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BCHCT-133
CHEMICAL ENERGETICS, EQUILIBRIA AND FUNCTIONAL GROUP ORGANIC CHEMISTRY-I

VOL
1

CHEMICAL ENERGETICS AND EQUILIBRIA

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CHEMICAL ENERGETICS, EQUILIBRIA AND FUNCTIONAL GROUP ORGANIC CHEMISTRY-I: INTRODUCTION

Dear learners, welcome to the Core Course in Chemistry titled, “Chemical Energetics, Equilibria and Functional Group Organic Chemistry-I”. This course is designed as per the CBCS scheme of UGC and is worth four credits. It requires an average of about 120 hours of study time at your end. As is evident from the name of the course, it has been designed to cover the contents from the domains of Physical Chemistry as well as Organic Chemistry. The course content has been divided into a total of nineteen units (chapters) that are organised into four blocks. The first two blocks containing nine units cover the topics of Physical Chemistry and the remaining two blocks cover topics of Organic Chemistry. In order to facilitate the organisation of the course content it is presented in two volumes.

The **Vol-1** contains the first two blocks of the course

The first block in this volume is titled “Chemical Energetics” and contains four units (1-4) that broadly cover the introductory aspects of chemical energetics, the laws of thermodynamics, their significance and applications.

The second block titled,” Chemical and Ionic Equilibrium” contains five units (5-9) that cover the introduction to chemical equilibrium, its characteristics and a detailed account of its applications to aqueous solutions of acids, bases and salts.

The **Vol-2** contains third and fourth blocks of the course

The third block of the course contains five units (10-14) that deal with the preparation, properties and reaction of aromatic compounds and alkyl halides.

The fourth block of the course also contains five units (15-19) that deal with the chemistry of five classes of compounds, *viz*., (i) alcohols (ii) phenols (iii) ethers (iv) aliphatic aldehydes and ketones, and (v) aromatic aldehydes and ketones

Objectives

After studying the contents of this course, you should able to:

- state and explain the laws of thermodynamics and outline their significance;
- explain the concepts of internal energy, enthalpy, entropy and Gibbs energy; outline their significance and state the relationships between them;
- derive mathematical expressions for the determination of various thermodynamic properties of different systems under different conditions;
- discuss energy changes accompanying chemical reactions and describe their experimental determination
- explain spontaneous and non-spontaneous processes and state the criteria for their spontaneity;

- define and calculate absolute entropy for a system and differentiate it from residual entropy;
- explain chemical equilibrium and derive an expression for equilibrium constant in terms of Gibbs energy;
- state Le Chatelier's principle and explain its applications;
- describe different theories of acids and bases; and discuss their merits and demerits;
- define pH and calculate the same for aqueous solutions of acids, bases and salts;
- describe the stepwise ionisation of diprotic and polyprotic acids and write expressions for the respective ionisation constants;
- relate the strengths of acids and bases with their molecular structure;
- define buffer solutions, explain their mode of action and calculate their pH;
- discuss the preparations, important reactions of benzene and explain the effect of substituents on the reactivity and orientation in benzene ring;
- classify and draw structures of simple halogen derivatives, alcohols, phenols, ethers and aldehydes and ketones:
- list the general methods of preparation of aliphatic and aromatic halogen derivatives, alcohols, phenols, ethers, aliphatic and aromatic aldehydes and ketones; and
- explain the mechanism of electrophilic substitution reactions, nucleophilic substitution reactions, elimination reactions, and nucleophilic addition reactions

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Block

1

CHEMICAL ENERGETICS

CHEMICAL ENERGETICS

In this first Block of the course you would learn about the basic aspects of energetics, the laws of thermodynamics, their significance and applications. This block contains four units.

The **first unit** deals with the basic aspects of chemical energetics and covers terminology of thermodynamics; the concepts of heat, work and heat capacity; thermodynamic reversibility; thermal equilibrium and the Zeroth law of thermodynamics.

The **second unit** deals with the First Law of thermodynamics, its explanation in terms of internal energy; heat changes under different conditions; and application of the law to the gaseous systems undergoing expansion under isothermal and adiabatic conditions.

The **third unit** takes up thermochemistry and covers the energy changes accompanying chemical reactions and their measurement; the concepts of thermochemical equations, standard enthalpy changes, bond enthalpy; and the variation of enthalpy changes with temperature.

The **fourth unit** of the block deals with the Second and the Third Laws of thermodynamics and covers spontaneous and non-spontaneous processes; criterion for spontaneity; concepts of entropy, Gibbs energy, chemical potential, absolute and residual entropies; and statements and significance of Second and Third Laws of thermodynamics. In the next block we would take up Chemical and Ionic equilibria.

Objectives

After studying this block, you should able to:

- define chemical thermodynamics and outline its significance;
- explain the meaning of work and heat and discuss their inter-convertibility;
- explain the concept of thermodynamic reversibility with the help of suitable examples;
- explain the concepts of internal energy and enthalpy, outline their significance and the relationship between them;
- derive mathematical expressions for the work for expansion of gases under isothermal and adiabatic conditions;
- discuss energy changes accompanying chemical reactions under constant volume and constant pressure conditions and their experimental determination
- explain the effect of temperature on the enthalpy of a reaction and derive the Kirchhoff's equation;
- explain spontaneous and non-spontaneous processes and state the criteria for spontaneity;
- explain the concept of entropy, Gibbs energy and chemical potential and outline their significance;
- state and give significance of the Second and Third Laws of thermodynamics; and
- define and differentiate between residual and third law entropies.

UNIT 1

CHEMICAL ENERGETICS: BASIC ASPECTS

Structure

1.1 INTRODUCTION

‘Energetics’ refers to the study of energy in terms of its flow and transformation within a system or between a system and its surroundings. The energy could be in the form of heat, radiation, work or some other means. Energetics is very broad field and its applicability in a given area can be qualified by putting a suitable prefix before it. For example, the term chemical energetics implies the study of flow and transformation of energy in chemical systems. Similarly, the term bioenergetics refers to the study of flow and transformation of energy in biological systems and so on so forth. In this course we are going to focus our attention on the flow and transformation of energy within chemical systems or between the chemical systems and their surroundings.

We would begin the unit by defining thermodynamics and outlining its significance in Chemistry. It would be followed by definition and explanation of the terminology needed to understand and appreciate different aspects of thermodynamics. Many of these terms may sound quite familiar to you; however, we would be defining them precisely in the context of thermodynamics. Having defined these, we would revisit the concepts of heat, work and heat capacity. We would then explain the meaning of thermodynamic reversibility followed by the concept of thermal equilibrium. The understanding of thermal equilibrium would then be used to formulate the Zeroth law of thermodynamics.

In the next unit we would take up the First law of thermodynamics.

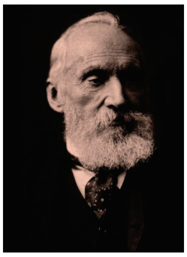
Expected Learning Outcomes

After studying this unit, you should be able to:

- define energetics;
- define chemical thermodynamics and outline its significance;
- explain different types of thermodynamic systems;
- explain the meaning of thermodynamic state of a system;
- define and differentiate between intensive and extensive variables giving examples;
- define different types of thermodynamic processes;
- explain the meaning of work and heat and discuss about their inter-convertibility;
- define heat capacity, discuss its different types and state relationship between them;
- explain the concept of thermodynamic reversibility with the help of suitable examples;
- differentiate between thermodynamic reversibility and irreversibility;
- define thermal equilibrium and outline the requirements to achieve the same; and
- state and explain the Zeroth law of thermodynamics.

1.2 CHEMICAL THERMODYNAMICS AND ITS IMPORTANCE

> *Thermodynamics is the only physical theory of a general nature of which I am convinced that it will never be overthrown.*
>
> **— Albert Einstein**



Lord Kelvin (William Thomson)

Thermodynamics is an experimental science based on certain generalisations formulated on the basis of extensive observations of the macroscopic world. Macroscopic means something that can be felt, seen or handled e.g., things that can be seen by naked eyes. These generalisations are termed as the laws of thermodynamics and are applicable to all macroscopic systems, irrespective of their physical state- solid, liquid, gas, or any combination of these states. The term thermodynamics was coined by Lord Kelvin (1824-1907) to signify the dynamic nature of heat, which was then considered to be a kind of fluid. The term is based on two Greek roots, viz., '*thermo'* meaning heat or temperature and '*dunamikos'* meaning movement. If we take literal translation, thermodynamics means dynamics (or motion) of heat. We would be talking about the laws of thermodynamics and their significance in this course.

Importance of Thermodynamics

It is important to note that the thermodynamics is concerned only with macroscopic or large-scale properties of matter and make no assumptions about the microscopic structure of matter i.e., the structure of atom or molecules. It implies that the laws of thermodynamics are independent of the structure of atom, which in turn means that *even if the structure of atom as we know today, is modified; the laws of thermodynamics and their applicability will not change.* In fact, the laws of thermodynamics were formulated mainly in the nineteenth century well before the classical and quantum mechanical description of the structure of atom was understood. It is worthwhile to mention that there has not been even a single example that violates these laws.

> Thermodynamics, like classical mechanics and classical electromagnetism, is an exact mathematical science. Each such science may be based on a small finite number of premises or laws from which all the remaining laws of the sciences are deductible by purely logical reasoning.
>
> **— Guggenheim**

Another important aspect of the thermodynamics is that it is an exact science and its laws can be expressed in terms of mathematical relationships. This allows us to derive mathematical equations that can describe and predict the outcome of many chemical and physical processes. This in turn allows us to apply these laws to practically all the branches of Science and Engineering.

In the context of chemical systems, the primary objective of thermodynamics is to establish a criterion for determining the feasibility (or spontaneity) of a given physical or chemical transformation. Secondly, thermodynamics can help in determining the criteria and conditions for the equilibrium state for a spontaneous process. The thermodynamic data can also be used to predict the direction in which the system would move to attain equilibrium and also provide the information about the extent of reaction for a given chemical reaction.

It's time that we take up the terminology used in thermodynamics. You should pay attention to the terms being discussed, as you would be using them extensively in the course of your learning thermodynamics. It is, therefore, essential that you have proper understanding of these terms. Answer the following simple question before moving ahead.

SAQ 1

What is the importance of thermodynamics in the context of chemical reactions?

1.3 THERMODYNAMIC TERMINOLOGY

A number of terms are used in the study of thermodynamics and these have specific meaning. Let us learn about some of the commonly used terms in the field of thermodynamics. Some of these may appear to be obvious or trivial but we need to define and understand them so that there is no ambiguity in their usage.

1.3.1 Thermodynamic System

A 'system' in thermodynamics is defined as *that part of the universe, which is under consideration for the study*. The system can be large or small; simple or complex. For example, a system could just be as small and simple as a beaker containing certain volume of distilled water or as large and complex as the ocean, Fig1.1.

(a) (b)

Fig. 1.1: A thermodynamic system can be of any size: (a) a beaker containing certain volume of distilled water (b) an ocean.

A thermodynamic system must have well defined boundaries that may be real (fixed or moveable) or imaginary. A capped glass vial containing water or a reaction mixture; Fig.1.2 (a) has defined physical boundaries whereas the ozone hole in the stratosphere layer of the earth's atmosphere; Fig.1.2 (b) does not have real boundary but it is also a thermodynamic system. Further, the boundaries of the system could be either fixed e.g., a fixed volume cylinder; Fig.1.2 (c) or movable e.g., a cylinder fitted with movable piston Fig. 1.2 (d).

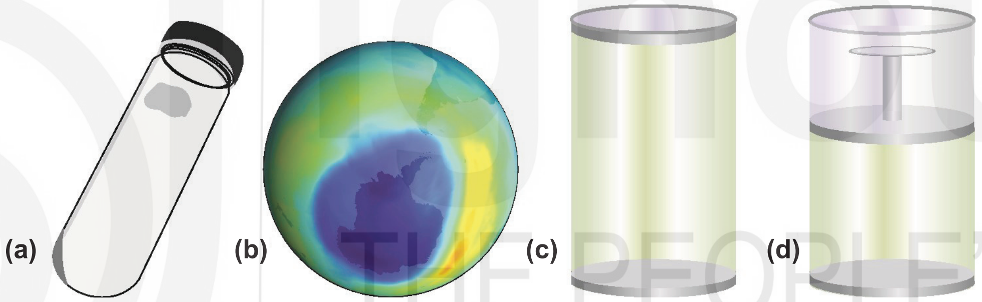
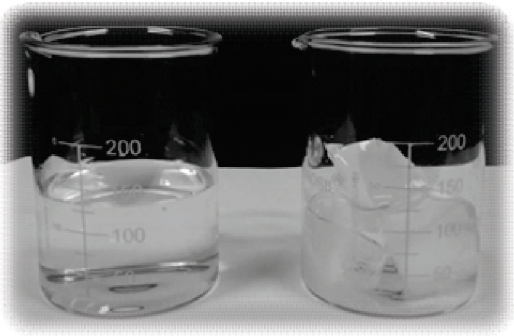


Fig. 1.2: The boundaries of a thermodynamic system can be: (a) real, (b) imaginary, (c) fixed, or (d) movable.

In addition, the system may be homogenous or heterogeneous; Fig.1.3 (a). A **homogeneous system** is the one whose properties are uniform throughout the system. A beaker containing an aqueous solution of salt or sugar in water is a common example of homogenous systems. On the other hand, a **heterogeneous system** consists of two or more homogeneous systems that are separated by physical boundaries. A beaker containing ice in water is a common example of heterogeneous systems; Fig.1.3 (b).



(a) (b)

Fig. 1.3: The thermodynamic system can be: (a) homogeneous (salt in water) or (b) heterogeneous (ice in water).

Surroundings

Theoretically speaking, the remaining (other than the *system*) part of the universe constitutes the ***surroundings*** of the system. The system and its surroundings put together constitute the ***universe***. However, *practically speaking, the surroundings are that part of the universe with which the system can interact*. For the examples given above,

i) The surroundings of the system of test tube containing distilled water, are its immediate surroundings-the laboratory bench, the people around or may be the laboratory as a whole.

ii) Similarly, for the ozone hole as the system, the surroundings may include the adjoining part of the stratosphere, the lower part of the mesosphere (the layer above the stratosphere) and the upper portions of the troposphere (the layer below the stratosphere).

Types of Systems

A system is always separated from its surroundings by a **boundary**. The type of thermodynamic system depends on the characteristics of the boundary. If the boundary of the system is such that it allows the transfer of matter and energy between the system and its surroundings through it, the system is classified as an **open system**. A glass test tube containing hot water is an example of an open system as water can be removed or more water or some other kind of matter can be added to it and also the temperature of water can be increased (by heating it) or decreased (by allowing it to cool down) by suitable transfer of energy.

The system, whose boundary does not permit the transfer of matter between the system and its surroundings but allows transfer of energy, is called a **closed system**. If the glass test tube containing hot water is suitably capped such that the matter exchange is not allowed, it would become a closed system. You may note here that the energy exchange can still happen and the temperature of water in the tube can be increased or decreased.

A closed system having a boundary that does not permit the transfer of heat to or from the surroundings is termed as an **isolated system**. In this case neither the matter nor the energy can be exchanged with the surroundings.

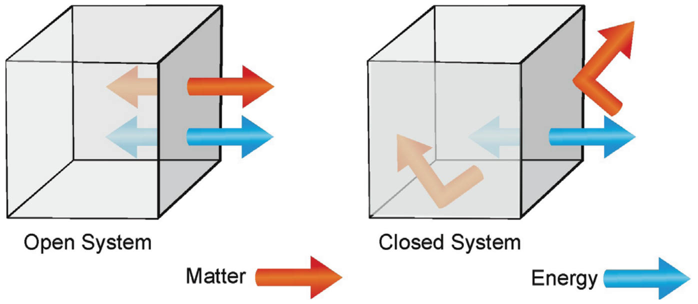


Fig. 1.4: Types of thermodynamic systems: in open system, both energy and matter can be exchanged with surroundings; closed system allows exchange of energy only whereas the isolated system does not allow exchange of either matter or energy.

If the suitably capped glass test tube containing hot water is placed inside a thermos flask or is wrapped with a thick thermally insulating material, it would become an isolated system, as then neither the matter nor energy exchange would be possible between the system and its surroundings. Different types of thermodynamic systems are schematically shown in Fig. 1.4.

Hope you have understood the types of thermodynamic systems, attempt the following simple question to assess your understanding of the types of systems.

SAQ 2

Differentiate between open, closed and isolated systems with the help of suitable examples. (Provide your own examples; do not use examples given above).

1.3.2 State of a System

The pressure, P; volume, V; temperature, T; and density, ρ, are examples of some of the thermodynamic properties or thermodynamic variables of a system. These are used interchangeably.

We have so far defined a thermodynamic system and its types. Let us raise a question, "How do we characterise or describe a thermodynamic system?" It is obvious that different systems say water in a test tube or the ozone hole would have different descriptions. One of the ways of characterising or defining a thermodynamic system is in terms of its measurable physical properties like pressure, temperature and volume etc. That is if we specify the physical properties of the system, we say that we have defined the state of the system. These properties are called **thermodynamic properties** or variables. The thermodynamic variables are also called **state variables** as these depend on the given state of the system and not on the past history of the system.

If we know the values of the thermodynamic properties of the system we say that the state of a system is defined or known.

Further, a state variable which depends on other variables is called a **dependent variable** and the variables on which it is dependent, are called **independent variables**. For example, if we have a sample of ideal gas taken in a cylinder fitted with a piston. Then according to the ideal gas equation, viz., $pV = nRT$, we can write $V = nRT/p$ i.e., the volume of the gas depends on the amount, n; temperature, T and pressure, p. Here, the volume is the dependent variable whereas the amount of gas, pressure and temperature are independent variables. On the other hand, if we wish to talk about the pressure of the gas in terms of other variables, then the pressure becomes dependent while n,T and V become independent variables. In other words, we can say that the choice of dependent and independent variables for a thermodynamic system is a matter of convenience.

1.3.3 Extensive and Intensive Variables

Thermodynamic variables of a given system can be divided into two groups' viz., intensive and extensive variables. An intensive variable is the one whose value is independent of the amount (mass) of the system whereas the extensive variables depend on the amount of the system. For example, temperature is an intensive variable; the temperature of a small chunk of ice broken from a slab of ice would be same as that of the slab. On the other hand volume is an extensive variable; the volume of 10 moles (1.8 kg) of glucose would be more than that of 1.0 mole (180 g) of glucose. It is important to note that the ratio of any two extensive variables is an intensive variable. For example, density- a ratio of two extensive variables viz., mass and volume, is an intensive variable.

