{\left(\frac{\partial T}{\partial P}\right)_V}$$

$$= \frac{\alpha}{\beta} = \frac{1}{\left(\frac{\partial P}{\partial T}\right)_V} = \left(\frac{\partial P}{\partial T}\right)_V$$ and again $\left(\frac{\partial V}{\partial T}\right)_V = \alpha V$

CP - CV = $T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$

CP - CV = $\frac{\alpha^2 TV}{\beta}$

Expression for $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2} = 0$ for ideal gas and $= \left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

Thermodynamic equation of state

$$\left(\frac{\partial U}{\partial V}\right)_T = P + T\left(\frac{\partial P}{\partial T}\right)_V$$

For n moles gas, $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$

Or, $P = \frac{nRT}{V - nb} - \frac{an^2}{V_2}$ or, $= \left(\frac{\partial P}{\partial T}\right)_V = P + T\frac{nR}{V - nb}$

Or, $= \left(\frac{\partial U}{\partial V}\right)_T = P + T\frac{nR}{V - nb}$

Or, $\left(\frac{\partial U}{\partial V}\right)_T = P + \left(P + \frac{an^2}{V^2}\right) = \frac{an^2}{V^2}$ The value decreases with increase of volume.

9.7 Work done in Reversible and Irreversible processes

Isothermal and Adiabatic Processes

An isothermal process occurs at a constant temperature throughout the transformation. In such a process, any expansion of the system against external pressure leads to cooling, as energy is expended in doing work. To maintain a constant temperature, the system must be in perfect thermal equilibrium with its surroundings, allowing heat to flow into the system to compensate for the energy loss. Conversely, during isothermal compression, heat must exit the system to prevent a temperature rise. The boundary that permits such heat exchange is known as a diathermic wall, ensuring continuous thermal communication between the system and its surroundings.

In contrast, an adiabatic process occurs without any heat transfer between the system and its surroundings. This means that all energy changes in the system arise solely from work done on or by the system. In adiabatic expansion, the system's temperature decreases as it does work on the surroundings, while in adiabatic compression, the temperature increases due to work being done on the system. The boundary that prevents any heat exchange is called an adiabatic wall, which ensures that thermal energy remains confined within the system.

Path in Thermodynamic Processes

The path of a thermodynamic process refers to the sequence of intermediate steps that a system follows as it transitions from its initial state to its final state.

In an irreversible process, the transition occurs in a finite number of steps-which could range from one, two, or even thousands-without maintaining equilibrium at every stage. The process cannot be reversed without external intervention, and the work done during such a process depends on the specific path taken.

In contrast, a reversible process consists of an infinite number of infinitesimally small steps, where the system remains in quasi-equilibrium at all times. In this case, the driving force and opposing force differ by an infinitesimally small amount, allowing the process to be reversed without any net change to the system or surroundings. The work obtained from a reversible isothermal expansion is always greater than that from an irreversible expansion under the same conditions.

Illustration

Consider a classroom where the teacher's chair is moved from one location to another. This change naturally raises questions: Who moved it? How did it happen? The rearrangement could have been done in a single step, or through multiple intermediate steps. The total effort (analogous to work in thermodynamics) varies depending on the path taken. Similarly, in thermodynamic systems, an irreversible process can have different work values depending on the number of steps involved, whereas a reversible process follows a unique, idealized path that maximizes work output.

Thermodynamic Reversibility

1. A process is considered thermodynamically reversible if both the system and its surroundings can be restored to their original states when the process is carried out in reverse, without leaving any net change in the universe.

2. In a reversible process, the system remains in internal equilibrium at all times, meaning that all intermediate states can be fully described using thermodynamic variables such as temperature and pressure. Moreover, at every step, the system maintains virtual equilibrium with its surroundings, allowing the process to be reversed by making an infinitesimally small adjustment to the opposing force relative to the driving force.

2. Since a reversible process requires the opposing force to differ from the driving force by an infinitesimal amount, it takes an infinitely long time to complete. This is because the process proceeds in an extremely slow and controlled manner. For example, in the reversible expansion of a gas, the internal gas pressure acts as the driving force, while the external pressure, which is only infinitesimally lower, serves as the opposing force.

4. Thermodynamic reversibility is an idealized concept that is rarely achieved in real-world processes. However, it serves as a theoretical benchmark, helping to establish the upper limits of efficiency and measurable quantities in practical thermodynamic systems.

Magnitude of w is Path Function

Work is one way by which energy can enter or leave the system. It has direction and order

so can be measured $w = \int_{\text{initial,path}}^{\text{final}} -P_{opp} dv$

Nature of Work	**Expression of work**	**Intensive Variable**	**Extensive Variable**
Mechanical Work	$-P\,dV$	P	V
Electrical Work	$-E\,dZ$	E	Z
Extension of surface film	$-\gamma\,d\sigma$	γ	σ

Comparison of q,w , ΔU and ΔH for different Types of Isothermal Processes

Process	Expansion	Compression	Cyclic
Reversible q, (-w)	$nRt\ln\frac{V^2}{V^1}$	$nRt\ln\frac{V^2}{V^1}$	0
$\Delta U, \Delta g$	0	0	0
Free q, (-w)	0	$P_{opp}(V_1-V_2)$	$P_{opp}(V_1-V_2)<0$
$\Delta U, \Delta g$	0	0	0
Intermediate q, (-w)	$0 < P /opp(V_2-V_1)$	$P_{opp}(V_1-V_2)$	$(P/_{opp}-P_{opp})(V_2-V_1)<0$
	$< nRTin\frac{V_2}{V_1}$	$< nRTin\frac{V_1}{V_2}$	
$\Delta U, \Delta H$	0	0	0

9.7 Joule's experiment and its consequence

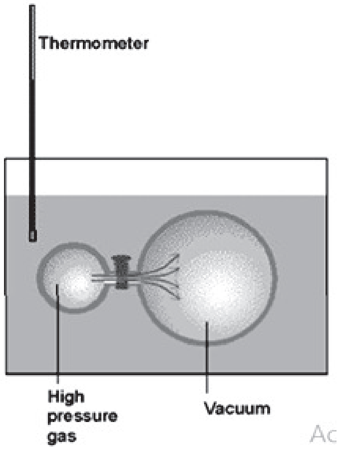
From the first-law point of view, heat and work are not different at all. However heat and work are very different from the second law point of view. Heat, temperature and energy belong to different scales, such as the motion of microscopic particles and the thermal state of a certain body. When the gas expands the molecules are slowed since they overcome attraction. Kinetic energy gets converted into potential energy, very similar to two magnets when they are separated attraction is reduced and the same is stored as potential energy in the magnet. Allowing molecule to be apart from each other, cools the gas which results by increasing volume without allowing any heat to enter from outside.

A schematic diagram of the apparatus used by Joule in an attempt to measure the change in internal energy when a gas expands isothermally (gas expands into a vacuum). The heat absorbed by the gas is proportional to the change in temperature of the bath.

Before expansion, the entire gas is present in the small vessel. Opening the stop cock, the gas freely expands against a zero pressure. Work involved in free expansion

$dw = 0$. Now $dU = dq + dw$,

we have dU = dq



Since there is no change in temperature of the bath, the amount of heat involved, dq, is also zero.

We know U = f (T,V)

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

Since dT = 0 and dU = 0 , $dV \left(\frac{\partial U}{\partial V}\right)_T dV = 0; dV \neq 0$

$\left(\frac{\partial U}{\partial V}\right)_T = 0$ known as Joule's law

Energy of the gas is function of Temperature only.

Joule Coefficient, $\mu J = \left(\frac{\partial T}{\partial V}\right)_U$

The results of Joule experiment involving any gas (real or ideal) can be expressed in terms of μJ

The Joule coefficient in terms of $\left(\frac{\partial U}{\partial V}\right)_T$ is $\mu_J = -\frac{1}{C_V}\left(\frac{\partial U}{\partial V}\right)_T$

The Joule coefficient J can be expressed in terms of the equation of state of the gas

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\mu_J = \frac{1}{C_V}\{T\left(\frac{\partial P}{\partial T}\right)_V - P\}$$

Joule Coefficient for ideal gas is 0 (zero)

μ_J depends on the relative magnitudes of P and $\left(\frac{\partial P}{\partial T}\right)_V$ for Real gas

$P > T\left(\frac{\partial P}{\partial T}\right)_V$ Then J is positive. μ_J is always positive in Joule experiment, $\left(\frac{\partial T}{\partial V}\right)_U$ $(dT)_U$ is positive, there is increase in temperature

$P < T\left(\frac{\partial P}{\partial T}\right)_V$ Then μ_J is negative (-ve).. Hence $(\partial T)_U$ is negative, that is, there occurs a decrease in temperature of the gas. Here $\left(\frac{\partial U}{\partial V}\right)_T$ = + ve.

Note. $\left(\frac{\partial U}{\partial V}\right)_T$ = - ve at very high pressures and is positive at ordinary pressures may be explained on the basis that the energy U consists of two types of energies, kinetic and potential energy. When the volume is increased at constant temperature, the kinetic energy remains constant but potential energy varies.

At ordinary pressures where the attractive molecular forces predominate, the potential energy increases on expansion and hence $\left(\frac{\partial U}{\partial V}\right)_T = +\text{ ve.}$

At very high pressures where the excluded volume plays the dominating role, the potential energy decreases on expansion and hence $\left(\frac{\partial U}{\partial V}\right)_T = -\text{ ve.}$

9.9 Summary

This unit introduces fundamental thermodynamic concepts, including the classification of thermodynamic systems (open, closed, and isolated) and thermodynamic variables (intensive and extensive properties). It explores different thermodynamic processes, such as isothermal, adiabatic, reversible, and irreversible processes, and establishes their defining characteristics.

A key focus of this unit is the First Law of Thermodynamics, which expresses the conservation of energy and its mathematical formulation $(\Delta U = q + w)$. The concept of internal energy (U) is discussed in detail, emphasizing its role as a state function and its dependence on system variables such as pressure, volume, and temperature. The unit also examines the mathematical background necessary for thermodynamics, including exact and inexact differentials, partial derivatives, Euler's reciprocity rule, and the cyclic rule.

The principles of work and heat transfer in thermodynamic processes are explored, highlighting the distinction between reversible and irreversible paths and their impact on work efficiency. The concept of thermodynamic reversibility is discussed as an idealized condition where the system maintains continuous equilibrium, setting theoretical limits for practical thermodynamic applications.

9.10 Self-Assessment Questions

1. Define internal energy (U). Why is it considered a state function?
2. State the First Law of Thermodynamics and explain its significance in energy conservation.
3. Differentiate between heat (q) and work (w) in thermodynamic processes.

4. Derive the mathematical expression for $\Delta U = q + w$ and explain its implications.
5. Define enthalpy (H) and derive the relationship between internal energy (U) and enthalpy.
6. Explain the relation between heat capacities at constant pressure (Cp) and constant volume (Cv). Derive the expression Cp - Cv = R for an ideal gas.
7. What is the physical significance of enthalpy (H) in thermodynamics?
8. How do you calculate q, w, ΔU, and ΔH for the reversible isothermal expansion of an ideal gas?
9. How do the values of q, w, ΔU, and ΔH differ in reversible and irreversible expansion of an ideal gas?
10. Compare the work done in free expansion versus reversible expansion of an ideal gas.
11. Explain the conditions required for a process to be isothermal and derive the work done in the isothermal expansion of an ideal gas.
12. Describe an adiabatic process and derive an expression for the work done in the adiabatic expansion of an ideal gas.
13. How does the First Law of Thermodynamics apply to Joule's experiment? What are its consequences?
14. Explain the significance of van der Waals gases in thermodynamics and how their expansion differs from that of an ideal gas.
15. In an adiabatic expansion, why does the temperature of an ideal gas decrease? How is this related to the First Law of Thermodynamics?

Unit 10 ❐ Thermochemistry

10.1 Objectives

10.2 Introduction

10.3 Calorimetry and Thermochemistry

10.4 Enthalpy of different processes

10.5 Laws of Thermochemistry

10.6 Temperature dependence of the Heat of reaction (Kirchoff Equation)

10.7 Bond Energy

10.8 Summary

10.9 Self-Assessment Questions

10.1 Objectives

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

- Apply the First Law of Thermodynamics to various thermodynamic processes, understanding energy conservation in closed and open systems.
- Explain the fundamental laws of thermochemistry, including Hess's Law, and their implications in energy calculations.
- Define and distinguish between different standard states and their role in thermochemical equations.
- Calculate enthalpy changes for various processes
- Determine bond dissociation energy from thermochemical data and assess its significance in chemical stability and reactivity.
- Illustrate and analyze the Born-Haber cycle for ionic compounds to understand lattice energy and formation enthalpies.
- Utilize Kirchhoff's equation to evaluate the temperature dependence of enthalpy changes in chemical reactions.
- Interpret and apply thermochemical data to solve problems related to energy changes in physical and chemical transformations.

10.2 Introduction

Thermochemistry is a vital branch of thermodynamics that deals with the study of heat changes occurring during chemical reactions and physical transformations. It provides a quantitative understanding of energy transfer in various processes, enabling scientists to predict reaction feasibility and efficiency.

The First Law of Thermodynamics, also known as the law of energy conservation, serves as the foundation of thermochemistry. It states that energy cannot be created or destroyed, only transferred or transformed between different forms. This principle allows us to track energy flow in chemical systems, providing essential insights into reaction energetics.

A key focus of this unit is the measurement and calculation of enthalpy changes associated with different processes. These include the enthalpy of formation, combustion, solution, dilution (including infinite dilution), neutralization, ionization, and the formation of ions. Each of these concepts plays a crucial role in understanding chemical behavior and reactivity.

Furthermore, thermochemical principles help determine bond dissociation energy, which reflects the stability of molecules and the strength of chemical bonds. The Born-Haber cycle is an essential tool for analyzing lattice energies in ionic solids, offering deeper insights into ionic bonding and crystal formation. Additionally, Kirchhoff's equation helps evaluate how enthalpy changes with temperature, allowing for precise thermochemical predictions under varying conditions.

Overall, this unit provides a strong theoretical and practical foundation for understanding energy transformations in chemical systems, equipping learners with essential problem-solving skills in thermodynamics and chemical energetics.

10.3 Calorimetry and Thermochemistry

Exothermic Reactions: These are reactions in which heat is released. In such cases, the energy content of the products is lower than that of the reactants. For a reaction occurring at constant pressure, the enthalpy change (?H) is negative.

Example:

$$N_2 + 3H_2 \rightarrow 2NH_3 + \text{heat}$$

Endothermic Reactions: These reactions absorb heat from their surroundings, resulting in products with higher energy content than the reactants. The enthalpy change (?H) for such reactions is positive.

Example:

$$PCl_5 + \text{heat} \rightarrow PCl_3 + Cl_2$$

Relationship Between ΔU and ΔH:

The energy change for a reaction varies depending on the conditions under which it occurs. At constant volume, the energy change is denoted as ?U, while at constant pressure, it is represented by ?H. The relationship between these two thermodynamic quantities, often referred to as the "heats of reaction," is given by:

$$\Delta H = \Delta U + P\Delta V = \Delta U + \Delta nRT$$

where ?n represents the difference in the number of moles of gaseous products and reactants in the balanced chemical equation.

10.4 Enthalpy of Different Processes

Heat or Δ enthalpy of formation (Δ Hf)

The enthalpy of formation of a compound is the enthalpy change accompanying the formation of one mole of the compound from the elements. If the compound and its elements are in the standard state, the heat of the above reaction is referred to as standard enthalpy of formation (?HOf). Eg. Formation of sucrose

$$12\ C\ (s) + 11H_2\ (g) + O_2\ (g) \rightarrow 1\ C_{12}\ H_{22}O_{11}\ (s) + \text{heat}$$

The enthalpy change for this reaction is the enthalpy of formation of sucrose. For H2 and O2 the gaseous state with a pressure of 1 atm (gases being assumed to be ideal) is the standard state. For carbon, graphite is taken as the standard state. It should be noted that the above reaction is a hypothetical one and does not actually take place.

Enthalpy of combustion is the enthalpy change accompanying the complete combustion of 1 mole of the substance. e.g. Combustion of benzoic acid

$$1C_6H_5COOH\ (s) + \frac{15}{2}O_2\ (g) \rightarrow 7\ CO_2\ (g) + 3\ H_2O\ (l) + \text{heat}$$

Δ H for this reaction is the enthalpy of combustion of benzoic acid.

Enthalpy of phase change (fusion of vaporization or sublimation or transition from one allotropic state to another) is the enthalpy change accompanying the required phase transition of 1mole of the substance at a fixed temperature. Under this head, we have enthalpies of fusion, vaporization, sublimation and allotropic transition.

Enthalpy of neutralization is the enthalpy change accompanying the neutralization of one gram equivalent of an acid by one gram equivalent of a base, both in dilute solution. The enthalpy of neutralization of a strong acid (HCl, H2SO4, HNO3) by a strong base (NaOH, KOH, etc.) is a constant, whatever be the acid or the base and it is -13.7kCals or -57.5kJ. This constancy is ascribed to the complete ionization of the strong acid and base and also the salt, the overall reaction being the formation of H2O from H+ and OH-. If in the neutralization, either the acid or the base or both are weak, Δ H of neutralization will be less, since dissociation of weak acid or base during neutralization requires energy. E.g. ?H of neutralization of acetic acid by NaOH is -55.2 kJ so that the difference , 57.5 -55.2 = 2.3 kJ, represents the energy required for ionizing 1 gm equivalent of the weak acid.

Enthalpy of solution (or heat of solution) is the enthalpy change accompanying the dissolution of 1 mole of the solute in a suitable amount of the pure solvent to give a solution of the desired concentration. It is also referred to as the integral heat of solution.

e.g. integral heat of solution of KCl in 200 moles of water is represented as:

KCl(s) + 200 H2O(l) ? KCl (solution) $\Delta H \approx 18.6$ kJ

A positive value of ?H means absorption of heat during dissolution and there is cooling. The above equation should be distinguished from the following:

$\mathrm{KCl\ (s) + aq \rightarrow KCl\ (aq)}$. In this case 1 mole of KCl is dissolved in an excess of water. By "excess" we mean that the water taken is in such large quantity that further addition of water to the solution will not produce any thermal change.