The ratio of an extensive variable to the mass of the system (i.e., property per unit mass) is called **specific property** and is intensive e.g., specific volume. Similarly, the ratio of an extensive variable to the number of moles of the substance in the system i.e., the property per mole is called **molar property** and is also intensive. Answer the following self assessment question to gauge your learning about the intensive and extensive variables.

All that is stated about intensive and extensive variables holds for a homogenous system. As regards the heterogeneous system consisting of number of phases, some of the intensive variables may be different for different phases.

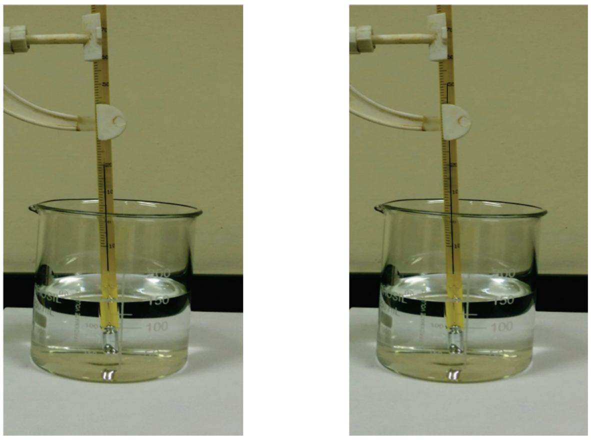
SAQ 3

Categorise the following properties into extensive and intensive properties:

Volume, area, density, refractive index, temperature, dielectric constant, pressure, energy

1.3.4 Thermodynamic Processes

In our discussion so far you have learnt about thermodynamic systems, their types and the variables that characterise the state of a given system. When a thermodynamic system undergoes a change in its state we say a **thermodynamic process** has occurred. Suppose we take 150 g of distilled water at 20°C in a beaker and heat it so that the temperature becomes 50°C; we have performed a thermodynamic process. In the course of a thermodynamic process the system can undergo an exchange of matter and/or energy with the surroundings. A thermodynamic process or a change in state is defined by clearly specifying the *initial* and *final states* of the system. The initial and final states in this example would be characterised as (p, 150 g, 20°C) and (p, 150 g, 50°C) respectively; here p is the atmospheric pressure (as the beaker is uncovered); Fig.1.5. It is assumed that there is no loss of water due to evaporation.



Initial state
(p, 150 g, 20°C)

Final state
(p, 150 g, 50°C)

Fig. 1.5: A thermodynamic process involves a change in at least one of the thermodynamic variables.

You may note here that in the process described here, only one thermodynamic parameter, viz.; the temperature has undergone a change whereas other parameters like volume and pressure have not changed significantly. Thus, *for a change of state or a thermodynamic process to occur, at least one of the thermodynamic variables must change.* Can you think of any process where none of the thermodynamic variables characterising the state of the system undergoes a change?

The answer is obvious, if none of the thermodynamic variables characterising the state of the system undergoes a change, the state of the system remains unchanged and it means that no process has occurred. However, sometimes it may so happen that the system undergoes a number of changes in state such that it comes back to its initial state with same characteristics. Such a process is referred to as a **cyclic process.**

Different types of thermodynamic processes are given below. Some of these thermodynamic processes occur in such a way that one of the variables does not change (remains invariant). These processes are given special names and are used very often.

You would learn about thermal equilibrium in Section 1.5

You would learn about bomb calorimeter in Unit 3

In addition to the thermodynamic processes given here, wherein some of the thermodynamic properties were allowed to change or remain constant we have two more types of processes which basically concern about the way the process is performed or allowed to occur. These are called reversible and irreversible processes. You would learn about these processes in Section 1.4

i) **Isothermal Process:** (pronounced as "eye-so-therm-al"): As is obvious from the name it is a process in which the temperature of the system remains constant. For example, the conversion of 1 mole of ice into water at its melting point (273.16 K; 1 atm) is an example of an isothermal process. Isothermal processes are carried out in such a way that any heat flow into or out of the system occurs so slowly that the thermal equilibrium between the system and the surroundings is maintained.

ii) **Adiabatic Process** (pronounced as "ay-dee-ah-bat-ic"): It is a process in which no energy as heat is allowed to enter or leave the system. Such a process occurs in systems that are thermally insulated and are accompanied by a change in the temperature of the system.

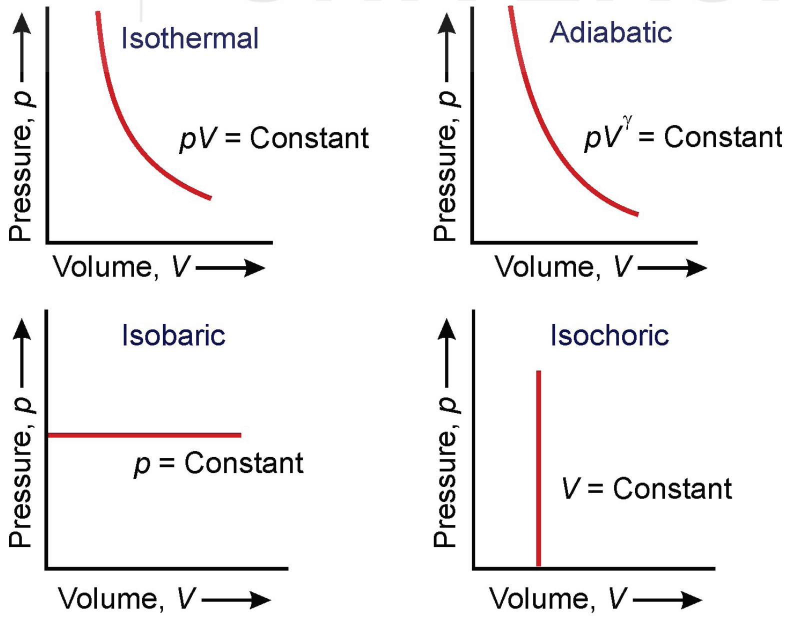


Fig. 1.6: Indicator diagrams showing the *pV* graphs for different types of thermodynamic processes for a gaseous system.

iii) **Isobaric Process** (pronounced as “eye-so-bear-ic”) sometimes also called as isopiestic process: It is a process, which is accompanied by no change in the pressure of the system. Heating of water in an open vessel or expansion of a gas in a cylinder fitted with a massless and frictionless piston are the examples of isobaric processes. In both of these cases the pressure is equal to the atmospheric pressure.

iv) **Isochoric Process** (pronounced as “eye-so-kor-ic”) sometimes also called as isovolumetric process: It is the process in which the volume of the system remains constant. Combustion of a substance in a bomb calorimeter about which you would learn in Unit 3, is an example of an isochoric process.

These processes for a gaseous system can be represented in terms of pV diagrams called **indicator diagrams**, Fig.1.6. In order to move on to the laws of thermodynamics, we need to recall a few important concepts viz., work, heat and heat capacity that you would have learnt in your earlier classes. It is essential to clearly understand the definitions of work and heat, and the distinction between the two so as to understand the exchange of energy between a thermodynamic system and its surroundings.

Solving the self-assessment question 4 would help you assess your understanding of thermodynamic state and processes.

SAQ 4

a) What is meant by the state of a thermodynamic system?

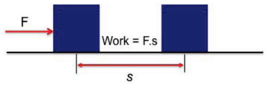
b) Can a cyclic process be a one step process? Comment.

1.4 WORK, HEAT AND HEAT CAPACITY

We all do work and know it as any activity that requires muscular or mental effort. The muscular effort typically involves pulling, pushing or lifting an object. In each of these, when we exert a force on a body such that the body moves from one place to another i.e., gets displaced; we say work has been done. Greater the displacement more the work, *if however, there is no displacement there is no work.* For example, suppose you start pushing a wall there is no work irrespective of the force applied by you, as the wall does not move. These examples on mechanical work can be used to give a definition for work.

Let us see the consequence of applying force in the examples given above. We find that the application of force causes an increase in the kinetic energy of the objects. Thus, there is transfer of some kind of energy from the person to the object. This transfer of energy is called **work**. Therefore, we may define work to be *transfer of energy via force*. You may see in the figure given in the margin that a force F is applied on the block and it moves by a distance s. In this case there has been a transfer of energy from the person to the object (block) we say the work has been done on the block. Mathematically, the work can be given as the product of the magnitude of force **F** applied and the magnitude of displacements:

$$w = \mathbf{F}.s \qquad \ldots(1.1)$$



There can be transfer of energy from the object also. Suppose an object is in motion and a person slows it down by applying force in a direction opposite to its motion. In such a case the kinetic energy of the object would decrease and an equivalent amount of energy will be transferred from the object to the person. We say that, the object has done work on the person. Such a work is called the negative work. Thus, we may define **work** as,

"The energy transferred to or from an object by means of a force acting on the object. The work is said to be positive if the energy is transferred to the object (its energy increases), and negative if the energy is transferred from the object (its energy decreases)"

Note:

We should keep in mind that work in **NOT** a material /substance that is physically transferred from the person to the object or vice-versa.

However, in thermodynamics we get more specific and define work as,

"A quantity of energy that flows across the boundary of a system by means of a force during a change in its state and is completely convertible into lifting of a mass in the surroundings." You should take note of two important aspects of this definition. First, work *appears only at the boundary of the system* and second; it appears only *during a change in the state of the system*. The SI unit of work is joule (J), which is the product of a unit force (one newton) acting through a unit distance (one meter); 1J = 1N.m

Here again, as in case of work, you have to keep in mind that heat also is **NOT** a substance or material. It is just energy in transit. There is nothing as 'the amount of heat in a body'

Though, historically the heat was thought to be a substance and was called 'caloric'. Around 1780 Benjamin Thompson (Count Rumford) demonstrated using boring of cannon barrels that the amount of heat was related to the amount of work done in the process. This was later, shown by Joule in 1840s that heat like work was energy and the two were inter-convertible.

Heat

Let us now understand what is heat? Heat is another type of energy in transit. Suppose we take two bodies at different temperatures (hot to different extent) and bring them in thermal contact with each other, what would we observe? Our common sense tells us that there would be transfer of energy from the hotter object to the cooler one. For example, if we add 100 cm^3 of water at 30°C to 100 cm^3 of water at 60°C taken in a beaker, mix the two and monitor the temperature of the mixture. We will find that the temperature of the mixture becomes about 45°C and starts decreasing gradually with time. The hot water has lost energy and the cold water has gained it hence the temperature becomes about 45°C. Further decrease is due to the loss of heat from the mixture to the surroundings (which are assumed to be at a lower temperature). Such an energy transfer that takes place because of a temperature difference is called heat flow or heat transfer, and energy so transferred is called **heat** and is symbolized as q. In terms of thermodynamics, we may define heat as,

"A form of energy that is exchanged at the boundary between a system and its surroundings by virtue of a difference in temperature between them and flows from a point of higher to a point of lower temperature and causes a change in the state of the system." You should take note of two important aspects of this definition. First, that the *heat appears only at the boundary* of the system and secondly, the heat appears *only during a change in the state* of the system.

Since heat is also a form of energy (in transit) so it's SI unit is joule, J. Further, you should note that heat is an algebraic quantity having magnitude as well as sign. Heat is said to be positive when energy is transferred to a system from its surroundings (we say that heat is absorbed by the system). On the other hand, heat is said to be negative when energy is transferred from a system to its surroundings (we say that heat is released or lost by the system).

Heat Capacity

Suppose we transfer a certain amount of heat, q to a system its temperature would increase by a certain value (ΔT) or for the temperature of the system to be increased by a certain value, ΔT we must supply a quantity of heat equal to q. The heat required is proportional to the change in temperature.

The heat capacity C of an object is the proportionality constant between the heat q that the object absorbs or loses and the resulting temperature change ΔT of the object.

$$q = C\,(T_f - T_i) = C\,\Delta T \qquad \ldots(1.2)$$

Where, T_f and T_i are the final and initial temperatures of the system. The proportionality constant, C is called **heat capacity**. Rearranging the equation, we get,

$$C = q / \Delta T \qquad \ldots(1.3)$$

For, $\Delta T = 1°C;\ C = q$ …(1.4)

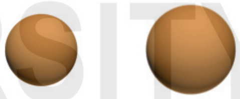
Thus, the ***heat capacity*** *C, of a given system is defined as the amount of energy as heat needed to raise the temperature of the system by 1°C.* Its units are energy per degree or energy per kelvin i.e., joule per kelvin, J K^{-1} or joule per degree Celsius, J $°C^{-1}$.

The word "capacity" here is somewhat misleading as it suggests that the system has some kind of a capacity of holding heat or has ‘heat’.

You must note that ‘heat’ is not a material that is contained in an object or the object has a capacity to hold ‘heat’. We can transfer any amount of heat to a system provided we have a body at temperature greater than the system.

It is observed that the quantity of *heat* required to raise the temperature of a given mass of the substance by a certain value depends on its nature. For example, 4 186 J of heat energy is required to raise the temperature of 1kg of water by 1°C, whereas to raise the temperature of 1kg of copper by 1°C we need only 387 J of heat.

Further, the transfer of heat to a system can be done under different conditions. If the transfer of heat is done under the conditions of constant volume, the associated heat capacity is called as **the heat capacity at constant volume, C_V** and if the transfer of heat is done under the conditions of constant pressure, the associated heat capacity is called as **the heat capacity at constant pressure**, C_P.



Let us take two balls of copper having different masses. These would require different amounts of heat to raise the temperature by a certain value say 1K. That is, these would have different heat capacities! This sounds ambiguous that two balls of same material have different heat capacities. In fact, it is due to the difference in their masses. It is therefore convenient to define a quantity like "heat capacity per unit mass" or **specific heat capacity,** *c*. The specific heat capacity would have the units of J $K^{-1}g^{-1}$ or J K^{-1} kg^{-1} (depending on the units of mass). For one mole of a substance the corresponding heat capacities are known as molar heat capacity at constant volume, $C_{V,m}$ and molar heat capacity at constant pressure $C_{p,m}$ respectively. The units for molar heat capacities are J $K^{-1}mol^{-1}$. The specific heat capacity and molar heat capacity are intensive properties whereas heat capacity is an extensive property.

Let us take an example, to understand the difference between different types of heat capacities.

The heat capacities per unit mass are called **specific heat capacities** c_p and c_v

$$c_p = C_p / m$$

According to IUPAC, the adjective specific before the name of an extensive quantity is often used to mean *divided by mass* and if the symbol for the extensive quantity is a capital letter, the symbol used for the specific quantity is often the corresponding lower case letter.

Example 1.1: 20.70 kJ of heat was supplied to 5.0 mole of water at 25°C and the temperature of water increased to 80°C. Calculate the heat capacity of the water sample, molar heat capacity and specific heat capacity of water.

Solution: As per the Eq.(1.3) the heat capacity, C is defined as

$$C = q / \Delta T$$

We are given,

$$q = 20.70 \text{ kJ} \quad \text{and} \quad \Delta T = (T_f - T_i) = 80 - 25 = 55\ ^\circ\text{C} = 55 \text{ K}$$

Substituting in the expression, we get, the heat capacity of the water sample,

$$C = \frac{20.70 \times 1000 \text{J}}{55 \text{K}} = 376.36 \text{ J K}^{-1}$$

The molar heat capacity can be obtained by dividing the value obtained above by 5.0, the number of moles of water in the sample.

⇨ Molar heat capacity, $C = \frac{376.36 \text{ J K}^{-1}}{5.00 \text{mol}} = 75.27 \text{J K}^{-1} \text{mol}^{-1}$

The specific heat capacity is the heat capacity per g; it can be obtained by dividing the molar heat capacity by the molar mass

⇨ Specific heat capacity, $c = \frac{75.27 \text{ J K}^{-1} \text{mol}^{-1}}{18.00 \text{ g mol}^{-1}} = 4.181 \text{ J K}^{-1} \text{g}^{-1}$

The values of C_P and C_V for a given solid or liquid systems are not much different. However for gaseous systems the difference in their values is significant and for an ideal gas it is given by the following expression.

$$C_{p,m} - C_{V,m} = R \qquad \text{…(1.5)}$$

Where, R is the gas constant. Further, the heat capacities depend on temperature implying that the amount of heat required to raise the temperature of a system by 1K is different at different temperatures. However, for small ranges of temperature, these do not change much and are usually taken as constant. We would talk more about the heat capacities and their temperature dependence in the Unit 3.

Solve the following question before moving ahead.

SAQ 5

0.5 mole of an ideal gas is taken in a container at 298 K. By what amount (give units also) would its heat capacity at constant pressure be more than its heat capacity at constant volume?

1.5 REVERSIBILE AND IRREVERSIBLE PROCESSES

The thermodynamic processes can be performed in two different ways i.e., 'reversibly' or 'irreversibly'. The thermodynamic reversibility and irreversibility is different from the reversibility and irreversibility that you have learnt in the context of chemical reactions. In a reversible process the change in the state of the system is made to happen slowly in an infinite number of infinitesimal steps. On the other hand, the same change can be achieved irreversibly in one or a few steps.

Let us try to understand these terms with the help of an experiment. Let us take a thermodynamic system consisting of a certain amount an ideal gas taken in a cylinder fitted with frictionless and massless piston having an area of cross section of A m^2. A mass of 1 kg is placed on the piston and the whole system is placed in a thermostat at temperature T, Fig. 1.7 (a). The gas occupies a volume V_1 at an initial pressure equal to the atmospheric pressure and the pressure exerted by the mass on the piston; let's us call this pressure p_1. The thermodynamic state of the system would be given as (p_1, V_1, T).

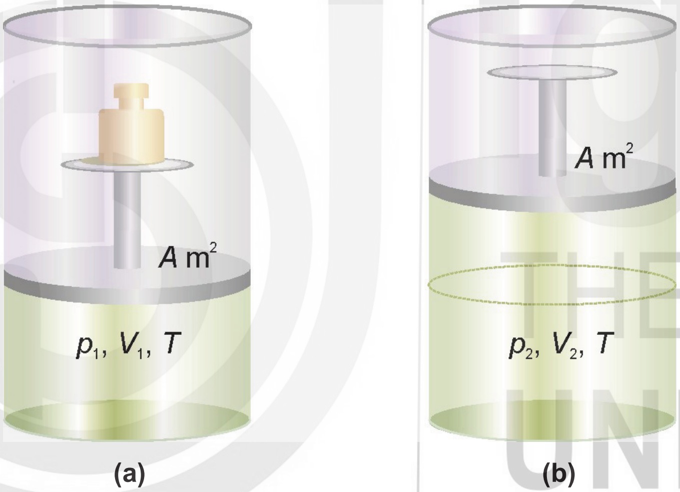


Fig. 1.7: Experimental design for understanding single step (irreversible) expansion of a gas.