There is another heat of solution, known as the differential heat of solution, defined by the expression $\left[\dfrac{\partial(\Delta H)}{\partial n_2}\right]_{T,P,n1}$. This is obtained by dissolving varying amounts of solute (n_2 moles) in a fixed amount of solvent (conventionally 1000gms). The slope of the plot of ΔH versus n_2 at any desired concentration (molality) gives the differential heat of solution.

It is also defined as the enthalpy change when 1 mole of solute is added to a large volume of solution at a specified concentration, temperature and pressure.

Enthalpy of dilution or the integral heat of dilution is the enthalpy change, when a solution containing 1 mole of the

10.5 Laws of Thermochemistry

1st Law : Law of Lavoisier and Laplace (1780)

"The enthalpy change of a chemical reaction in one direction is equal in magnitude but opposite in sign to that accompanying the same reaction in the reverse direction."

Illustration $H_2(g) + ½O_2(g) = H_2O\ (l); \Delta H°_{298K} = -68.3$kcal

So, $H_2O(l) = H_2(g) + ½O_2(g)\ ; \Delta H°_{298K} = +68.3$kcal

The law is a consequence of 1st law of thermodynamics. H is a state function, so it depends on the states of the reacting system. Let us suppose, the reactants A and B first change into products C and D with enthalpy of reaction. ?H1 and then C and D give reactants A and B back, the enthalpy of reaction is ?H2. Thus, for the whole cycle ?H= $\Delta H_1 + \Delta H_2$

2nd Law: Hess's Law of Constant Heat Summation (1840)

Statement: "For a chemical reaction, the net heat change (ΔH, ΔU) will be the same whether the process occur in one step or in several steps."

Illustration: A chemical reaction happening in two steps, $A \rightarrow C : \Delta H = \Delta H_1$

But when the same reaction occurs in two steps, $A \rightarrow B : \Delta H = \Delta H_2$ & $B \rightarrow C : \Delta H = \Delta H_3$

Then, according to the law, $\Delta H_1 = \Delta H_2 + \Delta H_3$

Application of the Law

This law is sometimes used to calculate the enthalpy of a reaction which is difficult to determine by experiments.

For example, $C(s) + \frac{1}{2}O_2(g) = CO(g)$, ΔH of the reaction is not easy to determine experimentally as some amount of CO_2 always forms in association with CO. The value of ΔH for the reaction can be calculated as follows.

$C(s) + O_2(g) = CO_2(g)$: $\Delta H^\circ_{298K} = -94.05$ kcal, when it occurs in a single step.

The same reaction can also occur in two steps.

$C(s) + \frac{1}{2}O_2(g) = CO(g)$: $\Delta H^\circ_{298K} = Q$ (say)

$CO(g) + \frac{1}{2}O_2(g) = CO_2(g)$: $\Delta H^\circ_{298K} = -67.63$ kcal

So, according to the law , (-94.05kcal) = Q + (-67.63kcal) or Q = -26.42 kcal

Thus, $C(s) + \frac{1}{2}O_2(g) = CO(g)$: $\Delta H^\circ_{298K} = -26.42$ kcal

Extension of Hess's Law

The changes in entropy and in Gibbs free energy can also be calculated by applying the concepts of Hess's law. The Bordwell thermodynamic cycle is an example of such an extension which takes advantage of easily measured equilibria and redox potentials to determine experimentally inaccessible Gibbs free energy values.

Thus change in free energy $\Delta G^\circ_{react} = \sum \Delta G^\circ_{f(pdts)} - \sum \Delta G^\circ_{f(reat)}$

But entropy can be measured as an absolute value thus entropy of formation is not required, simply absolute values of entropy are used. $\Delta S^\circ_{react} = \sum \Delta S^\circ_{f(pdts)} - \sum \Delta G^\circ_{f(reat)}$

Applications of Hess's Law

Hess's law of constant heat summation is useful in the determination of enthalpies of the following:

- Calculation of enthalpies of reactions
- Determination of enthalpy changes of slow reactions
- Calculation of enthalpies of formation
- Enthalpy of formation of reactive intermediates
- It helps in determining the lattice energies of ionic substances by building Born-Haber

cycles if the electron affinity to form the anion is known

10.6 Temperature dependence of the Heat of reaction (Kirchoff Equation)

If we know the $\Delta H°$ of a reaction at temperature, T1, Kirchhoff's equation provides the calculation of $\Delta H°$ of the same reaction at another temperature, T2.

Let us consider the chemical reaction,

$$\nu_1\ A_1 + \nu_2\ A_2 = \nu_3\ A_3 + \nu_4\ A_4 \text{ or, } -\nu_1\ A_1 - \nu_2\ A_2 + \nu_3\ A_3 + \nu_4\ A_4 \text{ or, } 0 = \sum_i \nu_i A_i$$

where ν_i = stoichiometric coefficient and it is (+ve) for the products and (-ve) for the reactants. Enthalpy of the reaction,

$$\Delta H° = (\nu_3\ H°_{3,m} + \nu_4\ H°_{4,m}) - (\nu_1\ H°_{1,m} + \nu_2\ H°_{2,m}) = \sum_i \nu_i H°_{i,m}$$

Since , P is fixed at the standard state of 1 atm, differentiating with respect to T at constant pressure, $\left[\frac{\partial(\Delta H°)}{\partial T}\right] = \sum_i \nu_i \left[\frac{\partial H°_{im}}{\partial t}\right]_p = \sum_i \nu_i C_{P,i} = \Delta C_p$, called standard constant pressure molar heat capacity change of the process.

Integrating within limits , $= \int_{\Delta H^\circ_1}^{\Delta H^\circ_2} d(\Delta H°) = \int_{T_2}^{T_2} \Delta C_P dT)$

When ΔC_P is assumed to be temperature independent, $\Delta H^\circ_2 = \Delta H^\circ_1 + \Delta C_p(T_2 - T_1)$

When ΔC_P is assumed to be temperature dependent, $C_{P,i} = a_i + b_i T + c_i T_2 + \ldots$

and $\Delta C_P = \sum_i \nu_i C_{P,i} = \sum_i \nu_i (a_i + b_i T + c_i T^2 + \ldots)$

$= \alpha + \beta T + \gamma T^2$

Where $\alpha = \sum \nu_i a_i , \beta = \sum \nu_i b_i$ and $\gamma = \sum \nu_i c_i$

Using this expression of ΔC_P we get $\Delta H_2^0 = \Delta H_1^0 + \int_{T_1}^{T_2} (\alpha + \beta T + \gamma T^2 + ...)dt$

Or, $\Delta H_2^{\circ} = \Delta H_1^{\circ} + \alpha(T_2 - T_1) + \frac{\beta}{2}(T_2^2 - T_1^2)$

The relation of internal energy of reaction with temperature is

$$\Delta U_2^{\circ} = \Delta U_1^{\circ} + \alpha(T_2 - T_1) + \frac{\beta^1}{2}(T_2^2 - T_1^2)$$

These are the Kirchhoff's equations which relate the heat of reaction with temperature.

10.7 Bond Energy

Bond energy of a given bond is defined as the average of energy required to dissociate the said bond present in different gaseous compounds into free atoms or radicals in the gaseous state. The bond energy differs from dissociation energy which is defined as the energy required to dissociate a given bond of some specific compound.

Let us consider O_H bond. The heat of dissociation of the O-H bond depends on the nature of molecular species from which the H-atom is being separated from O-atom.

Examples

For H_2O molecule ,

H2O molecule (g) → H(g) + OH(g): ΔH°_{298K}= 119.95kcal mol^{-1}.

But to break the O-H bond in the hydroxyl radical requires a different quantity of heat

O-H (g) → O(g) + H(g) ; ΔH°_{298K} = 101.19kcal mol^{-1}. The bond energy , ε OH is defined as the average of these two values:

i.e. ε OH = ½(119.96+101.9) = 110.57 kcal mol^{-1}.

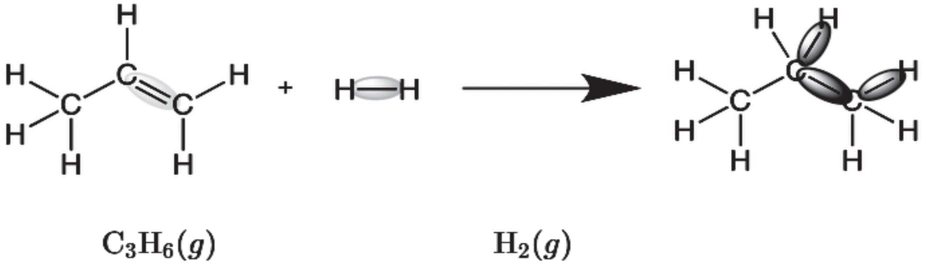
Energy in chemical bonds

Chemical bonds represent potential energy. Quantifying the energy represented by the bonds in different molecules is an important part of understanding the overall energy implications of a reaction. In this article, we'll explore two different concepts that help describe that energy: enthalpy of reaction and bond enthalpy.

Enthalpy of reaction

During chemical reactions, the bonds between atoms may break, reform or both to either absorb or release energy. The result is a change to the potential energy of the system. The heat absorbed or released from a system under constant pressure is known as *enthalpy*, and the change in enthalpy that results from a chemical reaction is the *enthalpy of reaction*. The enthalpy of reaction is often written as ΔH_{rxn}

To better understand enthalpy of reaction, let's consider the hydrogenation of propene, C_3H_6, to form propane, C_3H_8. In this reaction, propene gas reacts with hydrogen gas, $H_2(g)$, to form propane gas:



What is happening in this reaction? First we have to break the carbon C=C bond and H-H bond of the reactants. As a rule, breaking bonds between atoms requires adding energy. The stronger the bond, the more energy it takes to break the bond. To make the product propane, a new C-C and two new C-H. Since breaking bonds requires adding energy, the opposite process of forming new bonds always releases energy. The stronger the bond formed, the more energy is released during the bond formation process. In this particular reaction, because the newly formed bonds release more energy than was needed to break the original bonds, the resulting system has a lower potential energy than the reactants. This means the enthalpy of reaction is negative.

Mathematically, we can think of the enthalpy of reaction as the difference between the potential energy from the product bonds and the potential energy of the reactant bonds.

Reactions where the products have a lower potential energy than the reactants, such as the hydrogenation of propene described above, are exothermic. Reactions where the products have a higher potential energy than the reactants are endothermic.

In an exothermic reaction, the released energy doesn't simply disappear. Instead it is converted to kinetic energy, which produces heat. This is observed as an increase in temperature as the reaction progresses. On the other hand, endothermic reactions often require the addition of energy to favor the formation of products. In practice, this often means running a reaction at a higher temperature with a heat source.

In order to quantify the enthalpy of reaction for a given reaction, one approach is to use the standard enthalpies of formation for all of the molecules involved. These values describe the change in enthalpy to form a compound from its constituent elements. Subtracting the standard enthalpies of formation for the reactants from the standard enthalpies of the products approximates the enthalpy of reaction for the system.

An alternative approach is to estimate the enthalpy of reaction by looking at the individual bonds involved. If we know how much energy we need to make and break each of the bonds, then we can add those values to find the enthalpy of reaction.

10.8 Summary

This unit explores the principles of thermochemistry, focusing on the application of the First Law of Thermodynamics, which states that energy cannot be created or destroyed but can be transferred between a system and its surroundings. The concept of enthalpy (H) is introduced as a key thermodynamic function used to quantify heat changes in chemical reactions occurring at constant pressure.

10.9 Self-Assessment Questions

1. Differentiate between internal energy (U) and enthalpy (H). Under what conditions are they equal?
2. Define Hess's Law and illustrate its application with an example.
3. What is meant by the "standard state" of a substance? How is it relevant to enthalpy

calculations?

4. Define enthalpy of formation. How is it different from the enthalpy of combustion?
5. The standard enthalpy of combustion of methane (CH_4) is -890 kJ/mol. What does this value indicate about the reaction?
6. How does enthalpy of solution differ from enthalpy of dilution? Explain the concept of enthalpy of infinite dilution.
7. Why is the enthalpy of neutralization of a strong acid and strong base nearly constant?
8. What is enthalpy of ionization, and how is it related to the enthalpy of formation of ions?
9. How can bond dissociation energy be determined from thermochemical data? Explain with an example.
10. Derive Kirchhoff's equation and explain how it is used to determine enthalpy changes at different temperatures.
11. Given the following thermochemical data:

$$C(s) + O_2 \rightarrow CO_2(g) \quad \Delta H = -393.5 kJ/mol$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \quad \Delta H = -285.8 kJ/mol$$

Calculate the enthalpy change for the formation of methanol (CH_3OH) from its elements:

$$C(s) + 2H_2(g) + \frac{1}{2}O_2(g) \rightarrow CH_3OH(l)$$

Unit 11 ❒ Second Law of Thermodynamics

11.1 Objectives

11.2 Introduction

11.3 Need for a Second law

11.4 Thermodynamic Definitions

11.5 Statement of the Second law of thermodynamics

11.6 Carnot cycle, Carnot engine

11.7 Entropy

11.8 Entropy Change

11.9 Clausius inequality

11.10 Summary

11.11 Self-Assessment Questions

11.1 Objectives

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

- Understand the need for a Second Law of Thermodynamics.
- Recognize the limitations of the First Law in explaining spontaneity and directionality.
- Distinguish between Kelvin-Planck and Clausius statements and their equivalence.
- Study the Carnot cycle and its implications.
- Explain Carnot's theorem and efficiency limits of engines.
- Develop the thermodynamic scale of temperature.
- Interpret Clausius inequality and the concept of entropy.
- Calculate entropy changes for various processes.
- Understand the molecular basis of entropy.

11.2 Introduction

Thermodynamics is a fundamental branch of physical chemistry that deals with energy transformations and the principles governing them. It provides a systematic framework for understanding heat, work, and the properties of matter in equilibrium. The laws of thermodynamics define the limits of energy conversion and establish criteria for spontaneity and feasibility of chemical and physical processes.

The First Law of Thermodynamics addresses energy conservation, stating that energy cannot be created or destroyed, only transferred or converted. However, it does not explain why certain processes occur spontaneously while others do not. The Second Law of Thermodynamics introduces the concept of entropy, defining the directionality of natural processes and the limitations of energy utilization.

Through thermodynamics, we gain insights into the efficiency of engines, refrigeration cycles, and the fundamental nature of energy dispersal in the universe. This subject serves as a cornerstone for various scientific and engineering applications, including chemical reactions, phase transitions, and industrial energy systems.

11.3 Need for a Second law

In everyday experience, any difference in properties such as pressure, temperature, or electric potential tends to be eliminated through natural processes. When two systems with different properties are brought together, they are in a non-equilibrium state and move toward equilibrium by minimizing these differences-such as heat flow in the case of temperature variation. Once uniformity is achieved, the system remains in equilibrium unless disturbed by an external influence.

In analogy with mechanical systems, which seek to minimize potential energy, early theories suggested that chemical reactions should minimize heat content. This led to the idea that exothermic reactions must be spontaneous and endothermic reactions non-spontaneous. However, exceptions exist, such as the vaporization of water at low pressure or the dissolution of ammonium chloride in water, both of which are endothermic yet spontaneous. This indicates that internal energy (ΔU \ Delta UΔU) is not a sufficient criterion for spontaneity, and enthalpy (HHH) alone, as derived from the First Law of Thermodynamics, cannot predict it.

The First Law states that energy is conserved (ΔU =q+w), and for cyclic processes, $\Delta U = 0$, implying that heat can be entirely converted into work. This motivated the search for processes capable of achieving complete heat-to-work conversion. Carnot's reversible cycle was a breakthrough in this regard, laying the foundation for the theoretical development of heat engines.

While the First Law describes energy conservation, it does not determine the direction of a process. It permits heat transfer from a colder to a hotter body, yet such a process does not occur naturally. The Second Law of Thermodynamics addresses this limitation, establishing that processes occur in a specific direction. Before exploring this law in detail, it is essential to examine the limitations of the First Law.

First law allows us to calculate the energy changes in processes. But these changes do not suggest spontaneity. Examples: H, U

11.4 Thermodynamic Definitions

Heat reservoir

It is a large system which is in stable equilibrium and heat can be transferred to and from it without any change in its temperature.

The heat reservoir which is at high temperature and from which the heat is transferred is known as heat source while the heat reservoir which is at low temperature and to which heat is transferred is known as heat sink

Work reservoir

It is a very large system in stable equilibrium through which definite amount of work is transferred adiabatically without any change in pressure

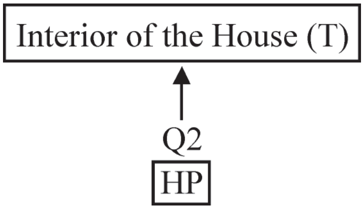
Thermodynamic cycle

If the system after undergoing series of processes reaches to its original state then the system is said to have completed a thermodynamic cycle. In this the properties of the system at the beginning and at the end of the cycle are same.

Thus Pf = Pi i.e. pressure of the system at initial (beginning) stage and at final (end) stage is same. Similarly, Tf = Ti

Heat engine

It is a thermodynamic system working in a thermodynamic cycle to which net heat is transferred and from which work is delivered.



Heat Pump

HP is used to warm the house in the winter by giving heat from outside, Outside the house temperature T1 is that of Low temperature reservoir.

Efficiency (ψ) = Heat pumped inside the room / work supplied

$$(\psi) = \frac{Q_2}{Q_2 = Q_1} = \frac{T_2}{T_2 = T_1}$$

11.5 Statement of the Second law of thermodynamics

The second law of thermodynamics is expressed in many ways, the most salient statements being given by Rudolf Clausius (1854), Lord Kelvin (1851), Max Planck(1926) etc. Although these statements are different but each one of them predicts the direction in which a change will take place spontaneously. Now discussing these statements in detail.

Kelvin statement of the second law

This statement for second law of thermodynamics was proposed by Lord Kelvin. It states that it is impossible to construct a device operating in a thermodynamic cycle to receive heat from a single heat source and produce a net amount of work. It also states that it is not possible to derive mechanical effect from any part of matter by cooling it below the temperature of the coldest of the surrounding objects.

NOTE

No Sink mentioned: qC = 0 or TH = TC Kelvin Statement

$$\frac{w}{q_H} = \frac{T_H - T_C}{T_H}$$; fot TC = TH , -w = 0, No work

No cyclic process is possible in which heat is taken from a hot source and completely converted into work.