Let's now remove the 1 kg mass from the piston; the pressure reduces to be equal to the atmospheric pressure; let's call it p_2. The gas would expand to volume V_2 against the opposing pressure P_2 and produce a work w_1. The new state of the system would be (p_2, V_2, T) Fig. 1.7 (b).

$$\text{Work} = w_1 = -p_2(V_2 - V_1) \qquad \ldots(1.6)$$

This work w_1 (done by the system) is generated in the surroundings. Let's move ahead and try to reverse the process by placing the 1 kg mass back on the piston. In this case the gas would undergo compression under the influence of the opposing pressure p_1 (1 atm + pressure due to 1 kg mass). The compression work would be

$$\text{Work} = w_2 = -p_{op}(V_1 - V_2) = -p_1(V_1 - V_2) \qquad \ldots(1.7)$$

You may note here that the amount of work (w_1) generated in the surroundings during the expansion process and work (w_2) that needs to be done by the surroundings to bring the system back to initial state are not equal. Let us compute the work in the cyclic process; state 1→ state 2 → state 1.

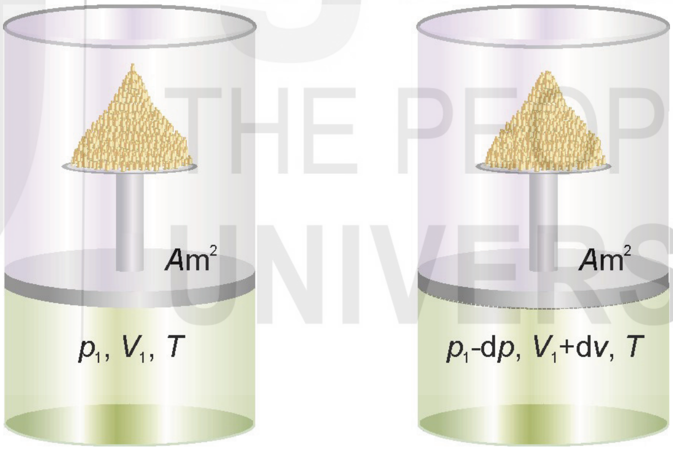
$$w_{\text{cyclic}} = w_1 + w_2 = -p_2(V_2 - V_1) - p_1(V_1 - V_2)$$

$$= -p_2(V_2 - V_1) + p_1(V_2 - V_1)$$

$$w_{\text{cyclic}} = (V_2 - V_1)(p_1 - p_2) \qquad \ldots(1.8)$$

As the terms in both the brackets of Eq.(1.8) are positive therefore w_{cyclic} is positive. When we analyse the system and the surroundings we find that the system has come back to its original state but the surroundings have not. The expansion process generated some work in the surroundings but much more work was required to be done by the surroundings to get the system back to its original state. We say that some work has been destroyed in the surroundings in this cyclic process. Such a process is called an **irreversible process.**

Let us again take the thermodynamic system consisting of same amount of the ideal gas taken in a cylinder fitted with frictionless and massless piston having an area of cross section of Am^2. Again a total mass of 1 kg is placed on the piston but in terms of 1000 masses of 1 g each, and the whole system as before is placed in a thermostat at temperature T, Fig. 1.8 (a). The gas would again occupy a volume V_1 at an initial pressure equal to the atmospheric pressure plus the pressure exerted by the 1 kg mass on the piston; i.e., p_1.



(a) (b)

Fig. 1.8: Experimental design for understanding reversible expansion of a gas.

Now let's remove one of the 1 g masses from the piston. The pressure would decrease slightly (say by dp_1) and the gas would undergo slight expansion (by a volume dV_1) against the new pressure (p_1-dp_1), Fig. 1.8 (b). This would generate a small amount of work (dw) in the surroundings.

We allow the system to attain equilibrium and remove another 1 g mass from the piston. Again the system expands a little and a work equal to dw_2 is obtained in the surroundings; again we let the system equilibrate. We continue the process of removing 1 g mass, allowing the system to equilibrate remove the next 1 g mass till all the 1 g masses are removed one by one. At the end of the process, i.e., when we remove the 1000th mass of 1 g, the system would reach state II (p_2, V_2, T); i.e., the gas expands from a volume V_1 to V_2.

Now we try to perform the reverse process, i.e., we place a 1 g mass on the piston. The pressure would increase slightly and the gas would compress by a small volume. A work +d*w* would be involved in this process. We allow the system to equilibrate and then put one 1 g mass on the piston. We repeat this process of placing 1g masses on the piston one by one; every time allowing the system to come to equilibrium. Once we place all the 1000 masses of 1g each on the piston we find that the system has come back to the state 1 (p_1, V_1, T).

It is found that the total work obtained from the system in the process of expansion ($V_1 \rightarrow V_2$) and the total work required to be done on the system during compression ($V_2 \rightarrow V_1$) are equal. In other words, no work is destroyed in the surroundings in the expansion-contraction cycle. Such processes are called thermodynamically reversible processes. If you think carefully you may note that the work done during the 2nd step of expansion process and the work obtained during the 999th step in the contraction process would be equal.

The process could be done in 10,000 steps using 100 mg mass each time or 100, 000 steps using 10 mg mass each time and so on. To make it even better we could use 1 kg of sand and remove a grain of sand each time.

We have taken an example wherein the change from state-I (p_1, V_1, T) to state-II (p_2, V_2, T) was achieved in say 1000 small steps. Such an approach is a reasonably good approximation to reversible processes. *Ideally speaking for a process to be truly reversible, the change must be brought in an infinite number of infinitesimally small steps.* Which means it would need an infinite length of time to complete. Thus, we can say that the reversible processes are not real processes; these are ideal. We may approach the true reversible behaviour but not achieve it. In other words we can say that ***all real processes are irreversible***.

SAQ 6

Outline the differences between the thermodynamically reversible and irreversible processes.

1.6 THERMAL EQUILIBRIUM: THE ZEROTH LAW OF THERMODYNAMICS

Temperature is a familiar property (we all seem to know it), however it is quite difficult to define. We are also familiar with the fact that when a hot body and a cold body are brought into contact, the hot body becomes cooler and the cold body becomes warmer. The concept of temperature is based on the qualitative ideas of something being ‘hot’ or ‘cold’ as felt by us on the basis of our sense of touch. However, a measurement of temperature on the basis of sense of touch can be very vague as our senses may deceive us and the outcome may be unreliable. For example, if we stand bare feet with one foot on dry grass and the other on an adjacent marble floor in open on a hot sunny day; the floor would appear much hotter than the grass even though the two may be at the same temperature. Similarly, a steel spoon may appear warmer than the wooden table on which it is kept. The difference is due to the fact that our skin measures the rate of energy transfer (heat) from the object rather than its temperature.

Now, suppose you ask anybody 'how can we measure temperature'? The immediate answer would be 'with the help of a thermometer'. In other words we all know that the thermometer as a device to measure temperature. Have you ever thought, what is the basis of this device? The principle of thermometer is based on two things: firstly, the concept of thermal equilibrium, and secondly, the fact that certain properties of materials depend on temperature. Let us first understand the meaning of thermal equilibrium. Let us bring two closed systems into a thermal contact with each other and observe the changes in the properties of both the systems. You may ask what are the systems and how do we observe changes?

For this, let us assume that we have got two identical cubes made up of a 'novel' material, which changes its colour with temperature. Let one of the cubes (system A) be 'hot' (red coloured) and the other (system B) be 'cool' (blue coloured) and we place these two in the two chambers (separated by an insulated partition) of an insulated box made up of a transparent material so that we can visually observe the colour changes taking place inside the insulated box (Fig. 1.9). Now when we remove the insulated partition what would we observe?

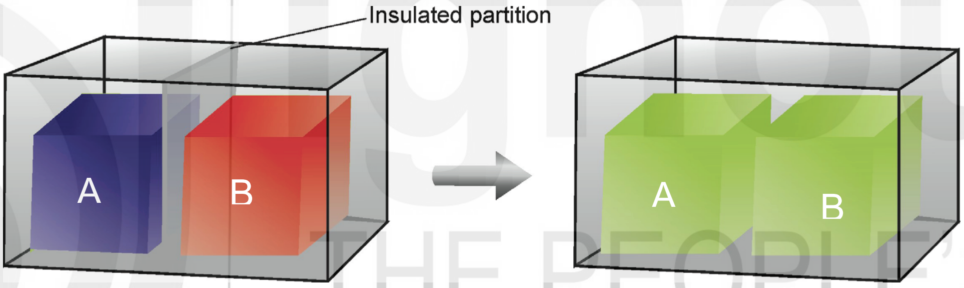


Fig. 1.9: A schematic diagram of a thought experiment (described in the text) designed to demonstrate the directionality of heat flow.

When two objects maintained at different temperatures are brought in thermal contact, they exchange heat with each other until they reach a state of thermal equilibrium and after that no further exchange of energy takes place between them.

We would observe that the colors of the two cubes change gradually and eventually become the same indicating the attainment of equality of temperature-a state of equilibrium. Thereafter, there is no further change in colour as there is no further exchange of energy between the systems. Such an equilibrium that is a consequence of temperature being the same is called **thermal equilibrium.** The heat flows from higher temperature to lower temperature and continues till the two objects attain same temperature. Now if one of the objects happens to be a thermometer, the reading on the thermometer would change and become constant. This would indicate the temperature of the other object.

The thermal equilibrium is characterized by the equality of a single parameter (temperature) was first stated by a Scottish chemist and physician, Joseph Black (1728–1799).

Let us extend our experiment and consider three systems, A, B, and C that are at different temperatures initially. The arrangement of the three systems is given in Fig. (1.10). In this arrangement we have separated system A and B by an insulating wall and have introduced thermally conducting slabs in such a way that these provide thermal contact between system A and system C and also between system B and system C. Thus, in our experiment system C can interact thermally with system A and B whereas system A and B cannot interact with each other.

Having set the experiment we observe the three systems from outside. Remember, our insulating box is made up of a transparent material that permits us to observe the systems inside. What would we observe?

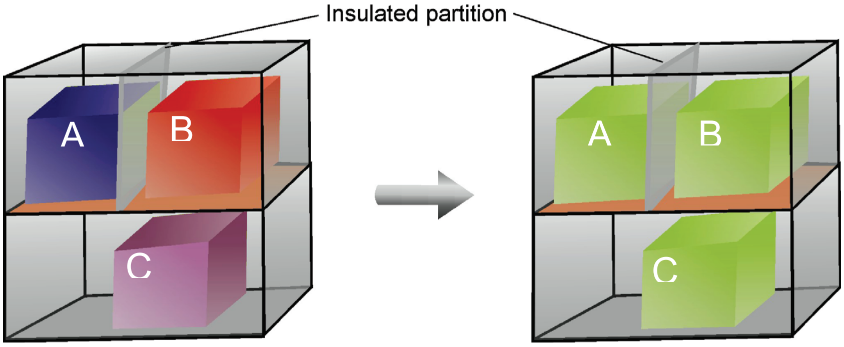


Fig. 1.10: A schematic diagram of a thought experiment (described in the text) to demonstrate the Zeroth law of thermodynamics.

The Zeroth Law is identical in form to a famous logical argument using deductive reasoning viz., if $\alpha=\beta$ (first premise), and $\beta=\gamma$ (second premise), then $\alpha=\gamma$ (conclusion). Herein we arrive at a conclusion based on two propositions. In mathematical terms, the Zeroth law of thermodynamics is said to be **transitive**.

We would observe that the colors of the three cubes representing the three systems change with time. After sufficient amount of time is passed the three systems, would be found to have same colour indicative of same temperature. Since there was a thermal contact between system A and system C we expect them to be at thermal equilibrium. Similarly, the thermal contact between system B and system C also allows for a thermal equilibrium to be achieved between them. The question comes up is that how do we explain the thermal equilibrium between system A and system B as we did not allow any thermal interaction between the two?

This observation, in fact, is the essence of the Zeroth law of thermodynamics which can be stated as, "*If two thermodynamic systems, A and B are in thermal equilibrium with a third thermodynamic system, C then the two thermodynamic systems (A and B) are also in thermal equilibrium with each other*". The importance of this law was recognized only after the other laws of thermodynamics were formulated and is fundamental to them, therefore is called the Zeroth law.

1.7 SUMMARY

In this unit we began by defining energetics as the study of energy in terms of its flow and transformation within a system or between a system and its surroundings. We highlighted its wide applicability and stated that in this course we are going to focus our attention on the flow and transformation of energy within chemical systems or between the chemical systems and their surroundings.

This was followed by introducing thermodynamics as a domain of science based on laws formulated by extensive observations of the macroscopic world. We defined thermodynamics as a branch of science that deals with the relationship between heat and other forms of energy and discussed the importance of thermodynamics in studying chemical reactions. Thereafter we took up the terms, like system, its types, state of system; the thermodynamic properties etc., commonly used in the study of this important scientific domain and explained them with the help of suitable examples. This was followed by a brief discussion on thermodynamic processes; any change in state of a given system is termed as a thermodynamic process.

Having defined the terms used in thermodynamics, we revisited the concepts of heat, work and heat capacity etc. and explained the sign convention for heat and work to be used in the context of thermodynamics. This was followed by a discussion on important concepts of thermodynamic reversibility and irreversibility. A thermodynamically reversible process is a process, which is accomplished, in an infinite number of infinitesimally small steps.

Thereafter we introduced the concept of thermal equilibrium and used the same to explain the way a thermometer works. The argument was extended to introduce the Zeroth law of thermodynamics whose significance was outlined.

1.8 TERMINAL QUESTIONS

1. What is energetics?

2. A 10 g spherical ball of copper was heated by passing electrical current. If a transfer 100 J of energy increased the temperature of the sphere by 22°C. Calculate the specific heat capacity of copper. Assume that no heat was lost during the heating process.

3. Define and differentiate between intensive and extensive variables giving examples.

4. Calculate the amount of heat required to increase the temperature of 1.00 mole of argon from a temperature of 100 K to 900 K in:

   a) an isobaric process and

   b) in a isochoric process.

   (Given: $C_{V,m}$ = 12. 47 J $K^{-1}mol^{-1}$ and $C_{p,m}$ = 20. 78 J $K^{-1}mol^{-1}$)

5. What is meant by thermodynamic reversibility?

6. State Zeroth law of thermodynamics.

1.9 ANSWERS

Self-Assessment Questions

1. In the context of Chemical reactions, the thermodynamics
   - Provides a criterion for determining the feasibility of a reaction
   - Provides the criteria and conditions for the equilibrium state for a spontaneous process
   - Helps in predicting the direction of the system to attain equilibrium
   - Can provide information about the extent of reaction in an equilibrium reaction

2. A thermodynamic system that allows the exchange of energy as well as matter with the surroundings is called an open system, for example, food being cooked in an open vessel. On the other hand if the system permits the exchange of energy but not the matter it is termed as closed, e.g., cooked food kept in a closed metallic container. The isolated system does not permit the exchange of either the energy or the matter. The food in an insulated closed container is an example of an isolated system.

3. The given properties can be categorized as follows:

Extensive properties	**Intensive properties**
Area	Density
Volume	Temperature
Energy	Dielectric Constant
Pressure	Refractive index

4. a) The state of a system refers to its current condition identified in terms of its characteristic physical properties. If the thermodynamic properties characterising the system are defined the state is said to be defined. The pressure, p; volume, V; temperature, T; and density, ρ, are examples of some of the thermodynamic properties of a system.

   b) No, a cyclic process cannot be a one step process. The requirement of the cyclic process is that the system must be back to its initial state, however, in a single step process the state of the system gets changed.

5. We know that for one mole of an ideal gas $C_{P,\text{m}} - C_{V,\text{m}} = R$ or in general, $C_P - C_V = nR$.

   Substituting the values $C_p - C_v = 0.5\ \text{mol} \times 8.314\ \text{J K}^{-1}\text{mol}^{-1}$

   $$= 4.157\ \text{J K}^{-1}\text{mol}^{-1}$$

   Therefore, the heat capacity for the given system at constant pressure will be 4.157 J K^{-1} more than the heat capacity at constant volume.

6. The following are the differences between the thermodynamically reversible and irreversible processes.

   - In a reversible process, the thermodynamic system undergoes a change in state through a specified sequence of infinite number of infinitesimal steps each giving a new state whereas the irreversible process occurs in one or a few number of steps.
   - In case of reversible process, the system and the surroundings acquire equilibrium at every step whereas in irreversible process such an equilibrium does not exist

- In case of reversible process, the change in state is reversed through the same sequence of states in the reverse order whereas in irreversible process the same sequence in the reverse order is not observed

Terminal Questions

1. 'Energetics' refers to the study of energy in terms of its flow and transformation within a system or between a system and its surroundings. The energy could be in the form of heat, light, radiation or mass etc.

2. The specific heat capacity is defined as the quantity of energy as heat required to raise the temperature of 1 g of a substance through 1°C. Mathematically

$$c = \frac{q}{m\Delta T}$$

we are given q = 85 J ; m = 10 g and ΔT = 22°C.

Substituting the values, we get

$$c = \frac{85\,\mathrm{J}}{10\,\mathrm{g}\times 22\,\mathrm{K}} = 0.386\ \mathrm{J\,K^{-1}g^{-1}}$$

3. The thermodynamic properties whose values do not depend on the amount of the substance are called intensive properties and the ones, which are dependent on the amount, are called extensive properties. For example, the mass and volume of a substance would depend on its amount. A sample of water having 1.00 moles of it will weigh 18 g and would occupy a volume of 18 $\mathrm{cm^3}$ (at room temperature; assuming ρ to be 1.0 g $\mathrm{cm^{-3}}$) whereas 5.00 moles of water would have five times the mass and the volume. On the other hand density is an intensive property, as any two samples of a substance (if they are from the same source) would have same density.

4. a) We know that for isobaric process (occurring at constant pressure), the heat required to raise the temperature is, $q_p = nC_{p,m}\Delta T$

Given: $C_{P,m}$ = 20. 78 J $\mathrm{K^{-1}mol^{-1}}$, n = 1.00 mol,
ΔT = 900 − 100 = 800K

Substituting in the expression,

$$q_p = 1.00\ \mathrm{mol}\,\mathrm{x}\,20.78\ \mathrm{J\,K^{-1}mol^{-1}}\,\mathrm{x}\ 800\ \mathrm{K} = 16624\ \mathrm{J} \Rightarrow 16.624\ \mathrm{kJ}$$

b) Similarly, for isochoric process (occurring at constant volume), the heat required to raise the temperature is, $q_V = nC_{v,m}\Delta T$

Given: $C_{V,m}$ = 12. 47 J $\mathrm{K^{-1}mol^{-1}}$, n = 1.00 mole,
ΔT= 900 − 100= 800K

Substituting in the expression,

$$q_v = 1.00\ \mathrm{mol}\,\mathrm{x}\,12.47\mathrm{J\ K^{-1}mol^{-1}}\,\mathrm{x}\ 800\ \mathrm{K} = 9976\mathrm{J} \Rightarrow 9.976\ \mathrm{kJ}$$

5. In thermodynamics a process implies a change in state of a system. Thermodynamic reversibility concerns the nature of process i.e., the way a process occurs. A reversible process is that process which takes place in infinite number of infinitesimally small steps. At each step there is an equilibrium between the system and the surroundings and on reversing the order of the steps the initial state can be regained.