Clausius statement of the second law

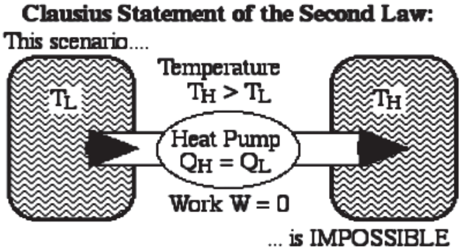
The second law of thermodynamics was founded by the German scientist, Rudolf Clausius in 1850. He developed the relationship between the heat transfer and work done. His formulation of second law is also known as Clausius statement. The concept of "passage of heat" was used in Clausius statement. This statement states that it is not possible to construct a device that operates in a cycle and develops no effect other than the transfer of heat from a lower temperature (cold region) body to higher temperature (hot region) body. In other words, heat cannot transfer from cold regions to hot regions spontaneously until some external work is done on the system for example in refrigerator.

Clausius also said that "the entropy increases towards a maximum and the energy of the universe is constant"

Note

Let us keep a sink at TC < TH but effectively qC= 0 The Clausius statement " heat does not pass from a body at low temperature to one at high temperature without change elsewhere."``

If the system violates Clausius statement and it will also violates Kelvin statement and vice versa. Thus both statements are equivalent



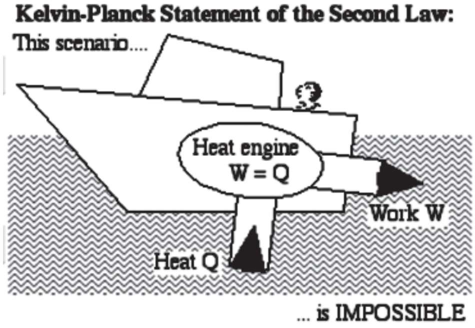
Planck statement for second law

Planck states that it is not possible to construct a device which will operate in a complete cyclic process and produce no effect except increasing of weight and cooling of reservoir. Or It is impossible to construct an engine which, working in a complete cycle, will produce no effect other than the raising of a weight and cooling of a heat reservoir.

Kelvin Planck statement

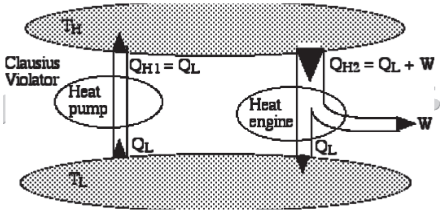
Heat cannot be completely converted into work. If it does so, the working system will suffer a permanent change. or

It is impossible for a system operating in a cycle and connected to a single reservoir (one Temperature) to produce a positive amount of work in the surrounding.

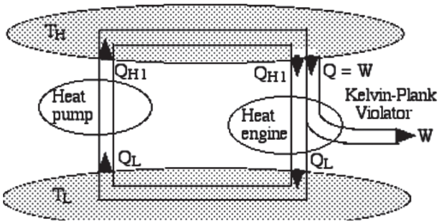


Equivalence of the Clausius and Kelvin-Planck Statements

It is remarkable that the two above statements of the Second Law are in fact equivalent. In order to demonstrate their equivalence consider the following diagram. On the left we see a heat pump which violates the Clausius statement by pumping heat QL from the low temperature reservoir to the high temperature reservoir without any work input. On the right we see a heat engine rejecting heat QL to the low temperature reservoir.



If we now connect the two devices as shown below such that the heat rejected by the heat engine QL is simply pumped back to the high temperature reservoir then there will be no need for a low temperature reservoir, resulting in a heat engine which violates the Kelvin-Planck statement by extracting heat from a single heat source and converting it directly into work.



11.6 Carnot cycle, Carnot engine

Carnot's principle for second law

Carnot Principle was proposed by French engineer Nicolas Sadi Carnot

He was the first who studied the principle of second law of Thermodynamics.

The concept of cyclic operation was also introduced by him.

Carnot's principle refers to a cycle of Carnot Heat engine which is working in a quasi-static mode so that transfer of heat and work takes place between subsystems which are always in thermodynamic equilibrium.

The efficiency of reversible Carnot cycle depends on the temperature of the two reservoirs and is the same whatever be the working substance.

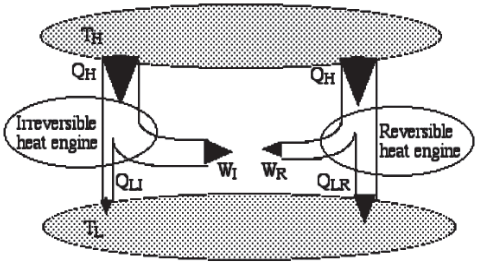
The Carnot cycle consists of four reversible processes i.e. two isothermal and two adiabatic.

Carnot's Theorem

Carnot's theorem, also known as Carnot's rule, or the Carnot principle, can be stated as follows:

No heat engine operating between two heat reservoirs can be more efficient than a reversible heat engine operating between the same two reservoirs.

The simplest way to prove this theorem is to consider the scenario shown below, in which we have an irreversible engine as well as a reversible engine operating between the reservoirs TH and TL, however the irreversible heat engine has a higher efficiency than the reversible one. They both draw the same amount of heat QH from the high temperature reservoir, however the irreversible engine produces more work WI than that of the reversible engine W_R.



Note that the reversible engine by its nature can operate in reverse, ie if we use some of the work output (WR) from the irreversible engine in order to drive the reversible engine then it will operate as a heat pump, transferring heat QH to the high temperature reservoir, as shown in the following diagram:

Notice that the high temperature reservoir becomes redundent, and we end up drawing a net amount of heat (QLR - QLI) from the low temperature reservoir in order to produce a net amount of work (W_I - W_R) - a Kelvin-Planck violator - thus proving Carnot's Theorem.

Corollary 1 of Carnot's Theorem:

The first Corollary of Carnot's theorem can be stated as follows:

All reversible heat engines operating between the same two heat reservoirs must have the same efficiency.

Thus regardless of the type of heat engine, the working fluid, or any other factor if the heat engine is reversible, then it must have the same maximum efficiency. If this is not the case then we can drive the reversible engine with the lower efficiency as a heat pump and produce a Kelvin-Planck violater as above.

Corollary 2 of Carnot's Theorem:

The second Corollary of Carnot's theorem can be stated as follows:

The efficiency of a reversible heat engine is a function only of the respective temperatures of the hot and cold reservoirs. It can be evaluated by replacing the ratio of heat transfers QL and QH by the ratio of temperatures TL and TH of the respective heat reservoirs.

HEAT ENGINE THERMAL EFFICIENCY

$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_L}{Q_H} = 1 - \frac{Q_L}{Q_H}$$

$$\eta_{rev} = 1 - \frac{T_L}{Q_H}$$

CARNOT CYCLE

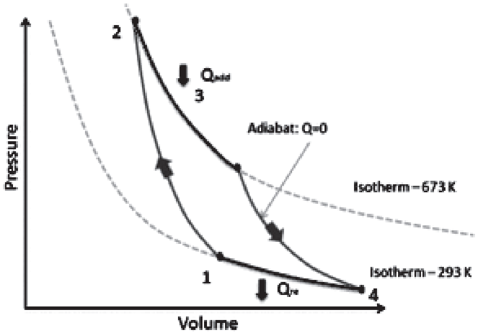
French engineer Nicolas Leonard Sadi Carnot in 1824 led to the discovery of heat engine called Carnot engine. He also showed that this engine is the most efficient engine which operates in an ideal reversible cycle called Carnot cycle. The Carnot engine establishes the maximum limit on the efficiency of all other engines. In other words, the system working through the Carnot cycle produces the maximum amount of work from given amount of energy supplied to the system.

A reversible process is the process by which system can be brought to its initial state along the same path, and for which every point along the path is an equilibrium state. In reversible process, the dissipative effects which convert mechanical energy to internal energy are not present.

An irreversible process is the process which violates the above requirement. The most natural processes are found to be irreversible in nature.

The heat engines are the device which are cyclic in nature and its working fluid returns to its initial state at the end of each cycle, and hence work is done by the working fluid during each part of the cycle. In one part of the cycle, work is done on the working fluid while in other part of the cycle, work is done by the working fluid. The difference between these two work is the net work done by the heat engine. The efficiency of heat engine cycle depends on the execution of individual processes involved in formation of the cycle. If reversible processes are used then the efficiency or net work produced by the system can be maximized. The best reversible cycle known is Carnot cycle. Carnot used a reversible cycle to derive the maximum convertibility of heat into work.

Carnot cycle consists of a system of one mole of ideal gas that is subjected to series of four reversible processes, commonly termed as four strokes. These are given below:



pV diagram of Carnot cycle. The area bounded by the complete cycle path represents the total work that can be done during one cycle.

Step 1: Reversible isothermal expansion at high Temperature, TH $2 \rightarrow 3$

Step 2: Reversible adiabatic expansion $(3 \rightarrow 4)$

Step 3: Reversible isothermal compression, TL $(4 \rightarrow 1)$

Step 4: Reversible adiabatic compression $(1 \rightarrow 2)$

$$\eta = \frac{\text{workoutput}}{\text{heatinput}} = \frac{W_{\text{cycle}}}{Q_H} = \frac{T_H - T_L}{T_H} = 1 - \frac{T_H}{T_L}$$

3.5.9. Discussion on the Efficiency of Carnot Engine

We have $\eta = 1 - \frac{T_1}{T_2}$ or $\frac{w}{Q} = \frac{T_2 - T_1}{T_2}$ or $w = Q \times \left(1 - \frac{T_1}{T_2}\right)$

1. Perpetual motion of the first kind

If no heat is supplied to the engine $Q = 0, w = Q \times \left(1 - \frac{T_1}{T_2}\right)$, i.e. w=0, no engine will work if heat is not added to it. This explains the impossibility of perpetual motion of the 1St kind

2. Perpetual motion of the second kind

If T_2=T_1 , then also w=0i.e., no engine can produce any positive work if it is connected to single reservoir and extracts heat from it.

3. Incompleteness of conversion of heat into work $\eta = 1 - \frac{T_1}{T_2}, \eta$ can be unity when T_1 = 0K or T= ∞. Both the condition are never realized in practice so $\eta < 1,$ i.e. $\frac{w}{Q} < 1$

W < Q. Heat is incompletely converted into work by an engine.

4. Unattainability of absolute zero temperature

Second Law of thermodynamics states that $\eta < 1$ (Planck-Kelvin statement). $\left(1 - \frac{T_1}{T_2}\right) < 1$ or - $\frac{T_1}{T_2} < 0$, or T_1> 0 so T1 can never be equal to zero. O Kelvin temperature can never be equal to zero.

5. Comparison of efficiency

The efficiency of the engine, $\eta = 1 - \frac{T_1}{T_2}$. So, η can be increased by lowering T_1 or increasing T2 or by both. If the efficiency of the engine is compared by decreasing the temperature of the sink (Low Temperature Reservoir, LTR) or increasing temperature of the source (HTR) to the same extent, is higher where the sink temperature is reduced.

When T_1 is decrease by dT_1 keeping T_2 fixed, $d\eta_1 = 0 - \frac{dT_1}{T_2}$

When T2 is increased by dT keeping T_1 fixed , $d\eta_2 = 0 + \frac{T_1}{T_2^2} dT_2$

But -dT_1 - dT_2

So $\frac{d\eta_1}{d\eta_2} = \frac{T_2}{T_1} > 1$

Decreasing temperature of the LTR leads to more efficiency than increasing temperature of the source keeping the same sink temperature or LTR, temperature.

6. We have w = $Q.\frac{T_2 - T_1}{T_2} = Q\frac{dT}{T_2}$ .. The engine converts fraction of heat supplied (Q) into work.

7. The efficiency ( ) depends on temperature difference of source and sink, and temperature of the source. It does not depend on the nature of the working substance used in the engine. Thus instead of using ideal gas, if van der Waals gas is used, the efficiency would be the same. The efficiency is also independent of the kind of work and it holds also for non mechanical work.

Refrigerator (R)

A refrigerator is a device that extracts heat from cold reservoir (LTR) and rejects to hot reservoir (HTR). The process of extraction of heat is called refrigeration.

A Carnot refrigerator acts in the same fashion as that of Carnot engine but in reverse direction. It takes away heat (Q_1) from LTR, work (w) is supplied to it and finally it rejects heat (Q_2) to HTR. The refrigerator starts from D of ABCD Carnot Cycle. The sequence of steps

Step[1: Reversible isothermal expansion at T_1, low temperature (D $\rightarrow$ C) Heat is taken from LTR = $Q_1 = w_1RT_1\ln\frac{V_3}{V_4}$

Step 2: : Reversible adiabatic compression (C $\rightarrow$ B). Temperature increases from T_1 to T_2.

Work done $w_2 = C_V(T_2 - T_1)$

Step[3: Reversible isothermal compression at T_2, (B $\rightarrow$ A) Heat rejected to HTR $= Q_2 =$

$$w_3 = RT_2 \frac{V_1}{V_2} \ln$$

Step 4: : Reversible adiabatic compression (A $\rightarrow$ D). Temperature decreases from T_2 to T_1.

Work done $w_2 = C_V(T_1 - T_2)$

Adding, $w = w_1 + w_2 + w_3 + w_4 = w_1 + w_3$

$$W = RT_1 \ \ln \frac{V_3}{V_4} + RT_2 \ln \frac{V_1}{V_4} = RT_1 \ \ln \frac{V_3}{V_4} - RT_2 \ln \frac{V_2}{V_1}, \text{ but } \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

$$= \ = R(T_1 - T_2) \mathrm{In} \frac{V_3}{V_4}$$

The efficiency of a refrigerator = Q_1 (heat extracted) / (-)w (work supplied)

$$\psi = (RT_1 \ln \frac{V_3}{V_4}) / -R(T_1 - T_2) \ln \frac{V_3}{V_4} = \frac{T_1}{T_2 - T_1}$$

The efficiency of refrigeration is also reported as the "coefficient of performance" of the arrangement. This quantity is defined as the ratio of heat removed from a cool object to the work that must be done in order to achieve that transfer. The higher the coefficient of performance the less work have to be done to achieve a given transfer. The best coefficient of performance that can be achieved by any arrangement when the object (the food) to be cooled is at a temperature Tcold and the surroundings (the kitchen) is at Tsurrounding is

$$\text{Coefficient of performance} = \frac{1}{\frac{T_{\text{surrounding}}}{T_{\text{cold}}}}$$

For instance,if the cold object is cold water at 0∘C (273 K) and the refrigerator is in room at 20∘C(293K), then the coefficient of performance is 14, and to remove 10kJ of energy from the freezing water, which is enough thfreeze about 30 g of the water to ice. Under ideal conditions we need to do about 0.71kJof work. Actual refrigerators are much less efficient than this thermodynamic limit, heat leaks in from outsideand not all the energy supplied to do the work joins the energy stream.

When a refrigerator is working , the energy released into the surrounding is the sum of that extracted from the cooled object and that used to run the apparatus. This remark is the basis of the operation of Heat Pump, adevice for heating a region (such as interior of house) by pumping heat from outside into the interior. A heat pump is essentially a refrigerator, with the cooled object the outside world and heat transfer arranged to be in the region to be heated. That is, our interst is in the back of the refrigerator, not its interior. The coefficient of performance of a heat pump is defined as the ration of the total energy released as heat into the region to be heated (at a temperature Tinterior), to the work done in order to achieve that release. By the same type of calculation as already done for the Carnot efficiency

$$\text{Coefficient of performance (heat pump)} = \frac{1}{1-\frac{T_{\text{surrounding}}}{T_{\text{int erior}}}}$$

Therfore the region to be heated is at 20 ∘ C (293K) and the surroundings are at 0oC (273K), the coefficient of performance is 15. Thus to release 1000J (1 kJ) into the interior, we need to do only 67J of work, In other words, a heat pump rated at 1kW behaves like 15kW heater.

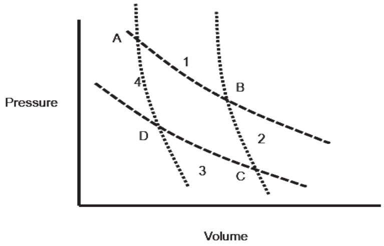
11.7 Entropy

Theory

The concept of entropy is vital for thermodynamics. The concept of temperature was used in zeroth law of thermodynamics while the concept of internal energy was used in first law of thermodynamics. These are state variables which define the state of the system. The state variable which is related to second law of thermodynamics is entropy (S). The concept of entropy was introduced by Clausius in 1865. It is considered as degree of randomness or disorderness in a molecular system. More the randomness, larger is the value of entropy. The word entropy has been made from energy (en) and trope (tropy) which is for chaos.

According to one of the statements of second law of thermodynamics, heat cannot be completely converted into work. This has been attributed to entropy. In thermodynamics, entropy is referred as the measure of the number of definite realizations or microstates that may realize a thermodynamic system, in a specified state defined by macroscopic variables. More precisely, the entropy is considered as a measure of molecular disorder within a macroscopic system. The second law of thermodynamics states that entropy of an isolated system never decreases. This kind of system spontaneously moves towards state with maximum entropy, i.e., at thermodynamic equilibrium. The system which is not isolated may lose entropy only when the entropy of environment is increased by same amount. As entropy is a state function, therefore the change in entropy of the system will remain constant for any process with known initial and final states. The change in entropy does not depend upon the nature of the process, i.e., whether the process is reversible or irreversible. But the irreversible processes raise the combined entropy of the system and its environment. As on increasing the temperature of the system, kinetic energy of the molecules increases; therefore the degree of randomness increases thereby increasing the entropy of the system.

Entropy from Carnot Cycle



In the Carnot Cycle ABCD the state of the system can be changed from A to C either along The path ABC or along the path ADC, as all steps are reversible.

For the paths ABC

$$\left(\frac{dq_{rev}}{T}\right)_{ABC=}\left(\frac{dq}{T}\right)_{AB+}\left(\frac{dq}{T}\right)_{BC}$$

High Temperature if T1 and heat absorbed reversibly q1

$$\left(\frac{dq_{rev}}{T}\right)_{ABC=}\left(\frac{dq_1}{T}\right)+0_{AB+}\left(\frac{dq}{T}\right)_{BC}$$

Along the path ADC, along DC , dq2 quantity of heat is absorbed reversibly as in the Carnot cycle dq2 quantityof heat is relwased during isothermal compression CD.