6. The Zeroth law of thermodynamics states that "If two thermodynamic systems, A and B are in thermal equilibrium with a third thermodynamic system, C then the two thermodynamic systems (A and B) are also in thermal equilibrium with each other".

UNIT 2

THE FIRST LAW OF THERMODYNAMICS

Structure

2.1 INTRODUCTION

In the previous unit you were introduced to the domain of energetics as the study of energy in terms of its flow and transformation between a system and its surroundings. In chemical energetics we focus our attention on the flow and transformation of energy within chemical systems or between the chemical systems and their surroundings. You have learnt about the basic aspects of thermodynamics like its definition, importance, and terminology etc. You have also learnt about the concept of thermal equilibrium and the Zeroth law of thermodynamics as its consequence. In this unit, we are going to take up the First law of thermodynamics.

We would begin by explaining the concept of internal energy and then use it to state and explain the first law of thermodynamics. This would be followed by the description of heat changes under different conditions. Here, we would introduce the concept of enthalpy and then relate internal energy and enthalpy with the measurable quantity-heat capacity. We would also establish a relationship between the heat capacities at constant volume and at constant pressure. We would then apply the first law of thermodynamics to the gaseous systems undergoing expansion under isothermal and adiabatic conditions.

In the next unit we would take up thermochemistry-application of the first Law of thermodynamics to the heat changes accompanying chemical reactions and their measurement.

Expected Learning Outcomes

After studying this unit, you should be able to:

- define internal energy;
- define and differentiate between the state functions and path functions;
- give different statements of the First Law of thermodynamics;
- formulate a mathematical expression for the first law of thermodynamics;
- discuss heat changes under constant volume and constant pressure conditions;
- explain the concept of enthalpy, its significance and the relationship with internal energy;
- relate the $\overline{C}_p$ and $\overline{C}_V$ respectively with enthalpy and internal energy;
- derive the relationship between $\overline{C}_p$ and $\overline{C}_V$ for an ideal gas;
- derive mathematical expressions for the work of expansion of gases under isothermal and adiabatic conditions; and
- establish relationships between different state variables for adiabatic expansion of an ideal gas.

2.2 THE FIRST LAW OF THERMODYNAMICS

You have learnt in the previous unit that heat and work are forms of energy in transit. Further, we know that a system may do work or the work is done on the system; accompanied by some energy transfer from or to the system. Similarly, we may give heat to the system or the system gives heat to the surroundings; again there is some energy transfer to or from the system. The question arises that when the energy (as heat or work) goes to the system where does it go? What change does it bring to the system? Similarly, when the system loses energy by doing work or by increasing temperature in the surroundings; what changes occur in the system? How do we represent such changes? In order to answer these questions we need to bring in the concept of internal energy symbolised as *U*.

2.2.1 Internal Energy, *U*

Internal energy is *the energy possessed by a given system by virtue of its very existence* and is composed of all possible types of energies, which all the constituents of the system put together can have. For example, chemical,

The internal energy does not include the kinetic energy due to the translation motion of the system as a whole.

translational, electronic, vibrational, rotational, and nuclear or any other types of energy all contribute to the internal energy of the system. Further, you must note that not all systems will have all the types of energies mentioned above. For example, a system containing certain amount of a monoatomic gas would not have vibrational energy. Can you think why? It is so because for the vibration motion to be executed there must be at least two bonded atoms (a diatomic molecule).

The internal energy is an extensive property however; the internal energy per mole i.e., the molar internal energy is an intensive property. Like heat, and work the internal energy is also measured in the units of energy, joule.

James Prescott Joule
(1818-1889)

In 1840s English physicist, **James Prescott Joule** (1818-1889) performed the experiments described in the text, in different ways like by rotating a paddle wheel, passing electric current, causing friction etc. He found that a given amount of work done on the system, irrespective of how it is done, produced the same change of state. The change in state was measured by the change in the temperature of the system. *Thus, to produce a given change of state, the adiabatic work required is independent of the path by which the change is achieved.*

As there are no means of measuring or knowing all these energies for a given system, the absolute value of the internal energy of any system cannot be known but every system has some value of its internal energy, U. However the change in internal energy ΔU is measurable. It refers to the change in internal energy when a system changes from an initial state having an internal energy U_i to a final state of internal energy U_f,

$$\Delta U = U_f - U_i \qquad \ldots (2.1)$$

Let us try to have an insight into internal energy by taking an adiabatic system (that does not allow any exchange of heat with the surrounding)in some state (say state 1) having a value of internal energy U_1 and do some work on it. This would lead to a change in state of the system and the system now would be in a new state (say state 2) having an internal energy U_2. As work is also a kind of energy the new internal energy U_2 would be higher than U_1. Since there is no other energy input, we can write,

$$\Delta U = U_2 - U_1 = w_{\text{adiabatic}} \qquad \ldots (2.2)$$

The added energy in the form of work would increase the kinetic energy of the molecules of the system and the temperature would increase. On the other hand, if the same adiabatic system in state with internal energy U_1 does some work on the surroundings it would be at the expense of its in internal energy. The final value of internal energy, U_2 will be smaller than U_1; the work would become negative.

$$\Delta U = U_2 - U_1 = -w_{\text{adiabatic}} \qquad \ldots (2.3)$$

A schematic representation of the sign convention on work in the context of thermodynamics is given in Fig. 2.1.

The sign convention on work: the work done by the system is negative while the work done on the system is positive.

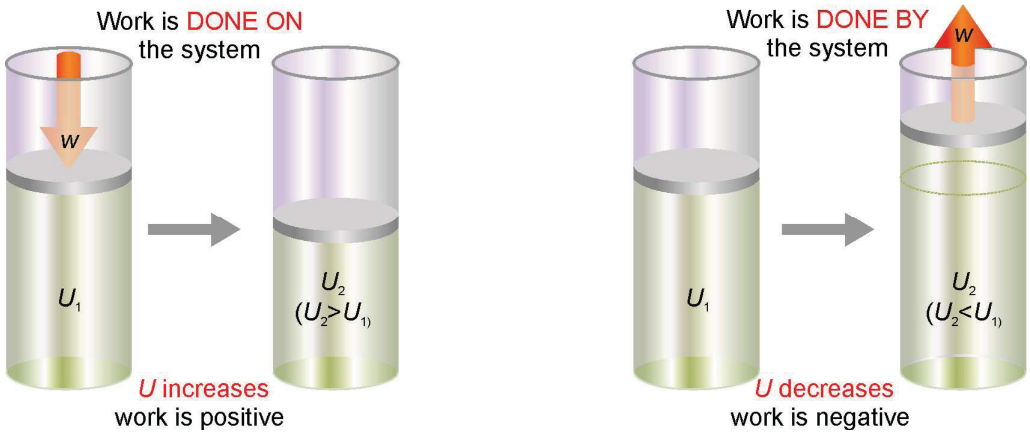


Fig. 2.1: A schematic representation of the sign convention on work.

Let us once again take the same system in same state having internal energy U_1 and perform another experiment. In this experiment we change the walls of the system such that the heat can be transferred to the system from the surroundings and also design the experiment in such a way that there is no work done on the system or by the system. Now let us transfer certain amount of heat from the surrounding to the system such that the system has same change in temperature as before. In other words the system comes to same state characterised by the internal energy $U_2 > U_1$; in such a case we can write,

$$\Delta U = U_2 - U_1 = q \text{ (no work; } w = 0) \qquad \dots (2.4)$$

Similarly, if the system lost heat to the surroundings under similar conditions, it would be at the expense of its internal energy and the value of U_2 will be smaller than U_1; the q would become negative.

$$\Delta U = U_2 - U_1 = -q \text{ (no work; } w = 0) \qquad \dots (2.5)$$

A schematic representation of the sign convention on heat in the context of thermodynamics is given in Fig. 2.2.

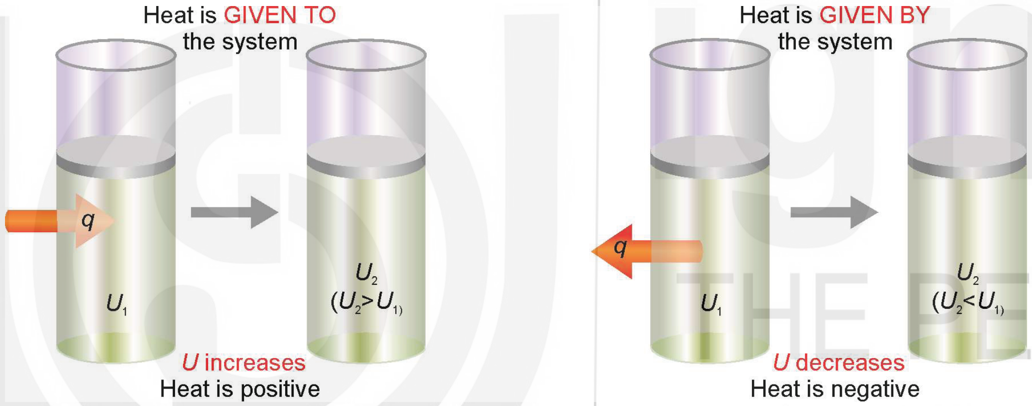


Fig. 2.2: A schematic representation of the sign convention on heat.

Going further, we may design a yet another experiment wherein we allow the transfer of certain amount of heat to the system and also perform some work on it adiabatically such that the system has same change in temperature as before. In other words the system comes to same state characterised by the internal energy U_2.

The sign convention on heat

The heat given to the system is positive while the heat given by the system to the surroundings is negative.

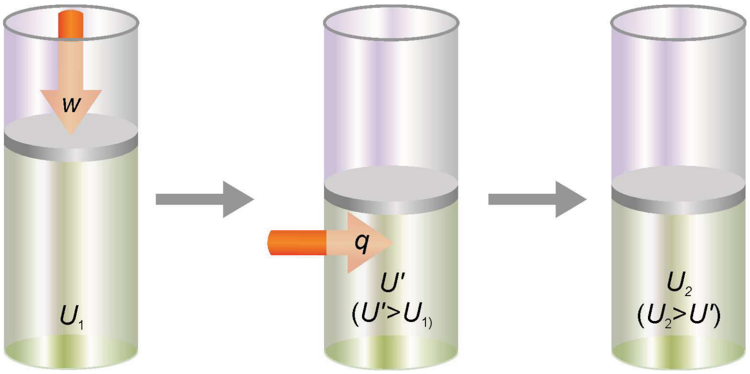


Fig. 2.3: A schematic representation showing effect of work and heat on internal energy.

Anything (heat or work) that increases the internal energy of the system is positive and the one that decreases the internal energy of the system is negative

The way we have defined internal energy here amounts to saying that the internal energy is a state function; the one which depend only on the state of the system and not on how that state has been achieved.

In such a case we can write,

$$\Delta U = U_2 - U_1 = q + w \qquad \ldots (2.6)$$

This leads us to the IUPAC definition of internal energy.

IUPAC defines internal energy as the quantity, the change in which is equal to the sum of heat, q, brought to the system and work, w, done on it, ΔU = q + w.

State and Path Functions

You may have noticed that we have used different types of symbols for three quantities used above, namely heat, q, work, w and internal energy, U. For internal energy we used a capital letter whereas for heat and work we have used lower case letters. This has been done to convey the fact that while internal energy is a state function, heat and work are path functions. *A '**state function**' is a property of the system that depends only on the current state of the system and is independent of the way the state is achieved.*

To understand the difference between a state function and a path function, let us take a thermodynamic system in state 1 having the internal energy as U_1 and transfer q amount of heat to it such that the system is now at state 2 with internal energy U_2. You would recall from the above, that the system with U_1 could also be taken to U_2 by doing work on it. Thus, we find that in the first case the change from state 1 to state 2 was associated with q amount of heat energy and no work whereas in the second case there was w work and no associated heat change.

We may take up another case where we start with the same system at state 1 and transfer q' ($q' < q$) amount of heat to it; the system will reach some state (state 1′) different from state 2 and then we do sufficient work on the system so as to make it reach state 2. In this case, the change in state (1→2) is associated with heat and work changes. We may take up a yet another case where we initially do some work on the system ($w' < w$) and then supply sufficient amount of heat to it to make it reach, state 2. The four cases are schematically given in Fig.2.4.

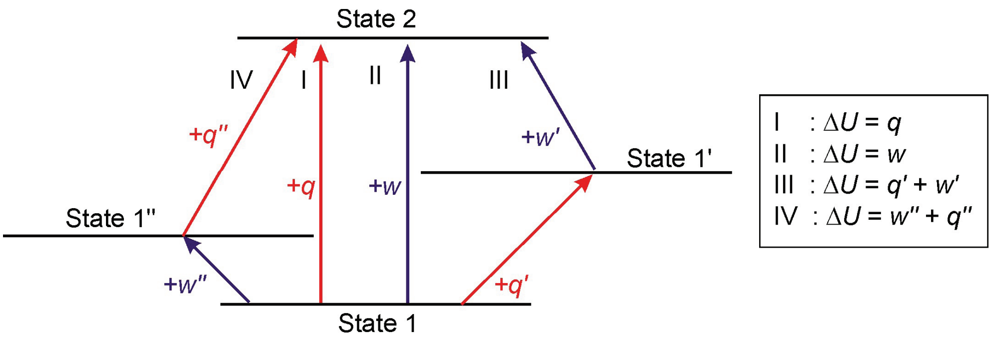


Fig. 2.4: A schematic diagram showing that work and heat are path functions.

You may note that in all the four cases taken here we go from state 1 (U_1) to state 2 (U_2) i.e., the change in internal energy is same but the amount of work done or the associated heat change is different in all the cases. In other words, the internal energy depends on the state of the system i.e., it is a **state function** whereas heat and work *depend on the path* taken for going from state 1 to state 2. Heat and work are accordingly called **path functions**.

Having learnt about the concept of internal energy we are now equipped to learn about the first law of thermodynamics.

2.2.2 The First Law of Thermodynamics and Internal Energy

Die Energie der Welt ist Konstant
-Clausius,1867

You have learnt about the first law of thermodynamics in your earlier classes as the law of conservation of energy i.e., *energy can neither be created nor be destroyed although it can be changed from one form to another*. You may also have come across many other statements for the First law of thermodynamics. Some of these are

- The total energy of universe is constant.
- It is not possible to construct a machine showing perpetual motion of the first kind. That is, a machine, which can work endlessly without the expenditure of energy.
- The internal energy of an isolated system is constant; $\Delta U_{\text{sys (isolated)}} = 0$

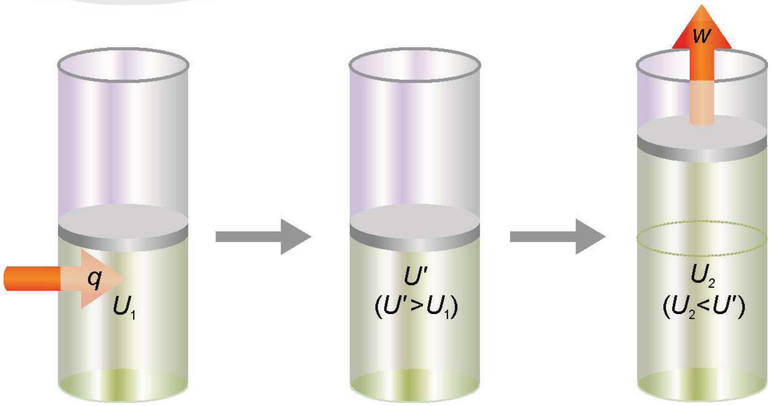
These statements are alternative expressions for the principle of conservation of energy.

Mathematical Expression of the First Law of Thermodynamics

There is no proof for first law of thermodynamics; the absence of any contradiction to it makes us believe in it.

The definition of first law in terms of $\Delta U_{\text{sys (isolated)}} = 0$ is not of wider applications as most of the systems we come across or work with are either open or closed systems. In such cases, the exchange of matter or energy between the system and the surroundings is allowed. Moreso, we are particularly interested in the energy changes of the system. Let us take up certain situations that we may come across.

Case I: We tranfer q amount of heat ($+q$) to a system having internal energy, U_1, that increases its internal energy to U' and the system in turn does certain work on the surroundings ($-w$) leading to decrease in the internal energy to U_2.

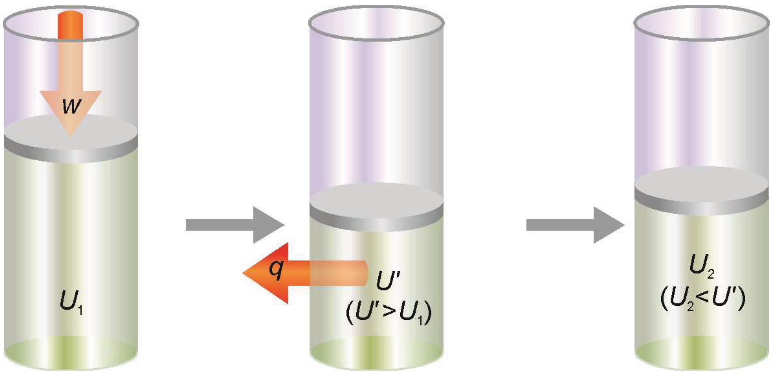


In such a case where the heat supplied to the system has caused some change in the internal energy and produced some work, we can write the following expression,

$$q = \Delta U + (-w) \qquad \dots (2.7)$$

This can be rearranged to get Eq. (2.6); $\Delta U = q + w$

Case II: We do certain amount of work (+w) on the system having internal energy, U_1, that increases its internal energy to U' and the system in turn transfers q amount of heat to the surroundings ($-q$) leading to decrease in the internal energy to U_2.