Again for the Carnot cycle

$$\frac{dq_1 - dq_2}{dq_1} = \frac{T_1 - T_2}{T_2} \text{ or } \frac{dq_2}{T_2} = \frac{dq_1}{T_1}$$

$$\text{Or } \left(\frac{dq_{rev}}{T}\right)_{ABC} = \left(\frac{dq_{rev}}{T}\right)_{ADC}$$

i.e $\left(\frac{dq_{rev}}{T}\right)$ is an exact differential for the given change of state of the system.

So it expresses the difference in magnitude of some state property of a system, which is termed entropy.

Units of entropy

Since change in entropy is given by ds = dqrev/T, i.e., heat term divided by the absolute temperature. Thus SI unit of entropy is given by Joules per degree Kelvin (J K-1). For molar entropy, the unit is J K-1mol-1.

Entropy of Reversible cyclic process

?U = 0 , For isothermal reversible expansion of ideal gas and for cyclic process

$$\oint \frac{dq_{rev}}{T} = \frac{q_h}{T_h} + \frac{q_c}{T_c} \text{ As only two steps have non-zero entropy } \frac{q_h}{q_c} = -\frac{T_h}{T_c}$$

$$\text{So, } \oint \frac{dq_{rev}}{T} = 0$$

Entropy is measure of the "quality" of the stored energy. When matter and energy are distributed in disorder way, as in gas, then entropy is high. when matter and energy stored in ordered manner, as in crystal , entropy is low.

Change in entropy is inversely proportional to first power of Temperature. Analogy drawn by Clausius, the change in entropy of a system at low temperature is similar to sneezing in a quiet library. A sudden sneeze is highly disruptive in a quite library. In a busy noisy street which is a metaphor for high temperature where the same sneeze will introduce relatively little additional disorder i.e. only a small increase in entropy.

Characteristics of entropy

1. Entropy is refers to as degree of randomness. As the degree of randomness increases, the entropy of the system increases.
2. Entropy can also be related to unavailable energy.
3. For a given substance, the vapour phase has maximum randomness and solid phase has least randomness. Therefore, Svapour > Sliquid > Ssolid
4. Entropy is a state function. Therefore, S = Sfinal - Sinitial = S2 - S1
5. It depends upon temperature, pressure, volume and amount.of substance
6. Entropy is an extensive property.
7. dS $\neq$ dqirr / T
8. Entropy increases with increase in temperature.
9. The entropy increases as the volume of the system increases.

11.8 Entropy Change

Change in entropy in an isothermal expansion of an ideal gas

When an ideal gas is expanded isothermally and reversibly, then the internal energy does not changes i.e. Δ U = 0 thus from first law of Thermodynamics (viz. ?U = q + w), we get

$$\text{qrev} = -\text{ w} = \text{PdV} = \text{nRT}\ \frac{dV}{V}$$

Thus change in entropy will be given by

$$\Delta S = \int_{V_1}^{V_2} \frac{q_{rev}}{T}$$

$$\Delta S = \int_{V_1}^{V_2} nR\frac{dV}{V}$$

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right)$$

Entropy change in reversible and irreversible processes

Suppose an ideal gas is expanded isothermally in vacuum keeping temperature to be constant. This process will proceed irreversibly. As no opposing force is applied, therefore the work done (w) by the system will be zero. As temperature is kept constant, thus change in internal energy will also be zero. According to first law equation then q = 0, i.e., no heat is exchanged between the system and surroundings during the process. Thus, the entropy of the surroundings does not change. The entropy of the system is defined by the state of the system, i.e., temperature and pressure (or volume). During this process let the volume changes from V1 to V2.

Therefore, the increase in entropy is given by (for one mole of S $R\ln\left(\frac{V_2}{V_1}\right)$

Δ S = nRln $\left(\frac{V_2}{V_1}\right)$ (for n moles of ideal gas).

Thus total increase in entropy of the system and its surroundings during isothermal expansion

$R \ln (V_2 / V_1)\ \ 0\ \ R \ln V_2 / V_1$

As $V_2 > V_1$thus we can say that there is increase in entropy of the system and the surroundings during the irreversible isothermal expansion. Now considering the reversible isothermal expansion of an ideal gas at the temperature T. Suppose the volume changes from V1 to V2 during infinitesimally slow expansion. Expansion is done such that the pressure on the frictionless piston remains always less than that of the gas by an infinitesimally small amount. Therefore some work is done by the system, i.e., $w = -P\Delta V$ Thus at this temperature T, equivalent amount of heat is absorbed by the system. Accordingly the increase in entropy is given by qrev/T. Similarly entropy of the surroundings decrease by qrev /T. Conventionally applying the negative sign for decrease of entropy and positive for increase of entropy, thus the net entropy change of the system and the surroundings is given by

$$\frac{q_{rev}}{T} - \frac{q_{rev}}{T} = 0$$

Thus total entropy change during isothermal expansion for a gas is zero

Note

During an irreversible isothermal expansion there is always increase in an entropy of the system and surroundings taken together while during reversible isothermal expansion the entropy of the system and surroundings remains same. This can be written as

$(\Delta S_{sys} + \Delta S_{surr}) = 0$ (for reversible process)

$(\Delta S_{sys} + \Delta S_{surr}) > 0$ (for irreversible process)

Combination of the above two $(\Delta S_{sys} + \Delta S_{surr}) \geq 0$

in which equal to sign stands for the reversible process and ' greater than' sign stands for irreversible process. Thus, the above equation helps in determining whether the process occurs spontaneously or not.

Since all the naturally occurring processes are spontaneous in nature thus we can say that the entropy of the universe increases continuously. This statement is also regarded as another statement of the second law.

The combination of first law and second law of thermodynamics is given by Clausius which is:

Entropy change of an ideal gas due to variation in P, V and T

Entropy of the system depends upon the state of the system, i.e., on T, P and V. For a pure gaseous substance the value of entropy is dependent only on two of the three variables P,V and T. Generally T is taken as one of the variable therefore two variables to be considered are either T and V or T and P.

Case 1: When the two variables are T and V

dS ? dq rev / T , where dqrev is the infinitesimal amount of heat absorbed by the system at temperature T. According to first law of thermodynamics ?U = q + w, we get dqrev = dU-dw

If work is done due to expansion of the gas , then infinitesimal change in volume will be given by: - dw = PdV.

Also $C_v = \left(\frac{\partial U}{\partial T}\right)V$, so, dU= CvdT and substituting

dq_{rev} = dU-dw; get $dq_{rev} = C_v dT + PdV$

Assuming the gas to be ideal, thus applying ideal gas equation in equation we get, (for one mole of gas) P= RT/V

dqrev CvdT + $\left(\frac{RT}{V}\right)$dv ;

Considering and rearranging dS= dq_{rev} = dS/T = $\frac{C_V dT}{T} + R \frac{dV}{V}$ and the above equation

on integration between initial state 1 and final state 2. And Cv is assumed to be constant within the

Temperature range T_1 and T_2

Therefore, the entropy change for finite change of state of the system is given by:

$$\Delta S = S_2 - S_1 = nC_v \ln \frac{T_2}{T_1} + nR\ln \frac{V_2}{V_1}$$

If we use the second basic equation dH = TdS + VdP and insert dH =nCPdT

$\Delta S = S_2 - S_1 = nCPln \frac{T_2}{T_1} - nRln \frac{P_2}{P_1}$ (ideal gas reversible process for the change of state

$(T_1,P_1 - T_2,P_2)$

Change in entropy of an ideal gas di{ in different processes

For isothermal Process, $T_1=T_2$ $\Delta S = nRln \frac{P_2}{P_1}$ and $\Delta S = nRln \frac{V_2}{V_1}$

For isochoric Process, $V_1=V_2$ $\Delta S = nCV \ln \frac{T_2}{T_1}$

For isobaric Process, $P_1=P_2$ $\Delta S = nCP \ln \frac{T_2}{T_1}$

S of a system in a reversible adiabatic process , Isoentropic process and $\Delta S = 0$. Thus a change of state from T_1,V_1 to T_2 , V_2 of a system containing n moles ideal gas in reversible adiabatic process $\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{T_1} + nR \ln \frac{T_2}{T_1} - R \ln \frac{V_2}{T_1}$. This leads to entropy change due to volume change compensates that due to temperature change in the reversible adiabatic process of an ideal gas.Again this relation shows that for reversible adiabatic compression $V_2 > V_1$, temperature of the system fall $T_2 < T_1$. i.e. increase in temperature.

S for reversible phase change of a pure substance

Change of a pure substance from one phase to another at constant temperature and pressure occurs reversibly. e.g. Ice to liquid water at 0oC and 1 atm pressure. Heat change in the process at constant pressure is the enthalpy change for this type of phase transformation and $\Delta S = \frac{\Delta H_1}{T_1}$ where ΔH_1 is the enthalpy change at the transition temperature.

S for the Mixing of Ideal gases at constant T and P

Consider the process where nA moles of ideal gas A are confined in a bulb of volume V_A at a pressure P and temperature T. This bulb is separated by a valve from bulb B of volume VB that contains nB moles of ideal gas B at the same (T,P). When the stop cock is opened, the gas molecules mix spontaneously and irreversibly and an increase in entropy $\Delta_{mix}S$ is then simply the sum of ΔS_A, the entropy change for the expansion of gas A from VA to $(V_A + V_B)$ and Δ SB, the entropy change for the expansion of gas B from VB to (VA + VB) / That is

$$\Delta_{mix}S = \Delta S_A + \Delta S_B$$

$$\Delta S_A = nA\ R \ln \frac{V_A + V_B}{V_A} \quad \& \quad \Delta S_B = nB\ R \ln \frac{V_A + V_B}{V_A}$$

$$\text{Hence} \quad \Delta_{mix}S = R[nA \ \ln \frac{V_A + V_B}{V_A} + nB \ \ln \frac{V_A + V_B}{V_A}]$$

Using ideal gas equation , $n_A = \frac{pV_A}{RT}$ nB = $\frac{pV_B}{RT}$

$n_A + n_B = \frac{p(V_A + V_B)}{RT}$, extensive property

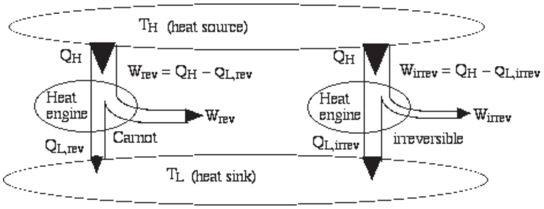
We know $\frac{n_A}{n_A + n_B} = \frac{V_A}{V_A + V_B} = x_A$ likewise xB are the mole fractions of A and B in the mixture.

We know $\Delta_{mix}S = - R[n_A \ln x_A + n_B \ln x_B]$ { note -ve sign}

To find $\Delta_{mix}S$, the entropy of mixing for a mole of mixture, we divide the above equation by total number of moles $\Delta_{mix}S = - R[x_A \ln x_A + x_B \ln x_B]$

11.9 Clausius Inequality

The First Law defines energy conservation, emphasizing equality, while the Second Law introduces inequality, stating that a reversible engine is always more efficient than an irreversible one operating between the same heat reservoirs. Additionally, the Second Law governs the directional nature of natural processes.



First in the reversible (Carnot) heat Engine, the reversible heat transfer can only occur isothermally, thus the cyclic integral of the heat transfer divided by the temperature can be evaluated as follows: $\oint \frac{\partial Q}{T} = \frac{Q_H}{T_H} - \frac{Q_{L,rev}}{T_L}$

For reversible machines, $\oint \frac{\partial Q}{T} = 0$

Or, $0 = \frac{Q_H}{T_H} - \frac{Q_{L,rev}}{T_L}$ -

Or, $\frac{Q_H}{T_H} = \frac{Q_{L,rev}}{T_L}$

Notice from the above diagram showing the two heat engines that for an irreversible engine having the same value of heat transfer from the thermal source QH as the reversible engine, the heat transfer to the thermal sink $Q_{L,irrev} > Q_{L,rev.}$

Let Qdiff = (QL,irrev- QL,rev), then the cyclic integral for an irreversible heat engine becomes:

= - (+) < 0

for any reversible or irreversible heat engine we obtain the Clausius Inequality: $\oint \frac{\partial Q}{T} \leq 0$

All properties (such as pressure P, volume V, etc) have a cyclic integral equal to zero.

For reversible machines, since $\oint \frac{\partial Q}{T} = 0$. This must be a property.

$dS \Rightarrow \frac{\partial q}{T}$ for reversible process (Entropy).

In case of an isothermal process at temperature T_0 we obtain : $\Delta S = \frac{q}{T°}$

Another statement of the second law is the Clausius Inequality which states that $\oint \frac{\partial q}{T} \geq 0$

The Clausius Inequality is used to generate two new functions, the Gibbs Energy and the Helmhlotz energy. These functions allow predictions to be made about the direction of change in processes for which the system interacts with its environment.

The Change of Entropy in the Surroundings and Δ Stotal = Δ S + Δ $Ss_{urroundings}$

The entropy of an isolated system increases in a spontaneous process. In general, a system interacts with the part of the Universe that is very close. Therefore in actual system and surroundings form interacting composites that is isolated from rest of the Universe. The part of the surroundings that is relevant for entropy calculations is a thermal reservoir at a fixed temperature, T. The mass of the reservoir is sufficiently large that its temperature is only changed by an infinitesimal amount dT when heat is transferred between the system and the surroundings. Therefore, the surroundings always remain in internal equilibrium during the heat transfer.

The entropy change (Δ S) in the surrounding which is either at constant Volume, V or constant Pressure, P. The amount of heat absorbed by the surroundings, $q_{surroundings}$, depends on the process occurring in the system. If the surroundings are at constant volume, $q_{surroundings} = \Delta U_{surroundings}$, and when the surroundings are at constant pressure P, $qs_{urroundings} = \Delta H_{surroundings}$. Because H and U are state functions , the amount of heat entering in the surroundings are independent of path. In particular, the system and the surrounding need not be at the same temperature and q is the same whether the transfer occurs reversibly or irreversibly.

Therefore $d_{Ssurroundings} = \frac{dq_{surr}}{T_{surroundings}}$ or for a macroscopic change, $\Delta S_{surroundings} = \cdot \frac{q_{surroundings}}{T_{surroundings}}$

NOTE. The heat that appears in change, ?Ssurroundings = , is the actual heat transferred. The ?S system is calculated using the heat flow , dqreversible, for a reversible process that connects the initial and final states of the system and not the actual dq for the process.

11.10 Summary

This unit explores the necessity of the Second Law of Thermodynamics and its role in defining the direction of natural processes. It introduces key concepts such as heat reservoirs, heat engines, and the Carnot cycle, establishing efficiency limits for energy conversion. The unit also presents the Kelvin-Planck and Clausius statements of the Second Law and their equivalence. The thermodynamic temperature scale, Clausius inequality, and entropy are discussed, highlighting their significance in determining spontaneity and unavailable work. Finally, the molecular interpretation of entropy provides a deeper understanding of disorder and energy dispersal in thermodynamic systems.

11.11 Self-Assessment Questions

1. Why is the Second Law of Thermodynamics necessary despite the First Law defining energy conservation?
2. Differentiate between the Kelvin-Planck and Clausius statements of the Second Law. How are they equivalent?
3. What is a heat engine? Explain its working principle with an example.
4. Describe the Carnot cycle and derive the expression for the efficiency of a Carnot engine.
5. Why is the efficiency of a reversible engine always greater than that of an irreversible one operating between the same two heat reservoirs?
6. What is Clausius inequality, and how does it lead to the definition of entropy?
7. Explain the thermodynamic concept of entropy. How does entropy change for reversible and irreversible processes?
8. How does the molecular interpretation of entropy explain the spontaneity of processes?

9. What is meant by unavailable work? How is it related to entropy changes in a system?
10. Why can heat not be completely converted into work in a cyclic process? How does the Second Law explain this limitation?

Unit 12 ❐ Free Energy Functions

12.1 Objectives

12.2 Introduction

12.3 Gibbs free energy (G) & Helmholtz / work function (A)

12.4 Maxwell's Relations

12.5 The effect of temperature and pressure on Free energy

12.6 Gibbs Helmholtz Equation

12.7 Joule Thompson expansion

12.8 Summary

12.9 Self-Assessment Questions

12.1 Objectives

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

- Understand the concepts of Gibbs free energy (G) and Helmholtz free energy (A) and their significance in thermodynamics.
- Analyze the variation of entropy (S), Gibbs free energy (G), and Helmholtz free energy (A) with temperature (T), volume (V), and pressure (P).
- Establish criteria for spontaneity and equilibrium based on Gibbs and Helmholtz free energy.
- Derive and apply Maxwell's relations to various thermodynamic processes.
- Understand and use the Gibbs-Helmholtz equation for studying energy changes with temperature.
- Explain the Joule-Thomson experiment, its consequences, and the concept of inversion temperature.
- Derive and interpret the Joule-Thomson coefficient for a van der Waals gas.
- Explore general heat capacity relations and their significance in thermodynamic transformations.
- Understand and apply thermodynamic equations of state to describe real and ideal gases.

12.1 Introduction

Thermodynamics not only describes energy conservation and the directionality of processes but also provides tools to predict spontaneity and equilibrium conditions. While the Second Law introduces entropy as a key factor in determining spontaneity, practical applications often require energy functions that directly relate to measurable quantities such as temperature, pressure, and volume.

Gibbs free energy (G) and Helmholtz free energy (A) serve as powerful thermodynamic potentials that help analyze equilibrium conditions and the feasibility of chemical and physical processes. Their variations with temperature, pressure, and volume provide essential insights into phase transitions, reaction spontaneity, and energy efficiency in thermodynamic systems.

This unit also explores key thermodynamic relations, including Maxwell's equations and the Gibbs-Helmholtz equation, which establish fundamental connections between thermodynamic variables. The Joule-Thomson experiment and the concept of inversion temperature explain the cooling or heating effects during gas expansion, while the Joule-Thomson coefficient provides a deeper understanding of real gas behavior. Additionally, general heat capacity relations and thermodynamic equations of state offer valuable tools for studying energy transfer in various systems.

By understanding these concepts, we can better predict and control thermodynamic processes in chemical reactions, industrial applications, and natural phenomena.

12.3 Gibbs free energy (G) & Helmholtz / work function (A)

The direction of spontaneous change for a process is predicted by

$$\Delta S_{total} = \Delta S + \Delta S_{surroundings} > 0$$

The spontaneity criteria can be used to derive two new state functions, the Gibbs and Helmholtz energies. These new state functions provide the basis for discussion of equilibrium.

The Clausius inequality

$$ds \geq \frac{dq}{T}$$

Or if written in the form

TdS $\geq$dq

dq = dU - dW_T, the equality is satisfied for reversible process

TdS $\geq$ dU - dWT , or equivalently, -dU + dW_T+ TdS $\geq$ 0 or dW_T ? dU - TdS

For isothermal process, TdS written as d(TS), dW_T $\geq$ d(U-TS) $\geq$ dAT.

When work is done by the system dWT ? dAT. For reversible process maximum work done by system d$W_{T, max}$ = -dA_T

Note. TdS represents the quantity of energy remaining associated with the change of entropy of the system and TS is called the bound energy.

A system can do different type of work on the surroundings, dW_T. It is particularly useful to distinguish between expansion work, in which the work arises from a volume change in the system, and non expansion work. -dU - $P_{external}$ dV + dw $_{non\text{-}expansion}$ + TdS$\geq$ 0

This equation expresses the condition of spontaneity for an arbitrary process in terms of the changes in the state functions U, V, S and T as well as the path-dependent functions PextdV and wnonexp. For an isolated system , WT =0 and dU = 0. Therefore the equation reduces dS$\geq$0.

Chemists are interested in systems that interact with their environment than in isolated systems. Hence defining equilibrium and spontaneity for such systems

d(U-TS) $\leq$ dwexpansion + dwnonexpansion

dA $\leq$ dwexpansion + dwnonexpansion

In Helmholtz energy, dT =0 is the only constraint. The additional constraint dV= 0.

The condition that defines spontaneity and equilibrium becomes d$A_{T,V}$ $\leq$ 0. The condition for spontaneity at constant (T,V) takes simple form using Helmholtz energy, A rather than the entropy, S.

Chemical reactions are commonly studied in test tube or under atmospheric pressure than constant volume conditions. Therefore, the condition for spontaneity is considered next for an isothermal transformation that takes place at constant pressure, P= Pexternal. At constant Pressure and Temperature, PdV = d(PV) and TdS = d(TS). The equation can be written

$d(U + PV - TS) = d(H-TS) \leq dw_{non\ expansion}$. The combination of $H - TS$, which has the units of energy, defines a new state function called the Gibbs energy. Using the Gibbs energy , the conditions for spontaneity and equilibrium for an isothermal process at constant pressure becomes $dGP,T \leq dw_{nonexpansion}$.

For a reversible process the equality hod and the change in the gibbs energy is a measure of the maximum non expansionwork that can be produced , the condtion for spontaneity and equilibrium is dG ? 0

The criteria of spontaneity and equilibrium are

(i) $\Delta S_{univ} \geq O$

(ii) $\Delta U_{s,v} \leq 0$

(iii) $\Delta H_{S,P} \leq 0$

(iv) $\Delta A_{V,T} \leq 0$

(v) $\Delta G_{P,T} \leq 0$

What is the advantage of using State function G and A as criteria for spontaneity rather than entropy?

The Clausius inequality can also be written as, $dS - \frac{dq}{T} \geq 0$

$dS_{surroundings} = -\frac{dq}{t}$, the Clausius inequality is equivalent to the spontaneity condition

$dS + dS_{surrounding} \geq 0$

G and A introduced are expressed in terms of the macroscopic state variables of the system. It is now not necessary to consider surroundings explicitly, ΔG, ΔA for the system alone is sufficient to predict the direction of natural change.

Equation $dG_{P,T} \leq dw_{nonexpansion}$ allows one to calculate the maximum nonexpansion work that can be produced by a chemical transformation.

Use of the Equation $dG_{P,T} \leq dw_{nonexpansion}$

To calculate the electrical work produced by a reaction in an electrochemical cell or fuel cell.

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

Note that there are two contributions to ΔG that determine if an isothermal chemical transformation is spontaneous. They are the energetic contribution, $T\Delta S$.

- The entropic contribution to ΔG is greater for higher temperatures.
- A chemical transformation is always spontaneous if and $\Delta H < 0$ (an exothermic reaction) $\Delta S > 0$
- A chemical transformation is never spontaneous if $\Delta H > 0$ (an endothermic reaction) and $\Delta S < 0$
- For all other cases, the relative magnitude of ΔH, $T\Delta S$ determine if the chemical transformation is spontaneous.

Similarly, for macroscopic changes at constant V and T in which no expansion work is possible the condition for spontaneity is $\Delta A < 0$, where $\Delta A = \Delta U - T\Delta S$

12.4 Maxwell's Relations

Free energy functions

The Differential Forms of U, H, A, G

The differential forms dU, dH, dA, dG are developed . Starting fro definitions

$H = U+PV$

$A = U - TS$

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

The following differentials known as Gibbs equation can be formed

$dU = TdS - PdV$	$U = f(S,V)$
$dH = TdS - PdV + PdV + VdP = TdS + VdP$	$H = f(S,P)$
$dA = TdS - PdV - TdS + SdT = -SdT - PdV$	$A = f(T,V)$

dG = TdS + VdP - TdS - SdT = -SdT + VdP G = f(T, P)

Maxwell's Relations

The expressions or equations which relate internal energy (U), enthalpy (H), Helmholtz free energy (A) and Gibbs free energy with parameters like entropy, pressure, etc., are called Maxwell's relations. Some of these are

i) dU = TdS - PdV

ii) dH = TdS + VdP

iii) dA = -SdT - PdV

iv) dG = -SdT + VdP

If volume of the system remains constant, i.e., dV=0 then equation (i) becomes;

(?U / ?S)V =T

If entropy of the system does not change, i.e., dS=0, then equation (i) becomes
(?U / ?V)S = - P

Differentiating $\left(\frac{\partial U}{\partial S}\right)_V = T$ with respect to V keeping S constant $\left(\frac{\partial T}{\partial V}\right)_S$

Differentiating $\left(\frac{\partial U}{\partial V}\right)_S = -P$ with respect to S keeping V constant $-\left(\frac{\partial P}{\partial S}\right)_V$

Similarly following the same procedure some following relations were derived

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

The above relations are known as Maxwell's relations. Some more relations are:

$$\left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial H}{\partial S}\right) = \text{ from (i) and (ii) ; } \left(\frac{\partial U}{\partial V}\right)_S = \left(\frac{\partial A}{\partial V}\right)_T = \text{from (i) and (iii)}$$

$$\left(\frac{\partial H}{\partial P}\right)_S = \left(\frac{\partial G}{\partial P}\right)_T = \text{ from (ii) and (iv); } \left(\frac{\partial A}{\partial T}\right)_V = \left(\frac{\partial G}{\partial T}\right)_P = \text{from (iii) and (iv)}$$

Free Energy Functions - Generalization

Although they are derived assuming a reversible process, as total differentials they apply to both reversible and irreversible processes. They are starting points for the derivation of general differential expressions in which we express U, H, A and G as a function of p, V, T C_p, C_v

Partial Differential Relationships

We want to express the partial derivatives

Z	$\left(\frac{\partial Z}{\partial T}\right)_V$	$\left(\frac{\partial Z}{\partial T}\right)_P$	$\left(\frac{\partial Z}{\partial V}\right)_T$	$\left(\frac{\partial Z}{\partial P}\right)_T$	$\left(\frac{\partial Z}{\partial V}\right)_P$	$\left(\frac{\partial Z}{\partial P}\right)_V$

As functions of p, V, T, C_V and CP where Z is U, S, H, A, G.

Already derived

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

$$\left(\frac{\partial H}{\partial P}\right)_P = C_P$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{P}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

The next two equations are derived and obtained as the Maxwell relationships

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Derive the equations for

(i) $\left(\frac{\partial U}{\partial T}\right)_P$ (ii) $\left(\frac{\partial U}{\partial V}\right)_T$ (iii) $\left(\frac{\partial U}{\partial P}\right)_T$

In each case we start with the first Gibbs equation

dU = TdS - pdV

(i) divide by dT to obtain $\frac{dU}{dT} = T\frac{dS}{dT} - P\frac{dV}{dT}$ the equation is true for all condition, including constant Pressure condition

We can substitute partial derivatives for the ratio of differentials in equation $(\frac{dU}{dT})P$ = $(\frac{\partial U}{\partial P})P$

This can be shown as follows U = f (P,T) so that

$$dU = \left(\frac{\partial U}{\partial T}\right)_P dT + \left(\frac{\partial U}{\partial P}\right)_T dP$$

If we specify constant P, then dP = 0 so that $dU = \left(\frac{\partial U}{\partial T}\right) dT$

Dividing by dT indicating the condition of constant P, we write $(\frac{dU}{dT})P = (\frac{\partial U}{\partial T})P$

Henceforth we will make substitution of the type represented by equation

$$\frac{dU}{dT} = T\frac{dS}{dT} - P\frac{dV}{dT}$$

$$\left(\frac{\partial U}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P - P\left(\frac{\partial V}{\partial T}\right)_P = T\frac{C_P}{T} - P\left(\frac{\partial V}{\partial T}\right)_P$$

The expression for is obtained by starting with the same Gibbs equation dividing by dV

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right) \text{ -P} \qquad \text{Maxwell relation } \left(\frac{S}{V}\right)_T = \frac{\text{relatedtoVisP}}{\text{relatedtoSisT}} \text{ [cross multiply]}$$

Substituting

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$$

The expression for $\left(\frac{\partial U}{\partial P}\right)_T$

dU = TdS - pdV

Dividing by dP, specifying constant T

$$\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$$

Applications of the Differential Relationships

The relationships expanded to include differences and molar properties, serve as the starting point of many useful thermodynamic calculations.The calculation of ΔZ for a variety of processesin which p, V, T are changed. For any of the extensive variables Z = S, U, H A or G , we can write

Z= f (V,T) (usually for S,U, A)

So that $dZ = \left(\frac{\partial Z}{\partial V}\right)_T dV + \left(\frac{\partial Z}{\partial T}\right)_V dT$

Integration gives $\Delta Z = \int_{V_1}^{V_2} \left(\frac{\partial Z}{\partial V}\right)_T dV + \int_{T_1}^{T_2} \left(\frac{\partial Z}{\partial T}\right)_V dT$

The three commonly encountered processes

a) An isochoric process in which dV =0

$\Delta Z = \int_{T_1}^{T_2} \left(\frac{\partial Z}{\partial T}\right)_V dT$ (isochoric process)

b) an isobaric process in which dP =0

$\Delta Z = \int_{T_1}^{T_2} \left(\frac{\partial Z}{\partial T}\right)_P dT$ (isobaric process)

c) An isothermal process where dT = 0,

$\Delta Z = \int_{V_1}^{V_2} \left(\frac{\partial Z}{\partial V}\right)_T dV$ (isothermal process) or $\Delta Z = \int_{P_1}^{P_2} \left(\frac{\partial Z}{\partial P}\right)_T dP$

12.5 The effect of temperature and pressure on Free energy

Considering the equation G = H- TS and also H =U + PV. Then G = U + PV-TS. Differentiating the above equation dG = dU + PdV + VdP - TdS - SdT

For infinitesimal small change, the first law equation can be written as: dq = dU - dw, we know - dw = PdV. Then dq = dU + PdV. Making the use of equation dS = $\frac{dq}{T}$.

TdS = dq = dU + PdV. Combining dG = (dU + PdV)+ VdP - TdS - SdT = VdP -TdS

dG = VdP - SdT

The above equation gives the change in free energy on variation of temperature and pressure.

If pressure of the system kept constant then dP = 0,thus equation dG = -SdT

The temperature derivatives of G and $A\left(\frac{\partial G}{\partial T}\right)_P = -S;\left(\frac{\partial A}{\partial T}\right)_V = -S$ is thus Entropy S. We usually do not know S as a function of P, V, T these derivates have limitations. However when expressions derived for temperature derivative of G/T and A/T it do not involve S and they are used in application where the original derivative was desired

12.6 Gibbs Helmholtz Equation

The variation of Gibbs free energy change with temperature is known as Gibbs Helmholtz equation. This relation is derived as follows:

G = H - TS

Dividing by T and differentiating gives

$$\left(\frac{\partial\left(G/T\right)}{\partial T}\right)_P = \left(\frac{\partial\left(H/T\right)}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P$$

Expanding $\left(\frac{\partial\left(H/T\right)}{\partial T}\right)_P = \frac{TC_P - H}{T^2} = \frac{C_P}{T} - \frac{H}{T^2}$

$$\left(\frac{\partial\left(G/T\right)}{\partial T}\right)_P = \frac{C_P}{T} - \frac{H}{T^2} - \frac{C_P}{T} = -\frac{H}{T^2}$$

Similarly

$$\left(\frac{\partial\left(A/T\right)}{\partial T}\right)_V = -\frac{U}{T^2}$$

The Gibbs-Helmholtz equation can also be written in the form

$$\left(\frac{\partial \frac{G}{T}}{\partial \frac{1}{T}}\right) = \left(\frac{\partial \frac{G}{T}}{\partial}\frac{dT}{d\left(\frac{1}{T}\right)}\right)_P = -\frac{H}{T^2}\left(-T^2\right) = H$$

The derivatives $\left(\frac{\partial Z}{\partial P}\right)_V, \left(\frac{\partial Z}{\partial V}\right)_P$ are easily obtained by making use of the properties of the exact differential $\left(\frac{\partial Z}{\partial P}\right)_V = \left(\frac{\partial Z}{\partial T}\right)_V \left(\frac{\partial T}{\partial P}\right)_V$

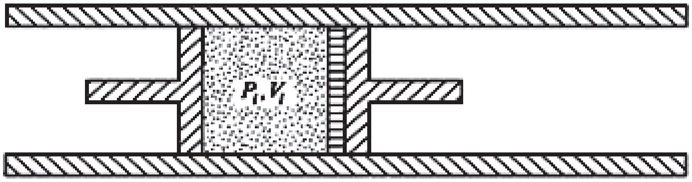
And $= \left(\frac{\partial Z}{\partial V}\right)_P = \left(\frac{\partial Z}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P$

For example $\left(\frac{\partial S}{\partial V}\right) = \left(\frac{\partial S}{\partial T}\right)_P \left(\frac{\partial T}{\partial V}\right)_P$ we know $\left(\frac{\partial S}{\partial T}\right)P = \frac{C_P}{T}$

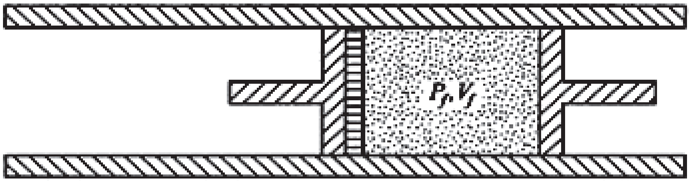
$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{T}\left(\frac{\partial T}{\partial V}\right)P$$

We need to remember the equations relating $\left(\frac{\partial S}{\partial T}\right)_V, \left(\frac{\partial S}{\partial T}\right)_P, \left(\frac{\partial U}{\partial T}\right)_V, \left(\frac{\partial H}{\partial T}\right)_P$

12.7 Joule Thompson expansion



(a) Initial state



(b) Final state

The Joule-Thomson effect also known as Kelvin-Joule effect or Joule-Kelvin effect is the change in fluid's temperature as it flows from a higher pressure region to a lower pressure.

Equilibrium states, which are described by thermodynamic coordinates. From the first law,

$(U_2 - U_1) = w + q$. The throttling process occurs in an adiabatic enclosure, so $q=0$.

The net work done by the piston on the gas causes the gas to flow across the boundary of the system enclosing the porus plug, that is

$$W = \int_{v_f}^{0} P_f dV - \int_{0}^{V_i} P_f dV$$

Since both pressures remain constant on either side of the porus plug , the net work is

$W = -(P_f V_f - P_i V_i)$ including the equation in $(U_2 - U_1) = w + q$.

$(U_2 - U_1) = -(P_fV_f - P_iV_i) + q(=0)$., shows that the internal energy U is different for the two equilibrium end-states of the Joule-Thomson expansion. A state function can be devised for which there is no difference in the end-states $(U_2 - U_1) = -(P_fV_f - P_iV_i)$

Then $U_i + P_iVI = U_f + P_fV_f$ likewise the characteristic enthalpy function is introduced.

In this process $U_i \neq U_f$; $P_i \neq P_f$ and $V_i \neq V_f$ but $U_i + P_iV_I = U_f + P_fV_f$.

H= U +PV

In a throttling process the initial and final enthalpies are equal. One is not entitled to say that the enthalpy remains constant, since one cannot spaeak on the enthalpy of a system while it is passing through non-equilibrium states during the irreversible process. In plotting a throttling process on any diagram, the initial and final equilibrium states may be represented by points. The intermediate non equilibrium states, however cannot be plotted.

A continuous throttling process may be achieved by a pump that maintains constant high pressure on one side of a porous wall or expansion valve, and a constant lower pressure on the other side.

In order to consider other properties of enthalpy, consider the change in enthalpy that occurs when an arbitrary system undergoes any infinitesimal quasi static process from an initial equilibrium state to a final equilibrium state.

We have dH = dU + PdV +VdP

dq = dU + PdV

dH = dq + VdP

Dividing both sides by dT, $\frac{dH}{dT} = \frac{dq}{dT} + V\frac{dP}{dT}$

And at constant P,

$\left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial q}{\partial T}\right)_P = C_P$ The equation shows that the enthalpy is related to an experimental quantity, the isobaric heat capacity, which is also a state function. $H_f - H_i = \int_i^f C_P dT$

For an ideal gas, the isobaric heat capacity is constant and H_f-H_i = $C_P(T_f$-$T_i)$. Enthalpy values for real vapours and gases at low pressures, with empirical temperature dependences of CP are calculated using $H_f - H_i = \int_i^f C_P dT$

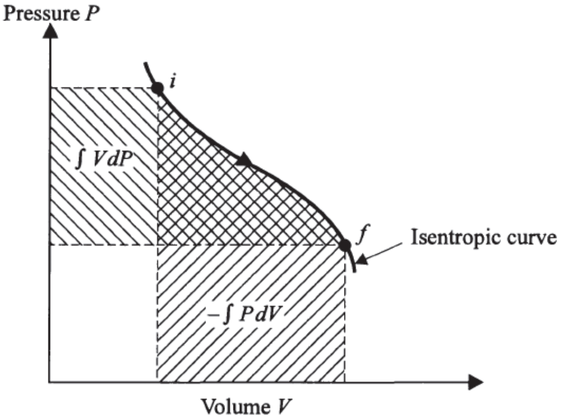
And the results are expressed as specific enthalpy or molar enthalpy as a function of temperature. Such data are extremely useful in experimental or practical work, even though , in theory, the characteristic function enthalpy H(P,S) is not expressly a function of temperature.