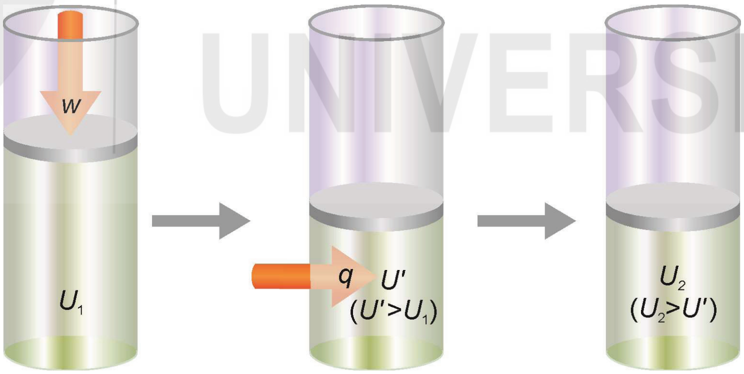


In such a case where the work done on the system has caused some change in the internal energy and produced some heat in the surrounding, we can write the following expression,

$$w = \Delta U + (-q) \qquad \ldots (2.8)$$

This again can be rearranged to Eq. (2.6); $\Delta U = q + w$

Case III: The third possibility is that we do certain amount of work (+w) on the system having internal energy, U_1, that increases its internal energy to U' and also transfer certain amount of heat (+q) to the system which increase the internal energy to U_2.



In such a case where the heat supplied to the system and the work done on the system cause change in the internal energy, we can write the following expression,

$$\Delta U = q + w \qquad \ldots (2.9)$$

Which is same as Eq. (2.6). We find that in all the three cases we get the identical expression for the change in the internal energy of the system. *This is the mathematical expressions for the first law of thermodynamics.* You must keep in mind that in this expression the q and w are inclusive of their signs. Let us take up a simple example to see the application of the mathematical expression for the first law of thermodynamics.

Example 2.1:380 J of heat was supplied to a thermodynamic system and its internal energy decreased by 72 J. Was any work destroyed in the surroundings?

If the surroundings do some work on the system we say that the work is destroyed in the surroundings.

Solution: As per the Eq. (2.6), we can write,

$$\Delta U = q + w$$

The amount of energy supplied to the system as heat, $q = 380$ J

The change in the internal energy, $\Delta U = -72$ J

Substituting in the Eq. (2.6) we get, $-72 \text{ J} = 380 \text{ J} + w$

Solving we get,

$$w = -452 \text{ J}$$

⇨ The work comes out to be negative implying that the **system** has done work on the surroundings. Thus, no work was destroyed in the surroundings.

For infinitisimal (very small) changes in state in which a small amount of heat dq is added to the system, the system does a small amount of work $-\mathrm{d}w$, and its internal energy changes by an amount $\mathrm{d}U$ we can write,

$$\mathrm{d}U = dq + (-dw) \qquad \dots (2.10)$$

dq and dw are often written as ∂q and ∂w or as đq and đw so as to emphasise the fact that these are inexact differentials as these depend on the path.

Now, suppose a system goes from state1 to state 2 in a number of small steps each associated with an infinitisimal change in heat, work and internal energy ($\mathrm{d}q$, $\mathrm{d}w$ and $\mathrm{d}U$ respectively),the overall changes for the process can be obtained by integrating the step wise changes. When we do so the following results are obtained,

$$\int \mathrm{d}w = w \qquad \dots (2.11)$$

$$\int \mathrm{d}q = q \qquad \dots (2.12)$$

$$\int \mathrm{d}U = \Delta U \qquad \dots (2.13)$$

That is, when dw and dq are integrated, the result is the absolute amountof work,w and heat,$q$respectively for the process, however when dU is integrated, the result isnot the absolute value of internal energy, U but the change in it i.e., ΔU, for the process. This is an important consequence of the fact that the internal energy is a state function whereas heat and work are path functions.Please answer the following self assessement question to assess your understanding of the first law of thermodynamics.

SAQ 1

416 J of heat was supplied to a system and its internal energy was found to have increased by 268 J, Was any work associated with the system? Determine the type and magnitude of the work involved.

2.3 HEAT CHANGES AT CONSTANT VOLUME

The heat change accompanying a process can be measured in terms of the change in the temperature of the system. The heat change in such a case would equal the product of the mass (m) of the system, its heat capacity (C) and the change in temperature ΔT i.e.,

$$q = m \times C \times \Delta T \qquad \dots (2.14)$$

This equation is valid for systems of any size, however, we generally deal with systems having 1 mole of the substance and the heat capacity as $\bar{C}_V$, molar heat capacity, which is an intensive property and has the units of $JK^{-1}mol^{-1}$.

A process occurring under the conditions of constant volume can be represented as:

$$\text{State 1 } (V_1, T_1) \rightarrow \text{State 2 } (V_1, T_2)$$

And the heat change accompanying it can be given as:

q_V or dq_V (*for infinitesimal change*)

We know that as per the First Law of thermodynamics, we have

$$dU = dq + dw \qquad \dots (2.15)$$

under the conditions of constant volume, the term, d*w* is equal to zero and we can write,

$$dU = dq_V \qquad \dots (2.16)$$

This implies that *all the heat supplied to the system at constant volume goes to increase its internal energy.*

Once again, from the first law of thermodynamics, we can write

$$dq_V = dU + pdV \qquad \dots (2.17)$$

Where $p\Delta V$ is the work involved in the process. Dividing both sides by dT we get,

$$\frac{dq_v}{dT} = \frac{dU + pdV}{dT} \qquad \dots (2.18)$$

At constant volume, d*V* = 0,i.e., there is no work of expansion, so we get

$$\left(\frac{dq_v}{dT}\right)_V = \left(\frac{dU}{dT}\right)_V \qquad \dots (2.19)$$

The term on the left hand side of Eq. (2.19)is the heat capacity at constant volume therefore we can write,

$$C_v = \left(\frac{dU}{dT}\right)_V \qquad \dots (2.20)$$

The subscript, v specifies that the volume is constant for the system. This equation *relates the rate of change of internal energy of the system with temperature under conditions of constant volume with the heat capacity*-a measurable quantity. Rearranging Eq. (2.20), we get

$$dU = C_v dT \qquad \dots (2.21)$$

We can integrate this equation for infinitesimal changes to obtain the change in internal energy for a finite change in temperature at constant volume.

$$\Delta U_V = \int_{T_1}^{T_2} C_V \, dT \qquad \ldots(2.22)$$

The heat capacity of most substances does not change much over short ranges of temperature.

For a small range of temperature, the heat capacity at constant volume is constant therefore we can take C_V out of the integral symbol and write,

$$\Delta U_V = C_V \int_{T_1}^{T_2} dT \qquad \ldots(2.23)$$

Integrating and applying limits

$$\Delta U_V = C_V [T]_{T_1}^{T_2} \qquad \ldots(2.24)$$

$$\Delta U_V = C_V [T_2 - T_1] = C_V \Delta T \qquad \ldots(2.25)$$

We showed above, that $\Delta U_V = q_V$, Eq. (2.16) therefore we can write,

$$q_V = C_V \Delta T \qquad \ldots(2.26)$$

$$\Rightarrow C_V = q_V / \Delta T \qquad \ldots(2.27)$$

This relation forms the basis for a simple method for the measurement of the heat capacity of a sample. In this method we transfer a measured quantity of energy as heat to the sample and note the change (increase) in the temperature of the system. The data is then used to compute the heat capacity of the sample under constant volume conditions. Let us take an example to understand it better.

Example 2.2 : A certain amount an organic compound was combusted in a bomb calorimeter of fixed volume having a heat capacity of 3.80 kJ K^{-1}. The temperature of the calorimeter increased from 22.70 °C to 26.10 °C. Calculate the amount of heat generated by the reaction.

You would learn about bomb calorimetry in Unit 3

Solution: As the reaction has occurred under the conditions of constant volume, we need to find q_V and as per Eq. (2.26), $q_V = C_V \Delta T$

Given: $C_V = 3.80 \text{ kJ K}^{-1}$ and ΔT= (22.70 – 26.10) = 3.40 °C = 3.40 K

Substituting in the expression for q_V ,

$$q_V = 3.80 \text{ kJ K}^{-1} \times 3.40 \text{ K} = 12.92 \text{ kJ}$$

⇨ Thus, the amount of heat generated by the reaction = 12.92 kJ

In the next unit you would be learning in details about such experiments on Calorimetry.

Let us now take up the heat changes accompanying the thermodynamic processes occurring under the conditions of constant pressure.

2.4 HEAT CHANGES AT CONSTANT PRESSURE: ENTHALPY

We had shown above that the heat transferred to a system under the conditions of constant volume (i.e., when there is no work of expansion) goes to increase the internal energy of the system. However, most of the chemical reactions are carried out under the conditions of atmospheric pressure or in other words at constant pressure. In such a situation, the system can change the volume i.e., it may expand. In such a process part of the energy given to the system goes back to the surroundings as work of expansion. This implies that a part of the energy supplied as heat at constant pressure, q_P,goes to increase the internal energy and rest comes back to the surroundings as PdV. We can, therefore, write,

Thus, in the process of relating the heat changes accompanying a process occurring under the conditions of constant pressure we have got a new thermodynamic property, enthalpy, H.

$$q_P = \Delta U_p + p\,\Delta V \qquad \text{…(2.28)}$$

$$\Delta U_p = q_P - p\,\Delta V \qquad \text{…(2.29)}$$

The thermodynamic process (state 1 → state 2) occurring under the conditions of constant pressure can be represented as

$$(p,\ V_1,\ T_1) \rightarrow (p, V_2, T_2)$$

The corresponding values of the internal energy would be U_1 and U_2 respectively; the Eq. (2.29) can be rewritten as

You may note here that as we cannot know the absolute value of internal energy of a system we cannot know its absolute enthalpy also. We can only measure the change in enthalpy and fortunately, for most of the processes we only need the changes in enthalpy.

$$U_2 - U_1 = q_p - p(V_2 - V_1) \qquad \text{…(2.30)}$$

The equation can be rearranged to

$$q_p = [U_2 + pV_2] - [U_1 + pV_1] \qquad \text{…(2.31)}$$

The terms given in the brackets of Eq. (2.31) consist of combination of state functions (U, p and V) therefore this combination also represents a state function. This new state function is called **enthalpy**, denoted as H, and is defined as

$$H = U + pV \qquad \text{…(2.32)}$$

The Eq. (2.31) can then be rewritten as

$$q_p = H_2 - H_1 = \Delta H \qquad \text{…(2.33)}$$

This implies that *the heat withdrawn from the surroundings in a process at constant pressure is equal to the change in enthalpy of the system if only work involved is pressure-volume work.*

If the pV work is the only kind of work, then the heat change accompanying a reaction in a constant-pressure calorimeter can be visualised as a measure of the decrease in enthalpy of the system.

For an infinitesimal change, we can write,

$$\mathrm{d}q_p = dH \qquad \text{…(2.34)}$$

From first law of thermodynamics we can write,

$$\mathrm{d}q = \mathrm{d}U + p\ \mathrm{d}V \qquad \text{…(2.17)}$$

Dividing both sides by dT we get,

$$\frac{dq}{dT} = \frac{dU + pdV}{dT} \quad \ldots(2.35)$$

At constant pressure, we get

$$\left(\frac{dq}{dT}\right)_p = \left(\frac{dU}{dT}\right)_p + p\left(\frac{dV}{dT}\right)_p \quad \ldots(2.36)$$

As mentioned above, generally the heat changes accompanying a chemical reaction are measured under the conditions of constant pressure i.e., we get the change in the enthalpy of the reaction. This can then be used to compute the change in internal energy with the help of the following equation.

$\Delta U = \Delta H - P\Delta V$

We defined enthalpy as, $H = U + pV$

Differentiating it with respect to T at constant pressure we get,

$$\left(\frac{dH}{dT}\right)_p = \left(\frac{dU}{dT}\right)_p + p\left(\frac{dV}{dT}\right)_p \quad \ldots(2.37)$$

Equating Eq.(2.36) and Eq.(2.37) we get,

$$\left(\frac{dq}{dT}\right)_p = \left(\frac{dH}{dT}\right)_p \quad \ldots(2.38)$$

The expression on the left hand side represents, C_P, heat capacity at constant pressure, we can write,

$$C_P = \left(\frac{dH}{dT}\right)_p \quad \ldots(2.39)$$

The subscript, *p* specifies that the pressure in the process is constant. This equation *relates the rate of change of enthalpy of the system with temperature under conditions of constant pressure with the heat capacity*-a measurable quantity.

This equation is valid for systems of any size, however, we generally deal with systems having 1 mole of the substance and the heat capacity as $\bar{C}_P$, molar heat capacity, which is an intensive property and has the units of $JK^{-1}mol^{-1}$.

Rearranging the equation, we can write,

$$dH = C_p dT \quad \ldots(2.40)$$

We can integrate this equation for infinitesimal change to obtain the change in enthalpy for a finite change in temperature at constant pressure.

$$\Delta H = \int_{T_1}^{T_2} C_p \, dT \quad \ldots(2.41)$$

For a small range of temperature, the heat capacity at constant pressure is constant therefore take C_p out of the integral symbol and write,

The heat capacity of most substances does not change much over short ranges of temperature.

$$\Delta H = C_p \int_{T_1}^{T_2} dT \quad \ldots(2.42)$$

Integrating,

$$\Delta H = C_p[\,T]_{T_1}^{T_2} \quad \ldots(2.43)$$

$$\Delta H = C_p[T_2 - T_1] = C_p \Delta T \quad \ldots(2.44)$$

As an increase in enthalpy can be equated with the energy supplied as heat under the conditions of constant pressure, we can write,

$$\Delta H = q_p = C_p \Delta T \qquad \text{…(2.45)}$$

This expression (Eq. 2.45) provides us a method to measure the heat capacity of a sample. For this we supply a measured quantity of energy as heat to the system under conditions of constant pressure and measure the rise in temperature. Having learnt about the heat changes under the conditions of constant volume and constant pressure respectively and relating them to the state functions, let us now try to establish the relationship between two types of heat capacities.

Relationship between C_p and C_V

We know that, $C_p = \left(\frac{\mathrm{d}H}{\mathrm{d}T}\right)_p$ and $C_V = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right)_V$

Also, $H = U + pV$ …(2.32)

For 1 mole of an ideal gas $pV = RT$

$$\Rightarrow \quad H = U + RT \qquad \text{…(2.46)}$$

Differentiating the expression w.r.t. T we get,

$$\left(\frac{\mathrm{d}H}{\mathrm{d}T}\right) = \left(\frac{\mathrm{d}U}{\mathrm{d}T}\right) + R \qquad \text{…(2.47)}$$

$$\Rightarrow \quad C_p = C_V + R \qquad \text{…(2.48)}$$

$$\Rightarrow \quad C_p - C_V = R \qquad \text{…(2.49)}$$

Therefore, for ideal gas the value of C_p is greater than C_V by R, the gas constant. You have so far learnt about the first law of thermodynamics, its significance and two very important state functions viz., internal energy and enthalpy. Let us now try to apply the first law to understand the behaviour of gases. We would be taking up the calculation of the work for the gases undergoing expansion under isothermal and adiabatic conditions. We begin with the isothermal expansion of gases. However, before moving ahead solve the following self assessment questions.

SAQ 2

Define enthalpy and give its significance.

SAQ 3

Calculate the amount of heat required to increase the temperature of 1.00 mole of argon from a temperature of 100 K to 900 K in

a) an isobaric process and

b) in a isochoric process.

(Given: $C_{V,\mathrm{m}}$= 12.47 J $\mathrm{K^{-1} mol^{-1}}$ and $C_{p,\mathrm{m}}$ = 20.78 J $\mathrm{K^{-1} mol^{-1}}$)

2.5 WORK OF EXPANSION

You know that the gases expand if the external pressure on them is lower than their own pressure. As the system alters its volume against an opposing pressure, it produces work in the surroundings; we say the system has done work. If however, the external pressure is more than the gas pressure the surroundings would perform work on the system and its volume would decrease, the process would be called **compression**. We would focus our attention on the work associated with the expansion of gases under isothermal and adiabatic conditions.

2.5.1 Isothermal Expansion

You have learnt in Unit 1 that an isothermal process is the one in which there is no change in the temperature of the system. You have also learnt that the thermodynamic processes could be reversible or irreversible depending on how do we perform it. It is advisable that you revisit Section 1.5 of Unit 1 where we have discussed about reversible and irreversible thermodynamic processes. Here, we would derive expressions for work obtained respectively in irreversible and reversible isothermal expansion of an ideal gas.

Irreversible Isothermal Expansion

Let us take a thermodynamic system consisting of a sample of ideal gas contained in a cylinder fitted with frictionless and massless piston of a cross-section area Am^2; and a mass of 1 kg is placed on the piston. Since we wish to perform the expansion under isothermal conditions, we immerse the cylinder in a thermostat to keep the temperature of the system constant throughout the process, Fig. 2.5 (a). The gas occupies a volume V_1 at an initial pressure equal to the atmospheric pressure and the pressure exerted by the mass on the piston; we call this pressure p_1. The thermodynamic state of the system would be given as (p_1, V_1, T).

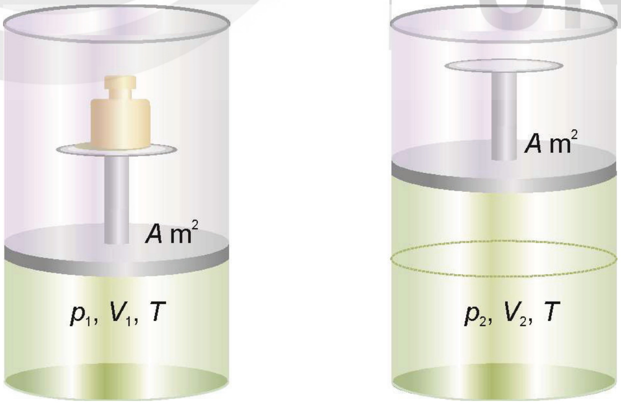


Fig. 2.5: Experimental design for isothermal irreversible expansion of a gas.

Let's now remove the 1 kg mass from the piston; the pressure reduces and becomes equal to the atmospheric pressure; let's call it p_2. The gas would expand to volume V_2 against the opposing pressure p_2; the new state of the system would be (p_2, V_2, T). The expansion of the gas would produce work produce work in the surroundings (work is done by the system) and is given as

$$\text{Work} = w_1 = -\,p_2(V_2 - V_1) \qquad \ldots(2.50)$$

This is the expression if the irreversible expansion happens in a single step. Let's ask if we perform the same expansion in two steps, what would be the work? Let's see!

Irreversible Isothermal Expansion in Two Steps

Let us take the same system again at state-1(p_1, V_1, T) however, we place the mass of 1 kg in terms of two masses of 500 g each as shown in Fig. (2.6).