The enthalpy is related to heat as shown dH = dq + VdP

Thus the change in enthalpy during an isobaric process (dP = 0) is equal to the heat that is transferred between the system and the surroundings. Hf- Hi = qP (isobaric). This very equation completes the explanation of the concept of heat began earlier with the mathematical formulation or explanation of the concept of heat in the first law . Where heat was explained as heat in transit due to a difference in temperature between the system and surroundings. For an isochoric (constant volume) process in hydrostatic system, heat is the flow of internal energy; whereas for an isobaric process in hydrostatic system, heat is the flow of enthalpy. The change of enthalpy of a system during an isobaric chemical process is commonly called the "heat of reaction", but the phase enthalpy of reaction is more informative.

If heat is added to the system during first order transition (e.g. melting, boiling or sublimation) then the change of enthalpy of the system is called "latent heat". The word "latent" acknowledges that there is no change in temperature of the system when the system during a phase transition, unlike heating without a phase transition. Again, it is more informative to use the the phrase latent enthalpy.

The change in enthalpy of a system undergoing a reversible adiabatic process has an interesting graphical interpretation. From the expression dH = dq + VdP, the change of enthalpy for an adiabatic process is $H_f - H_i = \int_i^f VdP$ (adiabatic).



PV diagram illustrating the difference between work and flow-work

The integral is represented by the area to the left of curve for an isotropic process on a PV diagram. The integral - $\int \text{Pdv}$ is represented by the are under an adiabatic curve on a PV diagram. There is a thermodynamic difference between the two integrals. The integral $\int \text{Pdv}$ - is adiabatic work, which changes the configuration of a system with constant mass by changing the volume. The integral $\int \text{VdP}$, known as (negative) flow-work in engineering practice, is energy that is received by a flowing gas in a region of higher pressures, perhaps from pump or piston, and then carried to a region of lower pressure, such as in the continuous Joule Thompson expansion. If a pure substance undergoes an infinitesimal reversible process, then we can write

dH = TdS + VdP, which of course, is the same as equation of enthalpy , H defined H =f(S,P) initiating from H= U +PV, since U, P and V are state function so H is also a state function in the differential form. $\left(\frac{\partial H}{\partial S}\right)_P = T$ and $\left(\frac{\partial H}{\partial P}\right)_S = V$

The properties of internal energy U(V,S) and enthalpy (P,S) are given in table for comparison of the two function. The free expansion of gas occurs in a rigid adiabatic container, which prevents work and heat from entering or leaving the system. Consequently the internal energy U is unchanged

Joule Thompson coefficient in terms of easily determinable Derivative

Since H = f(T,P), its differential is

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dt + \left(\frac{\partial H}{\partial P}\right)_T dP$$

Dividing by dP and introducing the condition of constant H, we get

$$0 = \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial P}\right)_T$$

$$\text{or, } \left(\frac{\partial T}{\partial P}\right)_H = -\frac{\left(\partial H/\partial P\right)_T}{\left(\partial H/\partial T\right)_P} = \frac{1}{C_P}\left(\frac{\partial H}{\partial P}\right)_T$$

According to Thermodynamic equation of state

$$= \left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial V}{\partial T}\right)_P + V$$

Substituting $\mu JT = \left(\frac{\partial T}{\partial P}\right)_H = \frac{T\left(\partial V/\partial T\right)_P - V}{C_P}$

Or $\mu JT = \frac{V}{C_P}\left[\frac{T}{V}\left(\frac{\partial V}{\partial T}\right)_P - 1\right] = \frac{V}{C_P}(T\alpha - 1)$

Joule Thompson Coefficient and van der waals equation of state

Expression for μJT is $\mu JT = \frac{V}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right]$

The expression for $= \left(\frac{\partial V}{\partial T}\right)_P = \frac{T}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}$

Substituting the same $\mu JT = \left[\frac{RT}{P - \frac{a}{V^2} + \frac{2ab}{V^3}} - V\right] = \frac{1}{CP}\left[\frac{\left(P + \frac{a}{V^2}\right)(V - b)}{p - \frac{a}{V^2} + \frac{2ab}{V^3}} - V\right]$

$= \frac{1}{C_P}\left[\frac{\frac{2a}{V} - \frac{3ab}{V^2} - Pb}{P - \frac{a}{V^2} + \frac{2ab}{V^3}}\right]$ Equation (i) $\frac{a}{V^2} + \frac{2ab}{V^3}$ ignored in comparison to P (ii)PV $\approx RT$

$\mu JT = \frac{1}{C_P}\left[\frac{2a}{RT} - \frac{3abp}{R^2T^2} - b\right]$ If the temperature of the gas is not too low and pressure not too high. The equation is reduced to $\mu JT \frac{1}{C_P}\left[\frac{2a}{RT} - b\right]$

OR $\left(P + \frac{a}{V^2}\right)(V - b) = PV + \frac{a}{V} - Pb - \frac{ab}{V^2}$

$$\therefore \left(\frac{\partial V}{\partial T}\right)_P \frac{\partial}{\partial v}\left[PV + \frac{a}{V} - Pb - \frac{ab}{V^2}\right] = \frac{\partial}{\partial T}(RT)$$

$\therefore T\left(\frac{\partial V}{\partial T}\right)_P \frac{R}{P - \frac{a}{V^2} + \frac{2ab}{V^3}} = \frac{R}{P - \frac{a}{V^3}}$ = neglecting $\frac{2ab}{V^3}$

$$=\frac{RT}{\frac{RT}{V-b}\left[1-\frac{2a\left(V-b\right)}{RTV^{2}}\right]}=\left(V-b\right)\left[1-\frac{2a\left(V-b\right)}{RT2^{2}}\right]^{-1}$$

$$T\left(\frac{\partial V}{\partial T}\right)_{P}-V\left(V-b\left[1+\frac{2a\left(V-b\right)}{RTV^{2}}\right]\right)-V \text{ neglecting higher terms}$$

$$=\left(V-b\right)+\frac{2a}{RT}\left(\frac{V-b}{V}\right)^{2}-V\approx\frac{2a}{RT}-b$$

$$\therefore \frac{V-b}{V}\approx 1$$

$$\therefore \mu JT=\frac{1}{CP}\left[\frac{2a}{RT}-b\right]$$

In J-T expansion cooling occurs when molecules have to do work to overcome the intermolecular attraction in order to pass through the porous plug and this occurs at low temperature where the effect of intermolecular attraction prevails. Heating occurs due to repulsive force and molecular size. In this case work is done on the molecules which are passing out through the porous plugby the molecules remaining behind the outgoing molecules within the porous plug. If the expression of $\left(\frac{\partial V}{\partial T}\right)_{P}, \frac{2ab}{V^{3}}$ is not neglected, two temperatures would be obtained.

Difference between J-T expansion and adiabatic expansion

J-T expansion:

The gas expands through porous plug under adiabatic condition. Ideal gas exhibits no change in temperature. For real gas, cooling or heating or no change of temperature depends upon , the initial temperature and pressure of the gas . $\Delta H = 0$; the process is isenthalpic. $dS_{sys}>0$

Reversible adiabatic expansion

For any gas always cooling effect is observed and this happens whatever may be the initial pressure and temperature of the gas Δ H=nCP Δ T and is (-) during expansion , dS_{sys}=0 if the expansion occurs reversibly and dSsys> 0 if it occurs irreversibly. $\left(\frac{\partial T}{\partial P}\right)_H < \left(\frac{\partial T}{\partial P}\right)_S$

12.8 Summary

This unit introduces Gibbs free energy (G) and Helmholtz free energy (A) as key thermodynamic potentials for predicting spontaneity and equilibrium. It explores their variations with temperature, pressure, and volume, establishing criteria for feasible transformations. Maxwell's relations and the Gibbs-Helmholtz equation provide fundamental thermodynamic interconnections. The Joule-Thomson experiment, inversion temperature, and Joule-Thomson coefficient explain the cooling and heating effects in gas expansion. Additionally, general heat capacity relations and thermodynamic equations of state offer insights into energy transfer and real gas behavior, enhancing our understanding of thermodynamic systems.

12.9 Self-Assessment Questions

1. What are Gibbs free energy (GGG) and Helmholtz free energy (AAA)? How do they differ in significance?
2. Derive the expressions for GGG and AAA in terms of enthalpy, entropy, and internal energy.
3. How do SSS, GGG, and AAA vary with temperature (TTT), volume (VVV), and pressure (PPP)?
4. What are the criteria for spontaneity and equilibrium based on Gibbs and Helmholtz free energy?
5. Explain the physical significance of Gibbs free energy in chemical reactions and phase transitions.
6. State and derive Maxwell's relations. How are they useful in thermodynamic analysis?

7. What is the Gibbs-Helmholtz equation? How is it applied in thermodynamic calculations?
8. Describe the Joule-Thomson experiment. What are its main observations and consequences?
9. Define the Joule-Thomson coefficient. How is it related to gas expansion and cooling?
10. What is inversion temperature in the Joule-Thomson effect? How does it determine the cooling or heating of a gas?
11. Derive the expression for the Joule-Thomson coefficient for a van der Waals gas.
12. Explain the significance of general heat capacity relations in thermodynamics.
13. What are thermodynamic equations of state? Provide examples and their applications.
14. How does Gibbs free energy predict the feasibility of a reaction at constant temperature and pressure?
15. Why is Helmholtz free energy particularly useful for systems at constant volume and temperature

Module 3:
Dynamics of Chemical Reactions -I

Unit 13 ❐ Chemical Kinetics - Rate Laws

Structure

13.1 Objectives

13.2 Introduction

13.3 The Concept of Reaction Rates

13.4 Rate Law and Rate Constant

13.5 Integrated Rate Equations

13.6 Half-Life of a Reaction

13.7 Pseudo First Order Reactions
(example using acid catalyzed hydrolysis of methyl acetate);

13.8 Determination of order of a reaction

13.9 Temperature dependence of rate constant - Arrhenius equation

13.10 Summary

13.11 Self-Assessment Questions

13.1 Objectives

After completing this unit, learners will be able to:

- Understand the Fundamental Concepts
- Differentiate between the order and molecularity of a reaction.
- Express rate laws in terms of the advancement of a reaction.
- Derive and interpret the differential and integrated rate expressions for zero, first, second, and n-th order reactions.
- Apply the concept of pseudo-first-order reactions with a focus on acid-catalyzed hydrolysis of methyl acetate.
- Use the half-life method and the differential method to determine the order of a reaction experimentally.
- Examine the effect of temperature on reaction rates using the Arrhenius equation.
- Calculate the energy of activation from experimental data.

13.2 Introduction

Chemical kinetics is a crucial branch of physical chemistry that deals with the rates of chemical reactions and the factors influencing them. Unlike thermodynamics, which predicts the feasibility and extent of a reaction, kinetics provides insight into how fast a reaction occurs and the mechanism by which reactants transform into products. Understanding reaction rates is essential in fields ranging from industrial chemistry to biological systems, where reaction speed dictates efficiency and functionality.

The study of reaction order and molecularity helps establish the relationship between reactant concentrations and reaction rates, offering a quantitative perspective on chemical transformations. Mathematical expressions for reaction rates, whether in differential or integrated forms, allow chemists to predict how concentrations evolve over time. Special cases, such as pseudo-first-order reactions, simplify complex reaction mechanisms, making it possible to study multi-step reactions with apparent first-order behaviour.

An important aspect of kinetics is the experimental determination of reaction order, which can be achieved using methods like the half-life and differential approaches. These techniques provide a systematic way to deduce the rate law and understand the underlying reaction mechanism. Additionally, temperature plays a significant role in influencing reaction rates. The Arrhenius equation quantitatively describes this dependence, linking the rate constant to activation energy-a key parameter in controlling reaction feasibility and optimization in both laboratory and industrial settings.

By studying chemical kinetics, one gains a deeper appreciation of reaction mechanisms, predictive modelling, and practical applications, from designing catalysts to optimizing energy production. This knowledge is indispensable for chemists, engineers, and researchers seeking to control and enhance chemical processes.

13.3 The Concept of Reaction Rates

The rate of a reaction tells us to what speed the reaction occurs. The rate of a reaction is defined as the change in concentration of any of reactant or product with time. Let us consider a simple reaction

$$A \rightarrow B$$

As you know during the progress of a reaction the concentration of A keeps on falling with time. The rate of reaction at any given instant is given by the expression

$$\text{rate} = -\frac{dC_A}{dt}$$

where dC_A is very small decrease in concentration of A in a very small time interval dt. Now the concentration of product B increases with time. Hence rate of reaction can also be expressed in terms of increase in concentration of the product B as well

$$\text{rate} = -\frac{dC_B}{dt}$$

where dC_B is very small increase in the concentration of product B in a very small-time interval of time dt. We can also write the concentrations in square brackets. So, the rate of the reaction can also be expressed as-

$$\text{rate} = -\frac{d[A]}{dt} = \frac{d[B]}{dt} \tag{13.1}$$

The negative sign in the expression signifies decrease in concentration. The units of rate are concentration time^{-1}. For example, if concentration is in mol L^{-1} and time is in seconds then the units will be mol $L^{-1}s^{-1}$. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s^{-1}.

Now let us consider a reaction

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

Where a, b, c and d are the stochiometric coefficients. It means in this reaction α moles of A reacts with *b* moles of B to form c moles of C and *d* moles of D. The rates of such a reaction can be expressed either in terms of decrease in concentration of a reactant per mole or increase in concentration of a product per mole divided by appropriate stoichiometric coefficients as follows-

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} \tag{13.2}$$

Advancement of a reaction

Suppose the reaction is -

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

If the above reaction is said to be advanced to ξ = 1mol, then, the changes in the number of moles of the reacting species are

$$\Delta n_A = -\alpha\Delta\xi = -\alpha(1\text{mol}) = -\alpha\text{mol}$$

and similarly $\Delta n_B = -\beta\Delta\xi = -\beta(1\text{mol}) = -\beta\text{mol}$,

$\Delta n_C = \gamma\Delta\xi = \gamma(1\text{m01}) = \gamma\text{mol}$,

$\Delta n_D = \delta\Delta\xi = \delta(1\text{m01}) = \delta\text{mol}$,

Now during the reaction, if the reaction be advanced from ξ to (ξ + dξ) over the time period t to (t + dt) then the changes in the number of moles

$dn_A = -\alpha d\xi$; $dn_B = -\beta d\xi$; $dn_C = \gamma d\xi$; $dn_D = \delta d\xi$

The rate of change of the number of moles of the component with time

$$\frac{dn_A}{dt} = -\alpha\frac{d\xi}{dt}; \qquad \frac{dn_B}{dt} = -\beta\frac{d\xi}{dt} \qquad \frac{dn_C}{dt} = \gamma\frac{d\xi}{dt}; \qquad \frac{dn_D}{dt} = \delta\frac{d\xi}{dt}$$

$$\frac{d\zeta}{dt} = -\frac{1}{\alpha}\frac{dn_A}{dt} = -\frac{1}{\beta}\frac{dn_B}{dt} = \frac{1}{\gamma}\frac{dn_C}{dt} = \frac{1}{\delta}\frac{dn_D}{dt}$$

Rate of reaction can now be defined as the rate of change of the advancement with time per unit volume of the reaction mixture. At constant volume, the rate of reaction

$$\nu = \frac{1}{V}\frac{d\zeta}{dt} = \frac{1}{-\alpha}\frac{d[A]}{dt} = -\frac{1}{\beta}\frac{d[B]}{dt} = \frac{1}{\gamma}\frac{d[C]}{dt} = \frac{1}{\delta}\frac{d[D]}{dt}$$

Note. $\frac{dn_A}{dT}$ where A is disappearing is negative quantity and it represents the rate of conversion, J, which is extensive quantity. Rate of reaction is $\frac{J}{V} = \frac{1}{V}\left(-\frac{1}{a}\frac{dn_A}{dT}\right)$ is intensive.

13.4 Rate Law and Rate Constant

The rate of reaction will be a function of temperature, pressure, and the concentrations of the various species in the reaction and may depend on the concentrations of species such as catalysts or inhibitors that may not appear in the overall reaction. Further-more, if the reaction occurs homogeneously (that is, exclusively within a single phase), the rate is proportional to the volume of the phase.

The mathematical expression that relates the reaction rate to the concentrations of reactants is known as the rate law, also referred to as the rate equation or rate expression.

For the general reaction

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

The rate is related to concentration as

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

$$\text{rate} = k[A]^x [B]^y \qquad (13.3)$$

Where x and y may or may not be equal to a and b. The above equation can also be written as

$$-\frac{1}{a}\frac{d[A]}{dt} = k[A]^x [B]^y \qquad (13.4)$$

The terms [A] and [B] represent the molar concentrations of species A and B, typically expressed in moles per liter (molarity, M). The exponents x and y denote the partial orders of reaction with respect to A and B, respectively, while the overall reaction order is determined by their sum. Although these exponents are often positive integers, they can also be zero, fractional, or even negative. The reaction order quantifies how the rate of a chemical reaction depends on the concentrations of the reactants. In other words, it specifies the exponent to which the concentration of a given reactant is raised in the rate equation. The constant k represents the reaction rate constant or rate coefficient, and in some cases, it is also referred to as the velocity constant or specific rate of reaction.

While the order of a reaction is determined experimentally from the rate law, molecularity refers to the number of reactant molecules involved in an elementary reaction-a single-step reaction that occurs exactly as written. The molecularity of a reaction is always a whole number (1, 2, or 3) and cannot be fractional or zero.

For an elementary reaction, the molecularity and order are the same since the reaction occurs in a single step. However, for complex reactions involving multiple steps, the overall reaction order does not necessarily match the molecularity of the reaction. Instead, the order is determined by the slowest (rate-determining) step in the reaction mechanism.

A reaction can be classified based on its molecularity as:

- Unimolecular reaction: Involves a single reactant molecule decomposing or rearranging (e.g., radioactive decay).
- Bimolecular reaction: Involves the collision of two reactant molecules to form the product (e.g., SN2 reaction in organic chemistry).
- Termolecular reaction: Involves the simultaneous collision of three reactant molecules, though such reactions are rare due to the low probability of three molecules colliding simultaneously with the correct orientation and energy.

It is important to note that, unlike reaction order, molecularity is a theoretical concept based on reaction mechanism, whereas order is determined from experimental data.

13.5 Integrated Rate Equations

We have already established that the dependence of reaction rate on concentration is expressed through the differential rate equation. However, determining the instantaneous rate experimentally can be challenging, making it difficult to deduce the rate law and reaction order directly.

To overcome this, we integrate the differential rate equation to derive a relationship between experimentally measurable quantities-reactant concentrations at different time intervals-and the rate constant. These integrated rate equations vary based on the reaction order. In this section, we will derive the integrated rate equations for zero, first, and second-order reactions.

Zeroth Order Reaction

Zero order reaction means that the rate of the reaction is proportional to “zero” power of the concentration of reactants. For a zeroth order reaction $A \rightarrow$ Products the rate equation will be

$$-\frac{d[A]}{dt} = k[A]^0$$

$$\Rightarrow -\frac{d[A]}{dt} = k$$

Let the initial concentration at initial time of the reaction, t = 0 be c0. Subsequently at any other time t, the concentration will be ‘c’. On integration we obtain

$$\int_{[A]_0}^{[A]} d[A] = -\int_0^t k dt$$

$$[A] - [A]_0 = -kt \quad \text{or}$$

$$[A] = [A]_0 - kt \qquad (13.5)$$

If we plot concentration (c) against t, we get a straight line (Fig. 13.1) with slope = –k and intercept equal to c_0. Photochemical reaction between H_2 and Cl_2 over water (saturated with HCl) surface is an example of zero order reaction.

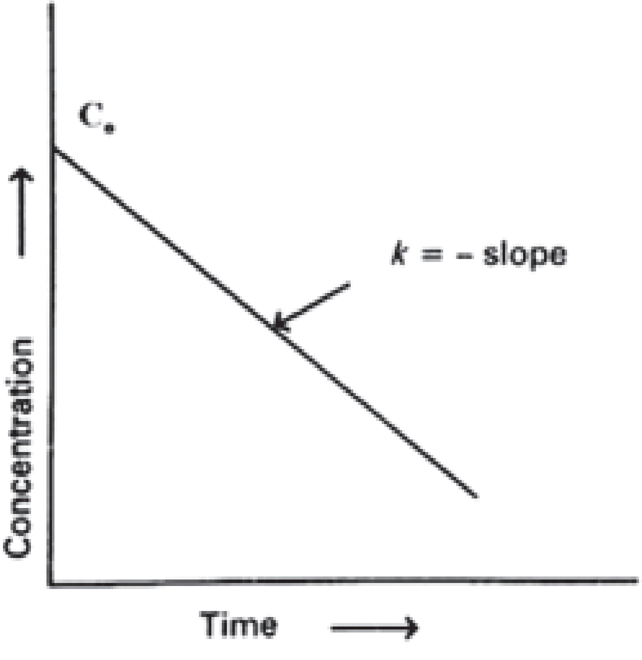


Figure 13.1: *Variation in the concentration vs time for a zeroth order reaction*

First Order Reaction

The differential rate expression for a first order reaction A $\rightarrow$ Products is given by

$$-\frac{d[A]}{dt} = k[A]^1$$

Rearranging the rate expression, we can write

$$-\frac{d[A]}{A} = kdt$$

Integrating the equation assuming the initial concentration at initial time of the reaction, t = 0 be c_0 and at time t = t concentration = c

$$\int_{[A]_0}^{[A]} -\frac{d[A]}{[A]} = \int_0^t kdt$$

$$-\text{In}\frac{[A]}{[A]_0} = kt$$

$$\Rightarrow [A] = [A]_0 e^{-kt} \tag{13.6}$$

Equation 13.6 can also be expressed as follows

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]} \tag{13.7}$$

Sometimes equation 13.7 is expressed in another format. If initial concentration of the reactant is a and x moles of it react in time t; then the concentration of the reactant left behind at time t will be a-x. In such a case the equation 13.7 can be written as

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \tag{13.8}$$

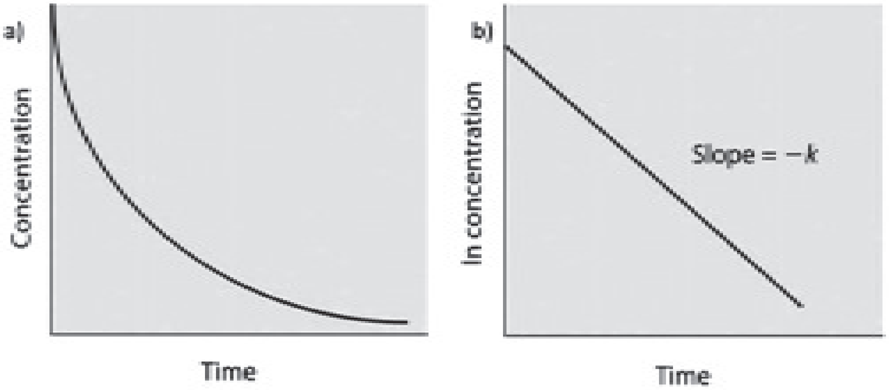


Figure 13.2. *The plot of concentration versus time (a) and ln(concentration) versus time (b) for a first order reaction.*

Second Order Reaction

There are two types of second order reactions

Case I: When both the reactants are same. This, in effect, means that two molecules of the same reactant are involved in the chemical reaction. The second-order reaction in this case would be represented as

$$2A \rightarrow P$$

The rate of the reaction can be expressed as

$$-\frac{d[A]}{dt} = k[A]^2$$

Where "k" is the second order rate constant. Now if "a" is the initial concentration of A, x is the concentration of the product formed after time t and (a – x) is the concentration of A remaining at time t, then,

$$\text{rate} = \frac{dx}{dt} = k(a-x)^2$$

By separating the variables and integrating, we get

$$\int_0^x \frac{dx}{(a-x)^2} = \int_0^t kdt$$

$$\frac{1}{a-x}-\frac{1}{a}=kt$$

$$k=\frac{1}{t}\left(\frac{1}{a-x}-\frac{1}{a}\right) \tag{13.9}$$

This is the integrated expression for the rate constant of a second order reaction in which two molecules of the same reactant are involved in the reaction. The most common example of the above type of the second order reaction is the gaseous decomposition of hydrogen iodide.

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

Case II: When the reactants are different

Consider a second order reaction

$$A + B \rightarrow P$$

where the initial concentration of A is “a” mol/lt and that of B is “b” mol/lt. After time t, “x” mol/lt of A and x mol/lt of B react to form x mol/lt of the product. Thus, the reactant concentration at time t is (a – x) and (b – x), respectively. The differential rate expression for the second order reaction is,

$$\text{rate}=\frac{dx}{dt}=k(a-x)(b-x)$$

where k is the second order rate constant. Separating the variables, we get

$$\frac{dx}{(a-x)(b-x)}=kdt$$

Resolving into partial fractions (assuming that a > b), we can write

$$\frac{1}{(a-x)(b-x)}=\frac{1}{(a-b)}\left[\frac{1}{b-x}-\frac{1}{a-x}\right]$$

Using this equation and integrating we can write

$$\int_0^x \frac{dx}{(a-x)(b-x)}=\frac{1}{(a-b)}\left[\int_0^x \frac{dx}{(b-x)}-\int_0^x \frac{dx}{(a-x)}\right]=\int_0^t kdt$$

By solving this integration and rearranging we get

$$k = \frac{1}{(a-b)t}\left[\text{In}\left(\frac{a-x}{b-x}\right) - \text{In}\frac{a}{b}\right] \tag{13.10}$$

This is the integrated expression for the rate constant of a second order reaction.

n-th Order Reaction

For a n-th order reaction, we can write

A → product

The differential rate equation is

$$-\frac{dA}{dt} = k[A]^n$$

We can find out the integrated rate law by integrating the above equation under the condition $n \neq 1$

$$-\int_{[A]_0}^{[A]} \frac{dA}{[A]^n} = k\int_0^t dt$$

$$\frac{1}{-n+1}\left([A]^{-n+1} - [A]_0^{-n+1}\right) = kt \tag{13.11}$$

When $n \neq 1$

13.6 Half-Life of a Reaction

The time required for a reaction to reduce the concentration of the reactant to the half of its initial concentration is called half-life period ($t_{1/2}$).

Half-life for a zero order reaction:

For a zero order reaction, from the integrated rate law we get

$$[A] = [A]_0 - kt$$

At $t = t_{1/2}, [A] = \frac{[A]_0}{2}$

So,

$$t_{1/2} = \frac{[A]_0}{2k} \tag{13.12}$$

So, for a zero-order reaction, the half-life period depends on the initial concentration of the reactant and the rate constant.

Half-life for a first order reaction:

For the first order reaction

$$k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$$

At $t = t_{1/2}; [A] = \frac{[A]_0}{2}$

$$t_{1/2} = \frac{2.303}{k}\log\frac{[A]_0}{\frac{[A]_0}{2}}$$

$$t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{0.693}{k} \tag{13.13}$$

Half-life for a second order reaction

For a second order reaction

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

The integrated rate equation is $\frac{1}{[A]} = \frac{1}{[A]^0} + kt$

For half-life, when $[A] = \frac{[A]_0}{2}$

$$\frac{1}{[A]_0/2} = \frac{1}{[A]_0} + kt_{1/2}$$

Rearranging

$$\frac{2}{[A]_0} = \frac{1}{[A]_0} + kt_{1/2}$$

$$t_{1/2} = \frac{1}{k[A]_0} \qquad (13.14)$$

This shows that the half-life of a second-order reaction depends on the initial concentration

For n-th order reaction

To find out the half-life of an n-th order reaction, we need to substitute $[A] = \frac{[A]_0}{2}$ in the equation 13.11 at t = $t_{1/2}$. So, we get

$$t_{1/2} = \frac{(2^{n-1} - 1)}{k_n(n-1)[A]_0} \qquad (13.15)$$

13.8 Determination of order of a reaction

The order of a reaction defines the dependence of the reaction rate on the concentration of reactants. Since reaction order cannot always be deduced directly from the balanced chemical equation, experimental methods are used to determine it. These methods involve analyzing how reactant concentrations influence the reaction rate and deriving the rate law.

Several approaches are commonly employed to determine reaction order, including the integrated rate equation method, half-life method, initial rate method, and graphical methods. Each method is suited for different types of reactions and experimental conditions. In this section, we will explore these techniques and their applications in determining reaction order.

Method of Initial Rate

The instantaneous rate of reaction extrapolated to the instant when the reagents were just mixed is called the initial rate of the reaction. Let us consider the reaction,

$A + B \rightarrow$ Products

Let the rate of reaction be represented as,

$$r = k[A]^m [B]^n$$

where the reaction is *m*-th order in A and *n*-th order in B. The rate constant for the reaction is *k*. We must obtain the initial rates from at least two experiments in which the initial concentrations of A (a_1 and a_2) are different while the initial concentration of B (b_1) is constant.

Rate in Experiment I : $r_1 = ka_1^m b_1^n$

Rate in Experiment II: $r_2 = ka_2^m b_1^n$

From the ratio $\frac{r_1}{r_2}$, we can calculate order m, since a_1 and a_2 are known

$$\frac{r_1}{r_2} = \frac{ka_1^m b_1^n}{ka_2^m b_1^n} = \left(\frac{a_1}{a_2}\right)^m$$

Taking logarithms, we can write

$$\log\frac{r_1}{r_2} = m\log\left(\frac{a_1}{a_2}\right) \qquad (13.13)$$

Similarly, the rate for one more experiment in which the initial concentration of A is a2 and the initial concentration of B is b2

So, rate in Experiment III: $r_3 = ka_2^m b_2^n$

$$\frac{r_2}{r_3} = \frac{ka_2^m b_1^n}{ka_2^m b_2^n} = \left(\frac{b_1}{b_2}\right)^m$$

$$\log\frac{r_2}{r_3} = n\log\left(\frac{b_1}{b_2}\right) \qquad (13.14)$$

Since r2, r3, b1 and b2 are known, n can be calculated. The overall reaction order = m + n.

Using Integrated Rate Expression:

We can determine the order of reaction

a) by substitution of experimental data into integrated rate law equations;

b) by graphical method using plots such as [A] against t, log[A] against t and 1/[A] against t. The order of the reaction is one, two or zero depending on which of the equations gives rise to a constant value for k or which of the plots givesa straight line.

Half-Life Method:

The half-lives are determined using different initial concentrations of the reactant. If the half-life is independent of initial concentration, the reaction is first order. If the half-life is inversely proportional to the first power of initial concentration, the reaction is second order. If the half-life is directly proportional to the first power of initial concentration, the reaction is zeroth order.

In general, half-life period ($t_{1/2}$) is proportional to $(a_0)^{n-1}$ where a_0) is the initial concentration of the reactant and *n* is the order of the reaction

If the half-life periods are $(t_{1/2})_1$ and $(t_{1/2})_2$ corresponding to the initial concentrations a_1 and a_2 of a reactant, then

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

So, ln $\frac{(t_{1/2})_1}{(t_{1/2})_2} = (n-1)\text{In}\frac{a_2}{a_1}$

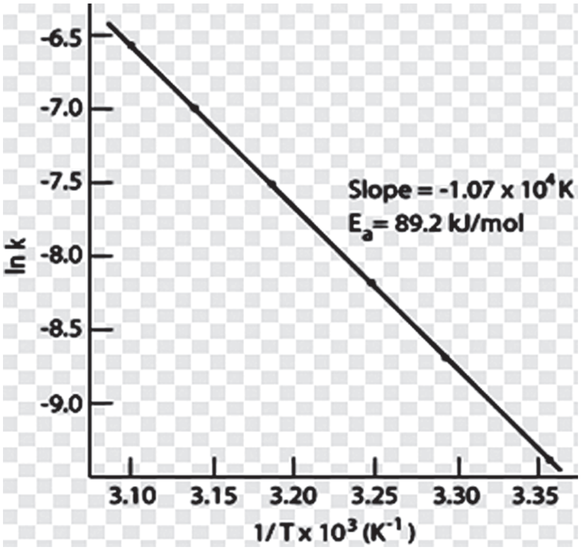
$$n = 1 + \frac{\text{In}\frac{(t_{1/2})_1}{(t_{1/2})_2}}{\text{In}\frac{a_2}{a_1}} \qquad (13.15)$$

Isolation Method

In the case of reactions having more than one reactant, the rate law can be simplified if the concentrations of all reactants except one are taken in excess. The reaction rate then depends on the reactant present in lesser quantity. The order of the reaction is determined by one of the methods given above. It is equal to the order in the reactant present in lesser quantity. This procedure is repeated in turn with each of the reactants being in lesser amount while others are in excess. This procedure is called van't Hoff s isolation method.

13.9 Temperature dependence of rate constant - Arrhenius equation

It is experimentally observed that for several reactions, an increase of temperature by about 10 degrees Kelvin increases the reaction rate (or rate constant) to a large extent; usually $\frac{k_T + 10}{k_T} = 2$. There is no rigidity about this ratio of 2; it may be less or more than 2, depending on the nature of the reaction and the temperature at which the difference of 10 K is considered.



By measuring the slope of the line, one can calculate the magnitude of activation energy.

Arrhenius observed that for a large number of reactions a plot of ln k versus $\frac{1}{T}$ is a straight line with a negative slope. The rate constant k increases exponentially with temperature:

$$k = Ae^{-\frac{E_a}{RT}},$$

where the proportionality constant A is called pre-exponential factor called the frequency factor. Ea is called the (experimental) energy of activation. A and Ea are known as Arrhenius parameters. From Arrhenius equation one may note that low activation energy means a fast reaction and high activation energy means a slow reaction. The rapid increase in k with increase of T is mainly due to the increase in the number of collisions between the molecules whose energy exceeded the activation energy

13.10 Summary

This unit covers the fundamental aspects of chemical kinetics, focusing on reaction order, rate laws, and temperature dependence of reaction rates.

Order of a reaction is an empirical quantity derived from the rate law, while molecularity refers to the number of reacting species involved in an elementary step. The rate of a reaction can be expressed in terms of the extent of reaction (ξ), leading to differential and integrated rate equations for various reaction orders.

Zero-order reactions proceed at a constant rate, independent of reactant concentration. In first-order reactions, the rate is directly proportional to the reactant concentration. Second-order and higher-order reactions follow rate laws where the reaction rate depends on concentration raised to the second or nth power.

Pseudo-first-order reactions appear to follow first-order kinetics due to the excess concentration of one reactant. A classic example is the acid-catalyzed hydrolysis of methyl acetate.

The order of a reaction can be determined using various methods. The half-life method examines how half-life changes with concentration, while the differential method uses experimental rate data to establish the rate law.

The temperature dependence of the rate constant is described by the Arrhenius equation, which explains how reaction rates increase with temperature due to an increase in molecular collisions and energy. The activation energy (E_a) is a critical parameter in this equation, indicating the minimum energy required for a reaction to proceed.

This unit provides essential tools to understand reaction kinetics, predict reaction rates, and analyze experimental data to determine reaction mechanisms.

13.11 Self-Assessment Questions

1. Define the order and molecularity of a reaction. How do they differ?
2. Derive the integrated rate law for a zero-order reaction.
3. A reaction follows first-order kinetics. Derive the integrated rate expression and explain how to determine the rate constant graphically.
4. What is the significance of the half-life of a reaction? Derive the half-life expression for a first-order reaction.
5. Explain the concept of pseudo-first-order reactions with a suitable example.
6. Derive the integrated rate equation for a second-order reaction when both reactants have the same initial concentration.
7. The half-life of a first-order reaction is independent of the initial concentration. Explain why.
8. How is the order of a reaction determined using the differential method?
9. Discuss the temperature dependence of reaction rates and explain the Arrhenius equation.
10. The rate constant for a reaction increases with temperature. Justify this observation using the concept of activation energy.
11. The rate constant of a reaction doubles when the temperature increases from 300 K to 310 K. Calculate the activation energy (E_a) using the Arrhenius equation.
12. A reaction follows second-order kinetics with a rate constant of 0.05 L mol^{-1} s^{-1}. Calculate the time required for the concentration of the reactant to decrease from 0.1 M to 0.02 M.
13. Derive the expression for the half-life of an nth-order reaction.
14. A reaction has an activation energy of 75 kJ/mol. Calculate the rate constant at 400 K if its value at 350 K is 1.2×10^{-3} s^{-1}.
15. Explain how the Arrhenius plot is used to determine the activation energy of a reaction.