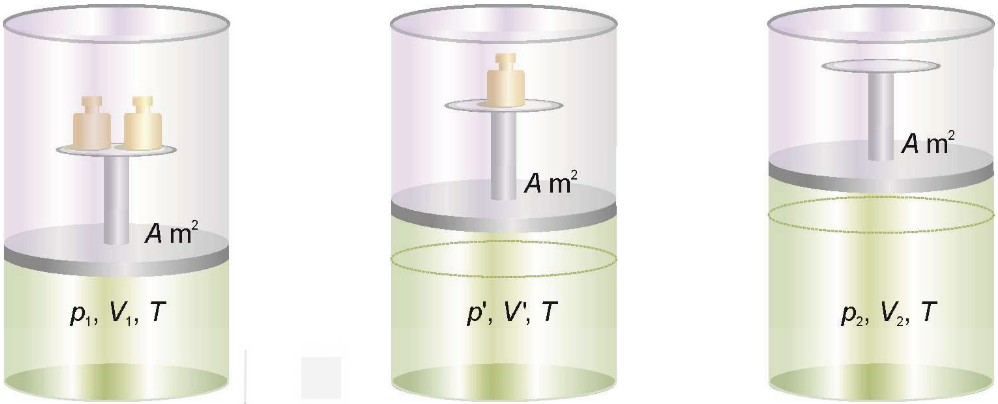


Fig. 2.6: Experimental design for isothermal irreversible expansion of a gas in a two-step process.

Let's now remove one of the 500 g masses from the piston; the pressure reduces to be equal to the atmospheric pressure plus that exerted by the 500 g mass; let's call it $p\,'$. The gas would expand to volume $V\,'$ against the opposing pressure $p\,'$ the new state of the system would be (p', $V\,'$, T). The expansion of the gas would produce work in the surroundings and is given as

$$w\,' \quad = -\,p'(V\,'-V_1) \qquad \text{…(2.51)}$$

Now when we remove the second 500 g mass from the piston; the pressure reduces to be equal to the atmospheric pressure; let's again call it p_2. The gas would expand to volume V_2 against the opposing pressure $p_{2;}$ the new state of the system would be (p_2, V_2, T). The expansion of the gas would again produce work in the surroundings and is given as

$$= w\,'' = -\,p_2(V_2-V\,') \qquad \text{…(2.52)}$$

The total work done by the system would be

$$=w' + w'' = -\,p'(V'-V_1)+ [-p_2(V_2-V') \,] \qquad \text{…(2.53)}$$

This work would be more than that obtained in the single step process. Can you think how? It is so because in the single step process the expansion was against pressure p_2 whereas in the two step process about half of the expansion was against the pressure p_2 and the rest was against a pressure $p\,'$ which is greater than $p_{2.}$ You may note that the overall change in the volume is same as in single step process.

Reversible Isothermal Expansion

You would recall from section 1.4 that a thermodynamic reversible process is the one, which occurs, in an infinite number of infinitesimally small steps. Let us workout an expression for the work done in a reversible expansion occurring under isothermal conditions. In order to do so we need to design a yet another experiment; we take the same system at state (p_1, V_1, T) as before and perform the expansion to volume V_2 in such a way that we slowly vary the opposing pressure created by the mass on the piston. We start with the external pressure, to be infinitesimally smaller than the pressure p_1 of the gas i.e., (p_1−dp). The gas expands to a volume (V_1+ dV_1) while the temperature remains T. The process for the first step of the expansion can be given as

$$(p_1, V_1, T) \rightarrow (p_1 - \mathrm{d}p, V_1 + \mathrm{d}V_1, T)$$

The infinitesimal amount of work obtained would be

$$= \mathrm{d}w' = -(p_1 - \mathrm{d}p)(V_1 + \mathrm{d}V_1 - V_1) \qquad \ldots(2.54)$$

$$=> -(p_1 - \mathrm{d}p)\,\mathrm{d}V_1 \qquad \ldots(2.55)$$

Once the equilibrium is achieved after expansion, we decrease the pressure infinitesimally again to let the gas expand to volume V'' and continue doing the same till the volume of the gas becomes V_2. Expressions similar to Eq. (2.55) would represent work done by the system in each successive step. The generalised expression for the work done by the system in an infinitesimal expansion can be given as follows.

$$\mathrm{d}w = -(p - \mathrm{d}p)\,\mathrm{d}V \qquad \ldots(2.56)$$

For a large number of steps, the work obtained from each step can be added to get the overall work.

$$w = \sum \mathrm{d}w = \sum [-(p - \mathrm{d}p)\,\mathrm{d}V] \qquad \ldots(2.57)$$

As each successive step happens to be infinitesimally small and number of steps is infinite, we can replace summation by integral and the expression for work becomes,

$$w = \int_{V_1}^{V_2} \mathrm{d}w = -\int_{V_1}^{V_2} (p - \mathrm{d}p)\,\mathrm{d}V \qquad \ldots(2.58)$$

$$w = -\int_{V_1}^{V_2} (p\mathrm{d}V - \mathrm{d}p\mathrm{d}V) \qquad \ldots(2.59)$$

Where, V_1 and V_2 are the initial and final volumes. Further, the second term in the bracket is much smaller than the first term and can be ignored. We get,

$$w = -\int_{V_1}^{V_2} (p\mathrm{d}V) \qquad \ldots(2.60)$$

Since this work is obtained in an infinite number of steps we call this work to be the maximum possible work that can be obtained from an expansion process. We can then write,

$$w_{\max} = -\int_{V_1}^{V_2} (p\mathrm{d}V) \qquad \ldots(2.61)$$

What we have just obtained is an expression for computing the maximum possible work of expansion for a given sample of gas. Let us get a little more specific and formulate the expression for the expansion of a sample of an ideal gas occurring at a constant temperature (isothermally).

We have shown that the work done by the system in two steps is more than that obtained in the same expansion performed in a single step. We can extend the argument and show that more the number of steps more the work. For infinite number of steps the work is maximum.

We know from the ideal gas equation that for n moles of an ideal gas, at a temperature *T*, the pressure can be given as

$$p = \frac{nRT}{V} \qquad \ldots(2.62)$$

Substituting in the Eq. (2.61) we get,

$$w_{\max} = -\int_{V_1}^{V_2} \frac{nRT}{V}\,\mathrm{d}V \qquad \ldots(2.63)$$

On simplifying, at constant temperature

$$w_{\max} = -nRT\int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} \qquad \ldots(2.64)$$

Integrating and applying limits, we get,

$$w_{\max} = -nRT\ln\frac{V_2}{V_1} \qquad \ldots(2.65)$$

$$w_{\max} = -2.303\,nRT\log\frac{V_2}{V_1} \qquad \ldots(2.66)$$

We know that for 1 mole of an ideal gas

$$p_1V_1 = p_2V_2 \Rightarrow \frac{V_2}{V_1} = \frac{p_1}{p_2} \qquad \ldots(2.67)$$

Substituting in Eq. (2.66), we get,

$$w_{\max} = -2.303\,nRT\log\frac{p_1}{p_2} \qquad \ldots(2.68)$$

The equations 2.66 and 2.68 are important expressions that can be used to compute the maximum amount of work that can be obtained from the isothermal expansion of an ideal gas. Let us take an example to see their applicability.

Here, In represents the natural logarithm or log to the base e. and log represents log to the base 10.

In X = 2.303 log X

(this can be worked out by using base changing formula for logs)

$\log_B A = \log_C A \times \log_B C$

$\log_e A = \log_{10} A \times \log_e 10$

$\ln A = \log_{10} A \times 2.303$

Example 2.3: 0.40 moles of argon behaving as an ideal gas is made to expand from a volume of 7.50 dm^3 to 11.25 dm^3 at 27 °C. What is the maximum work that can be obtained from this expansion?

Solution: As per the Eq. (2.66), the maximum work of expansion of an ideal gas is given as

$$w_{\max} = -2.303\,nRT\log\frac{V_2}{V_1}$$

The data given is as under:

$n = 0.4$ mol $\quad V_1 = 7.50$ dm^3 $\quad V_2 = 11.25$ dm^3

T = 273.15 + 27 = 300.15 K

Substituting the values in the expression, we get

$$w_{\max} = -2.303 \times 0.40\,\text{mol} \times 8.314\,\text{J K}^{-1}\text{mol}^{-1} \times 300.15\,\text{K} \times \log\frac{11.25}{7.5} = -404.82\,\text{J}$$

⇒ Thus a maximum work equal to 404.82 J can be done by the system on the surroundings

Having learnt about the isothermal expansion of ideal gases under different conditions let us take up adiabatic expansion, however before that answer the following simple question to gauge your understanding and applications of these expressions.

SAQ 4

One mole of an ideal gas at 25ºC is allowed to expand reversibly at constant temperature from a volume of 10 dm^3 to 20 dm^3. Calculate the work done by the gas.

2.5.2 Adiabatic Expansion

As you know, an adiabatic process is the one in which no heat can either enter or leave the system. As dq=0, the first law expression for such a case can be written as

$$\mathrm{d}U = \mathrm{d}w_{adi.} \qquad \dots (2.69)$$

For a sample of a gas at pressure p and a volume V, if there is an infinitesimal increase in the volume dV at pressure p, the work done by the gas would be $-p\mathrm{d}V$ and the corresponding decrease in the internal energy would be dU.If the work happens to be only the work of expansion the expression becomes

$$\mathrm{d}U = -p\mathrm{d}V \qquad \dots(2.70)$$

If the system expands adiabatically, dV is positive and therefore, dU is negative. This implies that as no energy enters the system as heat, the work done in the adiabatic process is at the expense of the internal energy. The decrease in internal energy means that the kinetic energy of the molecules fall, i.e., their average speed decreases, and hence the temperature falls. The relationship applies to any adiabatic process, reversible or irreversible, if only work of expansion is involved.

Thus, we can say qualitatively that a change in the volume of a gas against a non-zero opposing pressure, under adiabatic conditions causes change in its temperature. The question arises how are the temperature and volume related for an adiabatic expansion? How can we calculate the change in the temperature of the system? In order to do so we need to establish a relationship between the temperature and volume of the system for an adiabatic process.

Relationship between the Temperature and Volume for an Adiabatic Process

Let us work out the relationship between the temperature and volume for an adiabatic process.

We know that $\mathrm{d}U = C_V \mathrm{d}T$ …(2.21)

Equating the Eq. (2.70) and (2.21) we can write

$$C_V \mathrm{d}T = -p\, \mathrm{d}V \qquad \text{…(2.71)}$$

For an ideal gas we can write, $p = nRT/V$, we get

$$C_V \mathrm{d}T = -\frac{nRT}{V}\mathrm{d}V \qquad \text{…(2.72)}$$

Rearranging,

$$\frac{C_V \mathrm{d}T}{T} = -\frac{nR\mathrm{d}V}{V} \qquad \text{…(2.73)}$$

For the adiabatic change $[(V_1, T_1) \rightarrow (V_2, T_2)]$, and assuming that C_V is constant for the range of temperature we can integrate Eq. (2.67) to get,

$$C_V \int_{T_1}^{T_2} \frac{\mathrm{d}T}{T} = -nR \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V} \qquad \text{…(2.74)}$$

$$C_V \ln \frac{T_2}{T_1} = -nR \ln \frac{V_2}{V_1} \qquad \text{…(2.75)}$$

On rearranging,

$$\frac{C_V}{nR} \ln \frac{T_2}{T_1} = -\ln \frac{V_2}{V_2} = \ln \frac{V_1}{V_2} \qquad \text{…(2.76)}$$

Using the property of logarithm, we get

$$\ln\left(\frac{T_2}{T_1}\right)^{\frac{C_V}{nR}} = \ln \frac{V_1}{V_2} \qquad \text{…(2.77)}$$

Taking antilogarithms on both the sides

$$\left(\frac{T_2}{T_1}\right)^{\frac{C_V}{nR}} = \frac{V_1}{V_2} \qquad \text{…(2.78)}$$

$$\Rightarrow \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{nR/C_V} \qquad \text{…(2.79)}$$

Substituting $n = 1$ and $R = C_p - C_V$; we get,

$$\Rightarrow \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\frac{C_p - C_V}{C_V}} \qquad \text{…(2.80)}$$

$$\Rightarrow \qquad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \ldots(2.81)$$

where, $\gamma = \frac{C_p}{C_V}$

Rearranging, we get

$$\Rightarrow \qquad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1} \text{or } TV^{\gamma-1} = \text{constant} \qquad \ldots(2.82)$$

This gives the relationship between volume and temperature for a reversible adiabatic process.

Relationship between the Temperature and Pressure for Adiabatic expansion

In order to get the relationship between temperature and pressure for an adiabatic expansion process we recall the ideal gas equation for 1 mol, viz.,

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2} \quad => \quad \frac{V_1}{V_2} = \frac{p_2T_1}{p_1T_2} \qquad \ldots(2.83)$$

and substitute it into the Eq. (2.81), $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

$$\Rightarrow \qquad \frac{T_2}{T_1} = \left(\frac{p_2T_1}{p_1T_2}\right)^{\gamma-1} \qquad \ldots(2.84)$$

$$\Rightarrow \qquad \frac{T_2}{T_1} = \left(\frac{p_2}{p_1}\right)^{\gamma-1}\left(\frac{T_1}{T_2}\right)^{\gamma-1} \qquad \ldots(2.85)$$

$$\Rightarrow \qquad \frac{T_2}{T_1}\left(\frac{T_2}{T_1}\right)^{\gamma-1} = \left(\frac{p_2}{p_1}\right)^{\gamma-1} \qquad \ldots(2.86)$$

$$\Rightarrow \qquad \left(\frac{T_2}{T_1}\right)^{\gamma} = \left(\frac{p_2}{p_1}\right)^{\gamma-1} \qquad \ldots(2.87)$$

$$\Rightarrow \qquad \left(\frac{T_2}{T_1}\right) = \left(\frac{p_1}{p_2}\right)^{\frac{1-\gamma}{\gamma}} \qquad \ldots(2.88)$$

$$=> \qquad T_1p_1^{\frac{1-\gamma}{\gamma}} = T_2p_2^{\frac{1-\gamma}{\gamma}} \qquad \ldots(2.89)$$

It is the desired equation relating temperature and pressure for an adiabatic expansion process.

Relationship between the Pressure and Volume for Adiabatic Expansion

In order to get the relationship between the pressure and volume, we rearrange the gas equation,

$$\frac{T_2}{T_1} = \frac{p_2 V_2}{p_1 V_1} \qquad \ldots(2.90)$$

and substitute into the temperature-volume relationship, Eq.(2.81)

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

$$\Rightarrow \qquad \left(\frac{T_2}{T_1}\right) = \left(\frac{p_2 V_2}{p_1 V_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \qquad \ldots(2.91)$$

The expression can be rearranged as

$$\Rightarrow \qquad \left(\frac{p_2}{p_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma-1}\left(\frac{V_1}{V_2}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma} \qquad \ldots(2.92)$$

$$\Rightarrow \qquad \left(\frac{p_2}{p_1}\right) = \left(\frac{V_1}{V_2}\right)^{\gamma} \Rightarrow p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \qquad \ldots(2.93)$$

It is the desired equation relating pressure and volume for an adiabatic expansion process. We can summarise the relationships between the pairs of thermodynamic properties for reversible adiabatic expansion processes as

$$=> \qquad p_1 V_1^{\gamma} = p_2 V_2^{\gamma} \qquad \ldots(2.93)$$

$$=> \qquad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1} \qquad \ldots(2.82)$$

$$=> \qquad T_1 p_1^{\frac{1-\gamma}{\gamma}} = T_2 p_2^{\frac{1-\gamma}{\gamma}} \qquad \ldots(2.89)$$

Having learnt about the relationship between different thermodynamic properties for adiabatic expansion solve the follwing SAQ.

SAQ 5

2.00 moles of an ideal monoatomic gas, undergo adiabatic reversible expansion from a volume of 22.4 dm^3 to double its volume at 0 ^{o}C. Calculate the final temperature and pressure of the gas.
[Given: $C_{v,m}$= 12.47 J K^{-1}mol^{-1}]

2.6 SUMMARY

In this unit we discussed about the First law of thermodynamics. In order to understand the law we introduced the concept of internal energy and developed the relationships between heat, work and internal energy. We rationalised the effect of heat and work on the system in terms of the changes in the internal energy. In the process we developed the mathematical expression for the first law of thermodynamics and also emphasised that while heat and work are path functions, the internal energy is a state function. The application and the significance of the expression was clarified with the help of examples.

This was followed by discussion on the heat changes under constant volume conditions and realised the heat change accompanying a process under constant volume is related to the change in internal energy of the system. While discussing heat changes under constant pressure conditions we introduced the concept of enthalpy - a thermodynamic quantity equivalent to the total heat content of a system. It is defined as the internal energy of the system plus the product of pressure and volume. It is a state function whose change is equal to the heat withdrawn from the surroundings in a process at constant pressure.

This was followed by the derivation of mathematical expressions for isothermal irreversible and reversible expansion of an ideal gas. In this context we derived expressions for isothermal expansion in one, two and infinite number of steps. The importance of these expressions was clarified with examples. Towards the end of the unit we formulated relationships between different state variables for ideal gas undergoing adiabatic expansion.

2.7 TERMINAL QUESTIONS

1. Give different statements of the First Law of thermodynamics.
2. Formulate the mathematical expression for the First law of thermodynamics.
3. A sample of an ideal gas expands from an initial volume of 5.00 dm^3 to 20.00 dm^3 against an opposing pressure of 1 bar. In addition, 800 J of heat is also transferred to the system. Calculate the change in the internal energy of the system.
4. Define state and path functions and give suitable examples for the same.
5. Show that the heat absorbed by a system at constant volume is equal to increase in internal energy of the system
6. 1.50 moles of gas behaving ideally at a pressure of 4 bar and temperature of 300 K undergo isothermal expansion against a constant pressure of 1 bar. How much of the work is done by the gas?
7. Calculate the work done for the following processes on a sample of 0.500 mole of nitrogen gas occupying a volume of 5.00 dm^3 at 298 K

   a) Expansion to 10.00 dm^3 against a constant pressure of 1 bar

   b) Isothermal reversible expansion to 10.00 dm^3
8. 1.00 mole of helium gas at a temperature of 100 ^oC is made to undergo reversible adiabatic expansion from an initial volume of 4.00 dm^3 to 20.00 dm^3. Calculate the final temperature of the gas, assuming helium to behave ideally and has $C_{V,m}$ = 12. 47 J $K^{-1}mol^{-1}$

2.8 ANSWERS

Self-Assessment Questions

1. According to the First Law of thermodynamics, $\Delta U = q + w$

   The amount of energy supplied to the system as heat, $q = 416$ J

   The change in the internal energy, $\Delta U = 268$ J

   Substituting in the equation we get,

   $$268 \text{ J} = 416 \text{ J} + w$$

   Solving we get,

   $$w = -148 \text{ J}$$

   As the value for w is non-zero, some work is associated with the system. Further, as the work comes out to be negative, it implies that the system has done work on the surroundings.