Unit 14 ❐ Chemical Kinetics - Complex Reactions

Structure

14.1 Objectives

14.2 Introduction

14.3 Rate Determining Step

14.4 Opposing reactions

14.5 Parallel reactions

14.6 Consecutive Reactions

14.7 Chain Reactions

14.8 Summary

14.9 Self-Assessment Questions

14.1 Objectives

After studying this unit, learners will be able to:

- Understand the Concept of Rate-Determining Step
- Apply the Steady-State Approximation
- Analyze the Kinetics of Complex Reactions
- Study Opposing Reactions (Reversible Reactions)
- Examine Parallel Reactions (Competing Reactions)
- Understand Consecutive Reactions (Sequential Reactions)
- Explore Chain Reactions

14.2 Introduction

Chemical reactions often follow complex mechanisms involving multiple steps rather than a single transformation. In such cases, understanding the kinetics of these reactions requires identifying the rate-determining step, which is the slowest step that governs the overall reaction rate. The steady-state approximation serves as a useful mathematical approach to simplify rate equations for reactions involving reactive intermediates.

Many reactions proceed through opposing (reversible), parallel, consecutive, or chain reaction mechanisms, each exhibiting unique kinetic characteristics. Opposing reactions involve simultaneous forward and reverse processes, requiring equilibrium considerations. Parallel reactions occur when a single reactant follows multiple pathways to form different products, influencing selectivity. Consecutive reactions involve stepwise transformations where intermediates play a crucial role in determining the reaction rate. Chain reactions, commonly seen in combustion and polymerization, involve initiation, propagation, and termination steps, leading to rapid transformations.

This unit explores these fundamental concepts, providing theoretical insights and practical applications in reaction kinetics. Understanding these mechanisms helps in predicting reaction behavior, optimizing industrial processes, and designing efficient chemical pathways.

14.3 Rate Determining Step

The rate-determining step is the slowest step in a chemical reaction mechanism, controlling the overall reaction rate. It acts as a bottleneck, much like the narrow neck of a funnel that restricts the flow of liquid, regardless of how quickly it is poured in. Similarly, the reaction cannot proceed faster than its slowest step. However, not all reactions have a distinct rate-determining step—this occurs only when one step is considerably slower than the others in the sequence.

Consider this reaction:

$2NO_2 + F_2 \rightarrow 2NO_2F$,

which occurs via this mechanism

elementary step 1:

$NO_2 + F_2 \rightarrow NO_2F + F$(slow)

elementary step 2:

$NO + 2F \rightarrow NO_2F$(fast)

For elementary step 1 has a rate constant of k_1 and for elementary step 2 it has a rate constant of k_2. The slowest step in this mechanism is elementary step 1 which is our rate determining step. Looking at this mechanism I see Intermediates. Intermediates are molecules or elements that are found on the product of one step but are also located in the reactant of another step. In this case we have two intermediates NO_2 and F.

The rate equation is derived by the slowest step in the reaction. When writing a rate equation, you set up the equation by writing rate is equal to the rate constant of the slowest step times the concentrations of the reactant or reactants raised to there reaction order. Let's look at elementary step one.

elementary step one:

$NO_2 + F_2 \rightarrow NO_2F + F$

Here in this example rate = $k_1[NO_2][F_2]$.

14.4 Opposing Reactions

Certain reactions in which product of a chemical change react to form the original reactants are known as reversible or opposing reactions. In opposing reaction, the net rate of the reaction will be influenced by both forward and backward rates and that causes serious disturbance in the measurement of reaction.

Example : Muta rotation of α D glucose into β -D glucose; Conversion of ammonium cyanate into urea

There are several types of opposing reaction

- Both forward and backward reactions are of first order
- First order reaction is opposed by second order
- Both forward and backward reactions are of second order

Let us consider the case when the both forward and backward reactions are of first order

A □ B

here k_1 and k_2 represents first order rate constants for the forward and backward reactions respectively. Suppose 'a' is initial concentration of A, then after time t, x mole of A decomposed to form B. Thus, the concentration of A after a time t is a–x and that of B is x.

Therefore, the rate of forward and backward reactions equals to k_1 (a–x) and k_2 x. Thus, the net rate of formation of B is

$$\frac{dx}{dt} = k_1 (a - x) - k_2 x$$

At equilibrium the net rate is zero, $\frac{dx}{dt} = 0$

$0 = k_1 (a - x_e) - k_2 x_e$ (x_e is the equilibrium concentration)

$$k_2 = k_1 (a - x_e)/x_e$$

Substituting the k_2 into the original equation,

$$\frac{dx}{dt} = k_1 (a - x) - [k_1 (a - x_e)/x_e]\, x$$

$$\frac{dx}{dt} = k_1 (a - x) - k_1 \left(\frac{a - x_e}{x_e}\right) x = k_1 \frac{(x_e - x)a}{x_e}$$

Separating the variables,

$$\frac{dx}{x_e - x} = \frac{a}{x_e} k_1 dt$$

Integrating, t = 0, x = 0

$$-\frac{x_e}{a}[\text{In}(x_e - x)] = k_1 t - \frac{x_e}{a} \text{In } x_e$$

$$k_1 t = \frac{x_e}{a} \text{In} \left(\frac{x_e}{x_e - x}\right)$$

$$k_1 = \frac{x_e}{at} \text{In} \left(\frac{x_e}{x_e - x}\right)$$, (expressed in easily measurable quantities)

$$k_1 + k_2 = \frac{x_e}{at} \text{In}\left(\frac{x_e}{x_e - x}\right) + \frac{x_e}{at} \text{In}\left(\frac{x_e}{x_e - x}\right)\frac{(a - x_e)}{x_e}$$

$$k_1 + k_2 = \frac{x_e}{at} \text{In}\left(\frac{x_e}{x_e - x}\right)\left(1 + \frac{(a - x_e)}{x_e}\right)$$

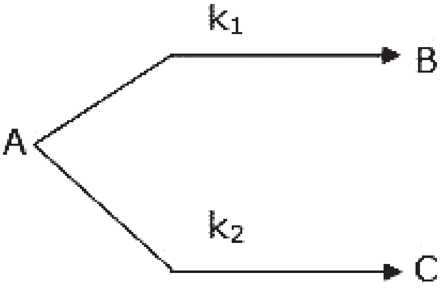
$$k_1 + k_2 = \frac{x_e}{at} \text{In}\left(\frac{x_e}{x_e - x}\right)\frac{a}{x_e} = \frac{1}{t}\text{In}\left(\frac{x_e}{x_e - x}\right)$$

$$k_1 + k_2 = \frac{1}{t}\text{In}\left(\frac{x_e}{x_e - x}\right)$$

knowledge of k1,a and xe The rate constant for reverse reaction can be obtained.

14.5 Parallel Reaction

The reactions in which a substance reacts or decomposes in more than one way are called parallel or side reactions.



If we assume that both of them are first order, we get

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A] = k_{av}[A]$$

k_1 = fractional yield of B × k_{av}

k_2 = fractional yield of C × k_{av}

If $k_1 > k_2$ then

A $\rightarrow$ B main and

A $\rightarrow$ C is side reaction

Let after a definite interval x mol/litre of B and y mol/litre of C are formed.

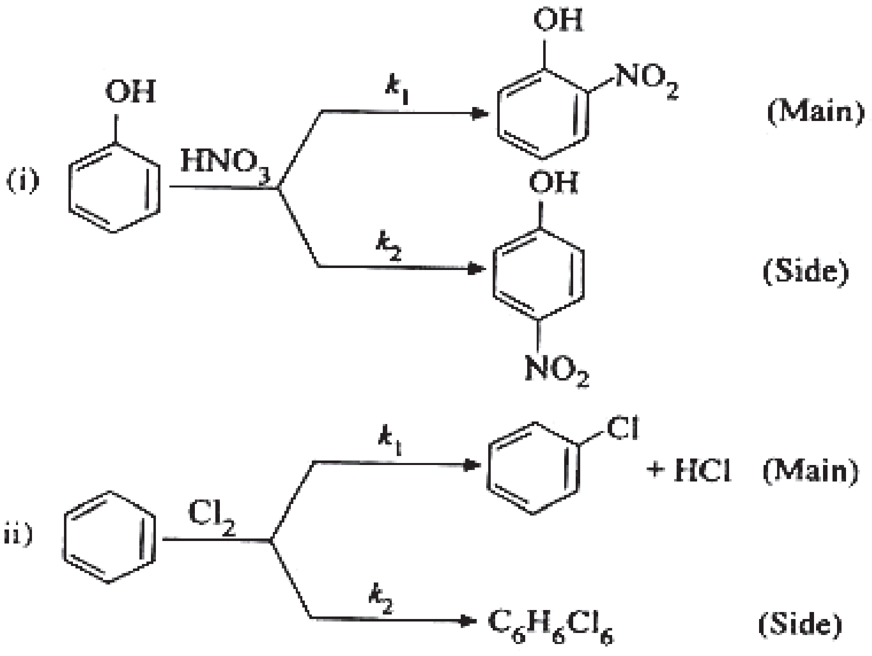
$$\frac{x}{y} = \frac{k_1}{k_2}$$

i.e

$$\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$$

This means that irrespective of how much time is elapsed, the ratio of concentration of B to that of C from the start (assuming no B and C in the beginning) is a constant equal to k_1/k_2.

Examples



14.6 Consecutive or Sequential Reactions

This reaction is defined as that reaction which proceeds from reactants to final products through one or more intermediate stages. The overall reaction is a result of several successive or consecutive steps.

$$A \rightarrow B \rightarrow C \text{ and so on}$$

Example of Sequential Reactions

Decomposition of ethylene oxide

$$(CH_2)_2O \xrightarrow{k_1} CH_3CHO$$

$$CH_3CHO \xrightarrow{k_2} CO + CH_4$$

The pyrolysis of acetone

$$(CH_3)_2CO \xrightarrow{k_1} CH_4 + CH_2 = C = O$$

$$CH_2 = C = O \xrightarrow{k_2} C_2H_4 + CO$$

For the reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

$$-\frac{d[A]}{dt} = k_1 [A] \ldots (i)$$

$$\frac{d[B]}{dt} = k_1 [A] - k_2[B] \ldots (ii)$$

$$\frac{d[C]}{dt} = k_2 [B] \ldots (iii)$$

Integrating equation (i), we get $[A] = [A]_0 e^{-kt}$ Now we shall integrate equation (ii) and find the concentration of B related to time t.

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \Rightarrow \frac{d[B]}{dt} + k_2[B] = k_1[A]$$

substituting [A] as $[A]_0e^{-k_1t}$

$$\Rightarrow \frac{d[B]}{dt}+k_2[B]=k_1[A]_0e^{-k_1t} \qquad ....(iv)$$

Integration of the above equation is not possible as we are not able to separate the two variables, [B] and t. Therefore we multiply equation (4) by an integrating factor e^{-k_1t}, on both the sides of the equation.

$$\left(\frac{d[B]}{dt}+k_2[B]\right)e^{k_2t}=k_1[A]_0e^{(k_2-k_1)t}$$

We can see that the left hand side of the equation is a differential of $[B]\,e^{k_2t}$

$$\therefore \frac{d}{dt}\left([B]e^{k_2t}\right)=k_1[A]_0e^{(k_2-k_1)t}$$

$$d\left([B]e^{k_2t}\right)=k_1[A]_0e^{(k_2-k_1)t}\ dt$$

Integrating with in the limits 0 to t

$$\left(\frac{d[B]}{dt}+k_2[B]\right)e^{k_2t}=k_1[A]_0e^{(k_2-k_1)t}$$

We can see that the left hand side of the equation is a differential of $[B]\,e^{k_2t}$

$$\therefore \frac{d}{dt}\left([B]e^{k_2t}\right)=k_1[A]_0e^{(k_2-k_1)t}$$

$$d\left([B]e^{k_2t}\right)=k_1[A]_0e^{(k_2-k_1)t}\ dt$$

14.7 Chain Reactions

A chain reaction is a self-sustaining sequence of reactions where the products of one step initiate further reactions. It consists of three main stages:

i. Initiation : A reactive species (like a free radical) is generated.

ii. Propagation : The reactive species reacts with other molecules, creating new reactive species that continue the reaction.

iii. Termination : The reaction stops when reactive species combine to form stable products or when they are removed.

Examples : Nuclear Chain Reaction: In nuclear fission, a neutron splits a heavy nucleus (like uranium-235), releasing more neutrons that trigger further fission. Chemical Chain Reaction: In the combustion of hydrogen and oxygen, free radicals propagate the reaction. Polymerization: In free-radical polymerization, monomers react in a chain-like sequence to form polymers.

In physical chemistry, a great example of a chain reaction is the thermal decomposition of hydrogen peroxide (H?O?), which follows a free-radical mechanism.

Reaction :

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

Mechanism :

1. Initiation : Heat or a catalyst (e.g., MnO_2) decomposes H_2O_2, generating hydroxyl radicals (●OH).

$$H_2O_2 \rightarrow 2.OH$$

2. Propagation : The hydroxyl radicals react with more H_2O_2, continuing the reaction.

$$.OH + H_2O_2 \rightarrow H_2O + .OOH$$

$$.OOH + H_2O_2 \rightarrow H_2O + O_2 + .OH$$

3. Termination : The radicals combine to form stable molecules, stopping the chain reaction.

$$.OH + .OH \rightarrow H_2O_2$$

$$.OOH + .OOH \rightarrow O_2 + H_2O_2$$

This reaction demonstrates how a small number of radicals can propagate a process, making it a classic chain reaction in physical chemistry.

Kinetics of a Chain Reaction

Let us take an example of a chain reaction. The reaction

$$Br_2 + H_2 \rightarrow 2HBr$$

proceeds via a chain reaction mechanism involving free radicals. The kinetic equations governing the reaction can be derived based on the mechanism.

Initiation- Formation of bromine radicals by homolytic dissociation

$$Br_2 \xrightarrow{k_1} 2.Br$$

Propagation- Bromine radical abstracts a hydrogen atom from H?, forming an H radical

$$.Br + H_2 \xrightarrow{k_2} HBr + .H$$

Hydrogen radical reacts with Br_2, regenerating Br radicals

$$.H + Br_2 \xrightarrow{k3} HBr + .Br$$

Termination- Radicals combine to stop the chain reaction

$$.Br + .Br \xrightarrow{k_4} Br_2$$

$$.H + .Br \xrightarrow{k_5} HBr$$

For bromine radicals (.Br)

$$\frac{d[.Br]}{dt} = k_1[Br_2] + k_3[.H][Br_2] - k_2[.Br][H_2] - 2k_4[.Br]^2 - k_5[.H][.Br]$$

For hydrogen radicals (.H\cdot\text{H}.H):

$$d[.H]dt = k2[.Br][H_2] - k3[.H][Br2] - k5[.H][.Br]\frac{d[.H]}{dt}$$

$$= k_2[.Br][H_2] - k_3[.H][Br_2] - k_5[.H][.Br]$$

In the steady-state approximation, the concentrations of radical intermediates Br and .H remain nearly constant. This means:

$$\frac{d[.Br]}{dt} \approx 0$$

$$\frac{d[.H]}{dt} \approx 0$$

Rearrange the equation for hydrogen radicals

$$k_2[.Br][H_2] = k_3[.H][Br_2] + k_5[.H][.Br]$$

Solving for [.H]:

$$[.H] = k2[.Br][H2]k3[Br2] + k5[.Br][.H] = \frac{k_2[.Br][H_2]}{k_3[Br_2] + k_5[.Br]}[.H]$$

$$= k3[Br2] + k5[.Br]k2[.Br][H2]$$

For simplicity, assume k_5 [.Br] is small compared to k_3 [Br_2]

$$[.H] \approx \frac{k_2[.Br][H_2]}{k_3[Br_2]}$$

Now substitute into the steady-state equation for bromine radicals:

$$k_1[Br_2] + k_3[.H][Br_2] = k_2[.Br][H_2] + 2k_4[.Br]^2$$

Substituting [?H]

$$k_1[Br_2] + k_3\left(\frac{k_2[.Br][H_2]}{k_3[Br_2]}\right)[Br_2] = k_2[.Br][H_2] + 2k_4[.Br]^2$$

For small k_4, we approximate

$$[.Br] \approx \sqrt{\frac{k_1[Br_2]}{2k_4}}$$

The overall rate of HBr formation is given by:

$$\text{Rate} = k_2[.Br][H_2]$$

Substituting for [.Br]

$$\text{Rate} = k_2\left(\sqrt{\frac{k_1[\text{Br}_2]}{2k_4}}\right)[\text{H}_2]$$

Rearranging

$$\text{Rate} = k_{\text{eff}}[\text{H}_2][\text{Br}_2]^{1/2}$$

$$k_{\text{eff}} = k_2\sqrt{\frac{k_1}{2k_4}}$$

This fractional order dependence on Br? is a hallmark of chain reactions.

14.8 Summary

This unit explores complex reaction mechanisms, focusing on different types of reactions and their kinetic characteristics. The rate-determining step (RDS) is the slowest step in a reaction mechanism that controls the overall rate. Opposing reactions involve reversible processes where the forward and backward rates establish equilibrium. Parallel reactions occur when a reactant follows multiple pathways to form different products, with the overall rate depending on competing steps. Consecutive reactions proceed through a sequence of steps where intermediates play a crucial role. Finally, chain reactions involve a self-sustaining sequence of initiation, propagation, and termination steps, commonly seen in free-radical and polymerization reactions. Understanding these mechanisms helps in predicting reaction behaviour and formulating appropriate rate laws.

14.9 Self-Assessment Questions

1. Define the rate-determining step. How does it influence the overall rate of a reaction?
2. Explain the steady-state approximation. Under what conditions is it applicable?
3. Provide an example of an opposing reaction and derive its rate expression.
4. What are parallel reactions? How is the rate expression derived for such reactions?
5. Explain the kinetics of a consecutive reaction with a suitable example and derive the rate laws.

6. Differentiate between chain initiation, chain propagation, and chain termination steps in a chain reaction.
7. Describe how the rate-determining step can be identified in a reaction mechanism.
8. Derive the rate equation for a first-order consecutive reaction $A \rightarrow B \rightarrow CA$ \to B \to $CA \rightarrow B \rightarrow C \cdot$
9. In a system with two parallel reactions, how does the selectivity of products depend on the rate constants?
10. Discuss the role of chain branching in explosive reactions, providing an example.

14.10 Reference

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