2. The enthalpy is a thermodynamic quantity equivalent to the total heat content of a system. It is defined as $H = U + pV$, i.e., the internal energy of the system plus the product of pressure and volume. It is a state function whose change (ΔH) is equal to the heat withdrawn from the surroundings in a process at constant pressure, q_p.

3. a) We know that for isobaric process (occurring at constant pressure), the heat required to raise the temperature is, $q_p = nC_{p,m}\Delta T$.

   Given: $C_{p,m} = 20.78$ J K^{-1}mol^{-1}, n = 1.00 mol, $\Delta T = 900-100 = 800$K

   Substituting in the expression,

   $$q_p = 1.00\text{mol} \times 20.78\text{J K}^{-1}\text{mol}^{-1} \times 800\text{K} = 16{,}624\text{ J} = 16.624\text{kJ}$$

   b) Similarly, for isochoric process (occurring at constant volume), the heat required to raise the temperature is, $q_V = nC_{V,m}\Delta T$

   Given: $C_{V,m} = 12.47$ J K^{-1}mol^{-1}, n = 1.00 mole, $\Delta T = 900-100 = 800$K

   Substituting in the expression,

   $$q_V = 1.00\text{ mol} \times 12.47\text{ J K}^{-1}\text{mol}^{-1} \times 800\text{ K} = 9976\text{ J} = 9.976\text{ kJ}$$

4. The maximum work of expansion is given as

   $$w_{\max} = -2.303\, nRT \log\frac{V_2}{V_1}$$

   The data given is as under:

   n =1.0 mol $V_1 = 10.00$ dm^3 $V_2 = 20.00$ dm^3

   T = 273.15 + 25 = 298.15 K

Substituting the values in the expression, we get

$$w_{\max} = -2.303 \times 1.0\,\text{mol} \times 8.314\,\text{J K}^{-1}\text{mol}^{-1} \times 298.15\,\text{K} \times \log\frac{20}{10}$$

$$= -1718.32\,\text{J} = -1.718\,\text{kJ}.$$

⇨ Thus a maximum work equal to 1.718 kJ is done by the gas on the surroundings

5. The temperature and volume for a reversible adiabatic expansion of an ideal gas are related as

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$

To begin with we need to compute the value for, $\gamma = \frac{C_p}{C_V}$

For ideal gas, $C_p - C_V = R \Rightarrow C_p = R + C_V$

➔ $C_p = 8.314\ \text{J K}^{-1}\text{mol}^{-1} + 12.47\ \text{JK}^{-1}\text{mol}^{-1} = 20.784\ \text{JK}^{-1}\text{mol}^{-1}$

Substituting above we get,

$$\gamma = \frac{20.784}{12.47} = 1.667$$

Now we can compute, T_2, T_1 is given as 0˚C = 273.15 K

Rearranging Eq. (2.81), we get,

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

Substituting the values,

$$T_2 = 273.15\,\text{K}\left(\frac{44.8\ \text{dm}^3}{22.4\ \text{dm}^3}\right)^{1.667-1}$$

Solving, we get T_2 = 433.70 K

Now, in order to find the final pressure we can simply use the ideal gas equation.

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

Substituting the values, $p = \frac{1.00\,\text{mol} \times 8.314\,\text{J K}^{-1} \times 433.70\,\text{K}}{22.40\,\text{dm}^3}$

On solving, $p_2 = 166.97\ \text{J dm}^{-3} = 1.67$ bar

$\Rightarrow$ $1\ \text{bar dm}^3 = 10^2\ \text{J} \quad \because 1\,\text{bar} = 10^2\ \text{J dm}^{-3}$

Thus, the final temperature and pressure would be 433.70 K and 1.67 bar respectively.

Terminal Questions

1. The First law of thermodynamics can be stated in a number of ways, some of these are

   - The total energy of universe is constant.
   - It is not possible to construct a machine showing perpetual motion of the first kind. That is, a machine, which can work endlessly without the expenditure of energy.
   - The internal energy of an isolated system is constant.

2. The mathematical expression for the First Law of thermodynamics can be formulated by more than one equivalent ways. As per one of the ways suppose we transfer $+q$ amount of energy to the system as heat and if the system does w amount of work then we can write,

   $$q = \Delta U + (-w)$$

   This can be rearranged to give the mathematical expression for the first law as $\Delta U = q + w$

3. According to the first law of thermodynamics, $\Delta U = q + w$

   We are given $q = +\ 800$ J (positive sign indicates that the heat is supplied to the system)

   We need to calculate the work done

   The work of expansion against a constant opposing pressure is,

   $$w = -\ p_{op}\ \Delta V$$

   $p_{op} = 1$ bar, $\Delta V = V_2 - V_1 = 20.00 - 5.00 = 15\ \text{dm}^3$

   Substituting in the equation we get,

   $$w = -1.00\,\text{bar} \times 15\ \text{dm}^3 = -15\,\text{bar dm}^3$$

   $$= -1500\ \text{J} \qquad (\because 1\,\text{bar dm}^3 = 100\,\text{J})$$

   Substituting the values of heat and work in the expression for change in internal energy, we get,

   $$\Delta U = 800\ \text{J} + (-1500\ \text{J}) = -700\ \text{J}$$

   The internal energy of the system would decrease by 700 J

4. A state function is the one whose value depends on the state of the system irrespective of how it is achieved. On the other hand, the path functions are the ones whose value depends on the path followed during the thermodynamic process. Internal energy, enthalpy, pressure, and temperature are some of the examples of state functions whereas the heat change and work associated with the process are path functions.

5. As per the first law of thermodynamics,

$$dU = dq + dw$$

As the heat is transferred under the conditions of constant volume, the term, dw is equal to zero and we can write,

$$dU = dq_V$$

This represents infinitesimal change in internal energy. We can get the finite change in internal energy at constant volume by integrating the equation as

$$\Delta U_V = \int dU = \int dq_V = q_V$$
$$\Rightarrow \Delta U_V = q_V$$

Thus, the heat absorbed by a system at constant volume is equal to increase in internal energy of the system,

6. The work of expansion against a constant opposing pressure is given as

$$w = -p_{\text{ext.}}\,\Delta V$$

Given: $p_{\text{op}} = 1.00$ bar $n = 1.50$ mol $p_1 = 4.0$ bar $p_2 = 1.0$ bar

In order to get the value of ΔV, we take the help of the ideal gas equation, $V = nRT/p$

$$\Delta V = V_2 - V_1 = \left(\frac{nRT}{p_2} - \frac{nRT}{p_1}\right) = nRT\left(\frac{1}{p_2} - \frac{1}{p_1}\right)$$

Substituting in the expression for w,

$$w = -p_{ext}.\,\Delta V \qquad = -p_{ext}.nRT\left(\frac{1}{p_2} - \frac{1}{p_1}\right)$$

$$= -1.00 \text{ bar} \times 1.50 \text{ mol} \times 8.314 \text{ J K}^{-1}\text{mol}^{-1} \times 300\text{K} \times \left(\frac{1}{1} - \frac{1}{4}\right)\text{bar}^{-1}$$

On solving, we get

w= + 2806 J = 2.806 kJ

Thus, a work equal to 2.806 kJ would be done by the system.

7. a) The work of expansion against a constant opposing pressure,

$$w = -p_{\text{ext.}}\,\Delta V$$

Given: $p_{\text{op}} = 1.00$ bar $n = 0.50$ mol $V_1 = 5.00\text{ dm}^3$ $V_2 = 10.00\text{ dm}^3$

Substituting in the expression for w,

$$w = -P_{ext}.\Delta V = -1.00\,\text{bar} \times (10.00\,\text{dm}^3 - 5.00\,\text{dm}^3)$$

$$= -5.00\text{ bar dm}^3$$

$= -500$ J ($\because 1.00\text{ bar dm}^3 = 100$ J)

c) The work of isothermal reversible expansion is given as

$$w_{\text{Re}v} = -2.303\, nRT \log\frac{V_2}{V_1}$$

Given: n= 0.50 mol V_1 = 5.00 dm^3 V_2 = 10.00 dm^3 T= 298 K

Substituting in the expression for w,

$$w_{\max} = -2.303 \times 0.50\,\text{mol} \times 8.314\ \text{J}\,\text{K}^{-1}\text{mol}^{-1} \times 298\,\text{K} \times \log\frac{10.00}{5.00}$$

On solving, we get w= − 858.73 J

Thus a work equal to 0.859 kJ would be done by the system.

8. We know that the temperature and volume for a reversible adiabatic expansion of an ideal gas are related as,

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

To begin with we need to compute the value for,

$$\gamma = \frac{C_p}{C_V}$$

For ideal gas, $C_p - C_\text{V} = R \Rightarrow C_p = R + C_\text{V}$

C_p = 8.314 J K^{-1}mol^{-1} + 12. 47 J K^{-1}mol^{-1} = 20.784 J K^{-1}mol^{-1}

Substituting above we get, $\gamma = \frac{20.784}{12.47} = 1.667$

Now we can compute, T_2, T_1 is given as 0˚C = 373.15 K

Rearranging Eq. 2.81, we get, $T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$

Substituting the values, $T_2 = 373.15\text{K}\left(\frac{20.0\,\text{dm}^3}{4.0\,\text{dm}^3}\right)^{1.667-1}$

Solving, we get T_2 = 1091.68 K

UNIT 3

THERMOCHEMISTRY

Structure

3.1 INTRODUCTION

In the previous units of this course you have learnt about the meaning and the importance of thermodynamics and its basic aspects. You have also learnt about the Zeroth and first law of thermodynamics and applications of the first law of thermodynamics to gaseous systems. In this unit, we would extend the application of the first law of thermodynamics and take up the study of the heat changes associated with chemical reactions. Such a study forms an important branch of thermodynamics and is called thermochemistry.

We would begin the unit by discussing the measurement of energy changes accompanying chemical reactions under the conditions of constant volume and constant pressure. We would also introduce the concept of thermochemical equations and discuss its significance. We would then introduce the concept of standard enthalpy changes and argue for the need for a standard state and define it. This will be followed by a discussion on the enthalpy changes accompanying chemical reactions. Herein we would introduce the concept of standard enthalpy of formation and discuss about its direct and indirect determination.

Since temperature is one of the important variables in thermodynamics; we would also be taking up the variation in the enthalpy changes with temperature. In this context we shall derive Kirchhoff's equation and discuss its importance. Towards the end of the unit we would introduce the concept of bond enthalpy and demonstrate how the bond enthalpies can be used to predict enthalpy of reaction.

Expected Learning Outcomes

After studying this unit, you should be able to:

- define thermochemistry and discuss the energy changes accompanying chemical reactions;
- describe the methods for experimental determination of energy changes accompanying chemical reactions under constant volume and constant pressure conditions;
- explain the significance of $\Delta_r U$ and $\Delta_r H$;
- derive the relationship between $\Delta_r U$ and $\Delta_r H$ and solve problems based on it;
- define the standard enthalpy of formation of substances and describe a method for their direct determination;
- enlist the standard states for reactants and products in different physical states;
- state Hess' law of constant heat summation and explain its significance;
- calculate the enthalpy of different reactions using enthalpies of formation of reactants and products;
- define enthalpy of combustion and use enthalpy of combustion values to determine the standard enthalpy of formation of compounds;
- explain the effect of temperature on the enthalpy of a reaction and derive the Kirchhoff's equation;
- compute the enthalpy of reaction at a given temperature from that available at some other temperature;
- define and explain the meaning of bond enthalpy; and
- predict the enthalpies of reactions from bond enthalpy data.

3.2 ENERGY CHANGES ACCOMPANYING CHEMICALREACTIONS

A chemical reaction can be seen as a process in which some of the chemical bonds of the reactants are broken and newer chemical bonds are formed in the products of the reaction. Such a process is expected to be associated with some kind of change in the chemical energy of the system. This change in chemical energy of the system may appear as heat or work or both in the surroundings. Here, we are concerned with the energy changes appearing in terms of heat. If the change in energy of the system appears as heat in the surroundings, the reaction is termed as **exothermic reaction.** For example, if we take some quick lime (CaO) and add it to water at room temperature, a chemical reaction would occur and the reaction mixture will become hot due to the heat released by the reaction. Since the energy as heat is given by the system; it would have a negative sign ($q_{\text{rexn.}} < 0$).

The chemical energy of a chemical system is the energy associated with the chemical bonds of the reactants and the intermolecular attractions between different species.

On the other hand if the chemical reaction is accompanied by absorbing heat from the surroundings, the reaction is termed **endothermic reaction**. For example, if we take some ammonium chloride (NH_4Cl) and put it in some water at room temperature, the mixture would become cold. The sign for the heat change would be positive ($q_{\text{rexn.}} > 0$). Let us see how do we measure these heat changes?

3.2.1 Measuring Heat Changes Accompanying Chemical Reactions: Calorimetry

The heat changes accompanying the chemical reactions are measured by observing the change in the temperature of its surroundings. These temperature changes along with the heat capacities of the surroundings provide the amount of heat change accompanying the reaction. The technique used for their measurement is called **calorimetry** and the reaction vessel in which the reaction is performed is referred to as a **calorimeter**. You are aware that a chemical reaction can be performed under two conditions, viz., under constant volume conditions or under constant pressure conditions. Let's first learn about heat changes under constant volume conditions. A reaction under constant volume conditions is performed in a closed vessel called **bomb calorimeter**.

Measuring Heat Changes under Constant Volume Conditions

Let us take the example of the combustion of an organic compound to learn about measuring heat changes with bomb calorimeter, Fig. 3.1. A bomb calorimeter consists of a double-walled container in which the reaction vessel (called bomb) is immersed in known quantity of water. The container is insulated from the surroundings and is fitted with a thermometer, a stirrer and an ignition system. The bomb is a steel container that contains a known quantity of the reactant and oxygen gas (also a reactant) under pressure. An electrical ignition starts the combustion (reaction with oxygen) of the organic compound. The reaction of the compound with excess of oxygen causes a minor explosion in the vessel that is why the reaction vessel is called a **bomb**.

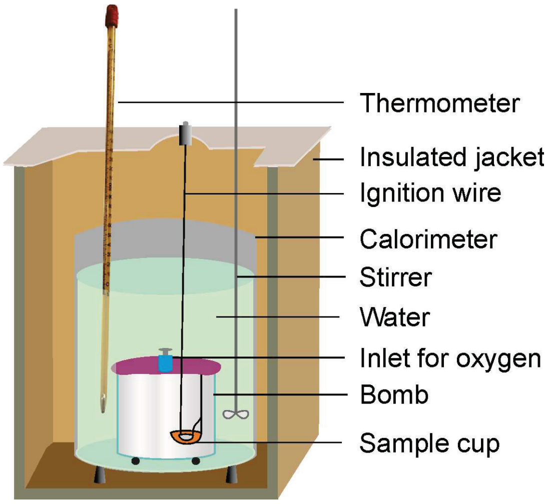


Fig. 3.1: A Bomb Calorimeter

In combustion reaction, there is an increase in the temperature of the surroundings; for some other reactions there may be a decrease in the temperature.

The heat liberated in the process is lost to the surrounding water and the calorimeter assembly causing their temperature to increase. In other words, the energy released by the combustion reaction in the form of heat is absorbed by the calorimeter and its contents. The calorimeter is so designed that no heat or mass is lost to the surroundings or we can say that the system (calorimeter with all the contents) is an isolated system. The increase in temperature due to the reaction is measured with the help of a sensitive thermometer. The increase in temperature along with the heat capacity of the calorimeter (including the bomb and the water) provides the amount of heat liberated during the reaction. Let us see how do we determine it?

In calorimetry, we need to ensure that in order to make a proper measurement of the heat change accompanying a chemical reaction we should ensure that the initial state (the reactants) and the final states (the products) of the system must have the same temperature.

As the calorimeter assembly is an isolated system, we can write,

$$q_{\text{calorimeter}} = -\, q_{\text{rexn.}} \qquad \ldots(3.1)$$

You would recall Eq. (2.21) from Unit 2

$$q_v = C\,\Delta T$$

for the calorimeter we can write,

$$q_{\text{calorimeter}} = C_{\text{calorimeter}}\,\Delta T \qquad \ldots(3.2)$$

The heat capacity of the calorimeter ($C_{\text{calorimeter}}$) is defined as the quantity of heat required for raising the temperature of the calorimeter assembly and its contents by one degree Celsius. The temperature change (ΔT) can be measured with the thermometer but we need to know the heat capacity of the calorimeter to determine $q_{\text{calorimeter}}$ and hence $q_{\text{rexn.}}$ The heat capacity of the calorimeter is determined in a separate experiment in which we take the same amount of water, the same bomb and use a known amount of a compound for which the heat change associated with combustion is known. Let's us take an example to understand the measurement of heat change under constant volume conditions.

Example 3.1: Combustion of 0.479 g of graphite with an excess of oxygen in a bomb calorimeter raised the temperature of the calorimeter from 298.09 K to 299.11 K. In a separate experiment, with the same calorimeter assembly under similar conditions, the combustion of 0.50 g of benzoic acid that released 13.21 kJ of heat caused the temperature of the calorimeter to increase by 0.86 K. Calculate the heat change associated with the combustion of graphite.

Solution: As per the Eq. (3.1) and (3.2) we can write,

$$q_{\text{rexn.}} = -q_{\text{calorimeter}} = -C_{\text{calorimeter}}\, \Delta T$$

The ΔT is given as 299.11K – 298.09 K = 1.02 K

We need to find the value of $C_{\text{calorimeter.}}$ For this we make use of the given data on the combustion of benzoic acid.

We know that the heat capacity = $C = q_{rexn} / \Delta T$

We are given, q_{rexn}= 13.21 kJ and ΔT = 0.86 K

Substituting the values, $C_{\text{calorimeter}} = \dfrac{13.21\ \text{kJ}}{0.86\ \text{K}} = 15.36\ \text{kJ K}^{-1}$

The value of $q_{\text{rexn}}$for combustion of graphite can be obtained by substituting the value of $C_{\text{calorimeter}}$ in the following equation,

$$q_{\text{rexn.}} = -C_{\text{calorimeter}}\, \Delta T$$

$$q_{\text{rexn.}} = -15.36\text{kJK}^{-1} \times 1.02\text{K} = -15.68\text{kJ}$$

Thus, the combustion of 0.479 g of graphite with an excess of oxygen is associated with the release (as the sign. Is negative) of 15.68 kJ of energy as heat.

Let us now learn about how to measure the heat changes under constant pressure conditions.

Measuring Heat Changes under Constant Pressure Conditions

In order to measure the heat changes under constant pressure conditions, in one of very simple methods, the reaction is performed in a calorimeter made from an insulating Styrofoam cup or in a thermos flask. In this set up the calorimeter is provided with a stirrer and a thermometer. The reactants are mixed in the calorimeter and the temperature changes accompanying the reaction are measured with the help of the thermometer. The insulation insures that there is no significant exchange of the heat energy with the surroundings.

The calorimeter and its contents (the reactants and the products) can be considered as an isolated system. As in the case of bomb calorimeter, here again we can write

$$q_{\text{calorimeter}} = -\, q_{\text{rexn.}} \qquad \ldots(3.1)$$

Let us take the example of neutralisation reaction between sodium hydroxide and hydrochloric acid to understand the determination of heat changes under constant pressure conditions. In a typical determination we take equal volumes of solutions of two reactants having same concentration and mix them in the calorimeter.

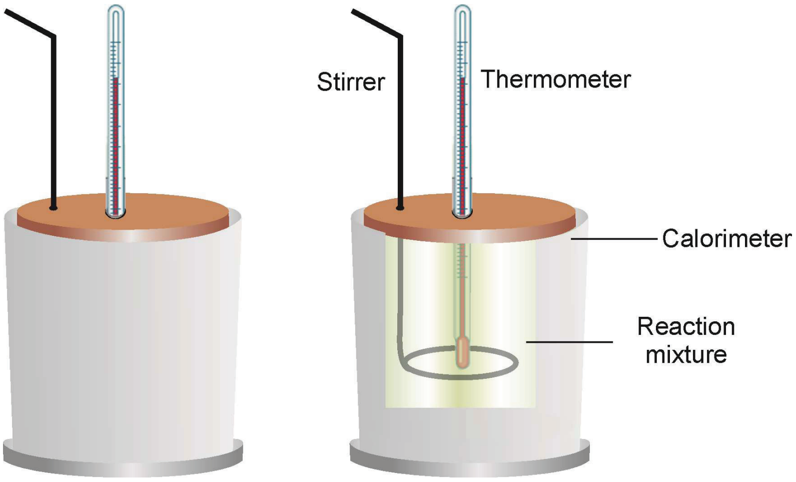


Fig. 3.2: A styrofoam calorimeter used for measuring heat change accompanying a reaction occurring at constant pressure.

The energy released in the reaction warms up the contents of the reaction mixture and the calorimeter. This fact, along with the masses, temperatures and the heat capacities of the products and the heat capacity of the calorimeter are used to determine the amount of energy released. You would actually be doing such measurements in the laboratory course BCHCL-134.

You have so far learnt about the heat changes accompanying a chemical reaction and the way to measure them under the constant volume or constant pressure conditions. We would now relate these changes with the enthalpy of reaction. However, before that why don't you answer the following simple question to assess your learning?

SAQ 1

1.75 g of ethanol (C_2H_5OH) was burned in a constant-volume bomb calorimeter and the temperature of the calorimeter assembly increased by 3.9 °C. If the heat capacity of the calorimeter assembly was 9.4 kJ K^{-1}, calculate the molar enthalpy of combustion of ethanol

3.2.2 Enthalpy of Reaction

Majority of chemical reactions are performed under the conditions of constant pressure, so the measured heat changes refer to the enthalpy change for the reaction. Such an enthalpy change associated with a given chemical reaction is termed as the **enthalpy of reaction**. It is denoted as $\Delta_r H$, where r signifies the reaction and Δ, as always refers to the change in the physical quantity (final value-initial value). The question arises is that when we measure the $\Delta_r H$ values in terms of the heat changes associated with the chemical reactions what do these imply? Let us try to answer this.

In a simplified way, a chemical reaction can be represented as a process wherein the reactants get converted into the products

$$\text{Reactants} \rightarrow \text{Products}$$

Here, the reactants and products respectively represent the initial state and the final state of the system. As per our understanding of the change in enthalpy ($\Delta H = H_f - H_i$) of a system we can write,

$$\Delta H = H_{\text{Products}} - H_{\text{Reactants}} \qquad \ldots(3.3)$$

As we know that generally we do not deal with a single reactant giving a single product; most of the times we have more species on either side of the chemical equation representing the reaction. Therefore, the enthalpy of the initial and the final state are the sum of the enthalpies of the reactants started with and the products obtained respectively. Thus,

$$\Delta_r H = (\text{sum of the } H_{\text{products}} - \text{sum of the } H_{\text{reactants}}) \qquad \ldots(3.4)$$

Mathematically,

$$\Delta_r H = \sum_j a_j H_{\text{m(products)}} - \sum_i a_i H_{\text{m(reactants)}} \qquad \ldots(3.5)$$

where, a_i's and a_j's are the stoichiometric coefficients for the reactants and the products respectively in the balanced chemical equation. For the reaction,

$$2\,CO(g) + O_2(g) \rightarrow 2\,CO_2(g) \qquad \ldots(3.6)$$

the enthalpy change can be represented as

$$\Delta_r H = 2H_{\text{m}(CO_2(g))} - (2H_{\text{m}(CO(g))} + H_{\text{m}(O_2(g))}) \qquad \ldots(3.7)$$

Two questions arise here,

- Can we predict the enthalpy of a reaction?
- Can we calculate the enthalpies of the reactants and products from the measured value of enthalpy of reaction?

We shall take up these questions later in the unit. Let's first learn about thermochemical equations.

3.2.3 Thermochemical Equations

You are familiar with chemical equations as the symbolic representation of a given reaction that consists of the chemical formulae of the reactants and the products along with their stoichiometric coefficients. In addition, the physical state of the reactants and the products and the reaction conditions are also generally indicated. In the thermochemical equations we include the associated energy changes along with all these. For example, the thermochemical equation for the combustion of methane to give carbon dioxide and water-an exothermic process would be represented as,

A thermochemical equation can be seen as a combination of the chemical equation and the associated enthalpy change.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l) \qquad \Delta_r H = -890.4\,\text{kJ mol}^{-1} \qquad \ldots(3.8)$$

The thermochemical equation has a specific meaning and we need to understand important points about it. These are explained below.

i) The chemical part of the equation shows that one mole of methane gas reacts with two moles of oxygen gas to give one mole of carbon dioxide gas and two moles of liquid water. We need to understand what does the energy part convey?

The minus sign in the energy part indicates that the reaction is exothermic, i.e., the reaction is accompanied by the release of 890.4 kJ of energy as heat to the surroundings per mole of the reaction. When we say per mole of the reaction we mean 'the reaction as written', i.e., in this case combustion of one mole of methane to give one mole of gaseous carbon dioxide and two moles of liquid water, releases 890.4 kJ of energy to the surroundings as heat.

As you know, the combustion of methane can also be represented by the following chemical equation.

$$\frac{1}{2}CH_4(g) + O_2(g) \rightarrow \frac{1}{2}CO_2(g) + H_2O(l) \qquad \dots(3.9)$$

If a substance can exist in different allotropic forms, the particular form used as reactant or formed, as product must be mentioned.

What would be the enthalpy for the combustion of methane as given by Eq. (3.9)? Will it be 890.4 kJ? Our common sense tells us that if half a mole (8 g) of methane undergoes combustion it will not give as much heat as is obtained in the combustion of 1 mole (16 g) of methane; it will be half of 890.4 kJ i.e., 445.2 kJ. Therefore, the thermochemical equation for the combustion of methane as per Eq. (3.9) would be

$$\frac{1}{2}CH_4(g) + O_2(g) \rightarrow \frac{1}{2}CO_2(g) + H_2O(l) \quad \Delta_r H = -\ 445.2 \text{ kJ mol}^{-1} \qquad \dots(3.10)$$

Similarly we can argue and say that the thermochemical equation for combustion of 2 moles (32 g) of methane would be

$$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(l) \quad \Delta_r H = -\ 1780.8 \text{ kJ} \qquad \dots(3.11)$$

We can generalise this fact and state that *if a thermochemical equation is multiplied by a factor 'n' on both sides, then the enthalpy change, $\Delta_r H$, for the reaction must also change by the same factor.*

ii) Another important aspect of thermochemical equations is that *it is mandatory to specify the state of the reactants and the products.* Let us understand why?

We once again take the example of combustion of methane but represent it as per the following chemical equation.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g) \qquad \dots(3.12)$$

What will be the enthalpy change for this reaction? Will it be 890.4 kJ? A little focus on the two equations, Eq. (3.8) and (3.12) would reveal that the products in the two equations are not same. According to the Eq. (3.8) the combustion of methane gives liquid water as one of the products whereas water is obtained in gaseous form as per Eq. (3.12). A little thinking reveals that a part of energy released in the combustion Eq. (3.12) would be used for the vaporization of 2 moles of water and accordingly the energy released, as heat in this reaction would be lesser than that obtained in Eq. (3.8). That is, the ΔH value would be lesser negative. In fact the enthalpy change for the combustion of methane as per Eq. (3.12) has been found to be –802.4 kJ mol^{-1}.

iii) Third important feature of the thermochemical equations is that *if we reverse the equation, i.e., we refer to the reaction where the products react to give reactants, then the sign of enthalpy change would reverse; magnitude remaining the same*. Let us take the following thermochemical equation,

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \ \Delta_r H = -285.8 \text{ kJmol}^{-1} \qquad \ldots(3.13)$$

The thermochemical equation for the reverse reaction would be

$$H_2O(l) \rightarrow \ H_2(g) + \frac{1}{2}O_2(g) \ \Delta_r H = 285.8 \text{ kJ mol}^{-1} \qquad \ldots(3.14)$$

The justification for this feature lies in the fact that the enthalpy is a state function.

This aspect of thermochemical equation is based on an important law of thermochemistry proposed by A. L. Lavoisier and P. S. Laplace (1780). The law follows directly from the First Law of thermodynamics and states that, *"the quantity of heat which must be supplied to decompose a compound into its elements is equal to the heat evolved when the compound is formed from its elements"*. This can be generalised as, *"the heat change accompanying a chemical reaction in one direction is exactly equal in magnitude, but opposite in sign, to that associated with the same reaction in the reverse direction".*

3.2.4 Standard Enthalpy Change for a Reaction, $\Delta_r H^o$

We have seen above that the enthalpy change for a reaction depends on the physical state of the reactants used and the products formed. In addition, the enthalpy change of a reaction is also found to depend on other factors also. Therefore, in order to report unambiguous and unique value for the enthalpy change for a reaction, it becomes necessary to specify the following parameters while reporting enthalpy values.

- The physical state (solid, liquid or gas, the proper allotropic form for the solid, if applicable) of the reactants and products
- Pressure
- Temperature
- Concentration (for reactions in solution)

The standard state of a substance at a specified temperature is its pure form at a pressure of 1 bar.

The specification of the parameters listed above makes the data on enthalpy change more reliable, but we may still have problem if we compare the data at different temperatures and /or pressures etc. Therefore, a new parameter called **standard enthalpy change** has been defined. *The standard enthalpy change is defined as the enthalpy change for a reaction in which the reactants and products are in their standard states and is denoted as,* $\Delta_r H^o$. This raises the need to define a standard state. The standard states for reactants or products in different physical states are defined as:

- The standard state of a solid substance is the pure crystalline substance, at a pressure of 1 bar and temperature of interest. For example, standard state of carbon at 298.15 K is graphite, and for tin it is the white form.
- The standard state of a liquid substance is the pure liquid substance, at a pressure of 1 bar and temperature of interest. For example, the standard state of mercury is liquid mercury at 298.15 K.

For phosphorus the standard state is defined to be white phosphorus as against the most stable red allotrope. The choice is based on the fact that the white phosphorous is the more reproducible form at 298.15 K.

- The standard state of a gaseous substance is the ideal gas (hypothetical) at a pressure of 1 bar and temperature of interest. For example, the reference state of nitrogen is N_2 gas at 298.15 K. Similarly, for oxygen as an element the molecular oxygen (O_2)- the more stable form at 298.15 K, than the allotropic form, ozone (O_3) is the standard state.

Though the definition of standard state is at the temperature of interest, usually the data is taken at 298.15 K.

3.2.5 Relationship between $\Delta_r U$ and $\Delta_r H$

You have learnt that the energy changes accompanying a chemical reaction can be measured under constant volume (in a bomb calorimeter) or under constant pressure conditions. These are equal respectively to the$\Delta_r U$ and $\Delta_r H$ for the reaction. Let us try to establish a relationship between them. For a generalised chemical reaction,

$$\mathrm{aA + bB \rightarrow cD + dD} \qquad \ldots(3.15)$$

Let the thermodynamic parameters for the initial state (reactants) and the final state (products) be as follows

Initial state	Final state
(p_1, V_1, U_1, H_1)	(p_2, V_2, U_2, H_2)

According to Eq. (2.32), we can write,

$$H_1 = U_1 + p_1V_1 \qquad \text{and} \qquad H_2 = U_2 + p_2V_2$$

The expression for the enthalpy change for the reaction would be,

$$\Delta_r H = H_2 - H_1 = (U_2 + p_2V_2) - (U_1 + p_1V_1) \qquad \ldots(3.16)$$

$$= (U_2 - U_1) + (p_2V_2 - p_1V_1)$$

$$\Rightarrow \qquad \Delta_r H = \Delta_r U + (p_2V_2 - p_1V_1) \qquad \ldots(3.17)$$

Under the conditions of constant pressure ($p_1 = p_2 = p$),

$$\Rightarrow \qquad \Delta_r H = \Delta_r U + (pV_2 - pV_1) = \Delta_r U + p(V_2 - V_1)$$

$$\Rightarrow \qquad \Delta_r H = \Delta_r U + p\Delta V \qquad \ldots(3.18)$$

Since for solids and liquids, ΔV, and hence $p\Delta V$ is negligible we can conclude that for reactions in solid and liquid phases,

$$\Delta_r H \approx \Delta_r U. \qquad \ldots(3.19)$$

However, in order to establish the relation for reactions involving gaseous reactants and/or products we need to make the following two assumptions

i) all gaseous species (reactants and products) behave ideally and

ii) the total number of moles of gaseous reactants and products are n_1 and n_2 respectively

We can then write, using ideal gas equation,

$p_1V_1 = n_1RT$ and $p_2V_2 = n_2RT$ …(3.20)

Since pressure is constant, we may write,

$p(V_2–V_1) = p\Delta V = (n_2–n_1)\ RT$ …(3.21)

➔ $p\Delta V = \Delta n_gRT$ …(3.22)

where $\Delta n_g = (n_2 - n_1) = n_g(\text{products}) – n_g(\text{reactants})$ …(3.23)

Substituting in Eq. (3.18), we get

$\Delta_rH = \Delta_rU + \Delta n_gRT$ …(3.24)

➔ $\Delta_rU = \Delta_rH – \Delta n_gRT$ …(3.25)

Let us take an example to understand the utility of this expression.

Example 3.2: Calculate the Δ_rU values for the chemical reactions given by following thermochemical equations at 298 K. What do you infer from the results obtained?

i) $2H_2O(g) \rightarrow 2H_2(g) + O_2(g)$ $\Delta_rH = 483\ \text{kJ mol}^{-1}$

ii) $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$ $\Delta_rH = –184.6\ \text{kJ mol}^{-1}$

iii) $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ $\Delta_rH = –114.6\ \text{kJ mol}^{-1}$

Solution: Part (i): $\Delta n_g = n_g(\text{products}) – n_g(\text{reactants}) = 3–2=1$

We know: $\Delta_rU = \Delta_rH – \Delta n_gRT$

Substituting the values in Eq. (3.25),

$$\Delta_rU = 483.6\text{kJ mol}^{-1} - (1 \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times 298\text{K})$$

$$= 483.6\text{kJ mol}^{-1} - 2.48\ \text{kJ mol}^{-1} = 481.12\ \text{kJ mol}^{-1}$$

Part (ii): $\Delta n_g = n_g(\text{products}) – n_g(\text{reactants}) = 2 – 2 = 0$

We know: $\Delta_rU = \Delta_rH – \Delta n_gRT$

Substituting the values in Eq. (3.25),

$$\Delta_rU = -184.6\ \text{kJ mol}^{-1} - (0 \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times 298\text{K})$$

$$= -184.6\text{kJ mol}^{-1}$$

Part (iii): $\Delta n_g = n_g(\text{products}) – n_g(\text{reactants}) = 2–3= –1$

We know: $\Delta_rU = \Delta_rH – \Delta n_gRT$

Substituting the values in Eq. (3.25),

$$\Delta_rU = -114.6\text{kJ mol}^{-1} - (-1 \times 8.314\,\text{JK}^{-1}\text{mol}^{-1} \times 298\text{K})$$

$$= -114.6\ \text{kJ mol}^{-1} + 2.48\ \text{kJ mol}^{-1} = -\ 112.12\ \text{kJ mol}^{-1}$$

From the results obtained we can infer that if the number of moles of gaseous reactants and gaseous products are equal then, $\Delta_r H = \Delta_r U$ and if the number of moles of gaseous reactants are more than the number of moles of gaseous products then $\Delta_r H < \Delta_r U$. On the other hand if the number of moles of gaseous products are more than the number of moles of gaseous reactants then, $\Delta_r H > \Delta_r U$.

Having learnt about the energy changes accompanying chemical reactions and the related concepts, you may assess your understanding by solving the following self assessment questions.

SAQ 2

Calculate $\Delta_r U$ for the following reaction

$$NH_3(g) \rightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \qquad \Delta_r H = 46.11 \text{ kJ}$$

SAQ 3

Complete the following thermochemical equation. (You may use suitable data from the example 2.2 given above)

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g) \qquad \Delta_r H = \text{............}$$

3.3 STANDARD ENTHALPY OF FORMATION AND ITS DETERMINATION

You have learnt that every chemical reaction is associated with a specific value of the enthalpy change. As the total number of chemical reactions known is very large it would be inconvenient and impractical to determine and compile the enthalpy of reaction for all of them. The requirement of such a compilation can be avoided by finding and tabulating the standard enthalpies of formation of different chemical compounds. These can then be used to calculate the enthalpy changes associated with reactions. Let us learn about standard enthalpies of formation and their determination.

The standard or reference state of an element is, *its most stable state at the specified temperature and a pressure of 1 bar*.

The standard enthalpy of formation, $\Delta_f H^o$, of a compound is defined as the standard enthalpy of reaction for the formation of the compound from its elements in their standard states. The standard enthalpies of formation of elements in their standard states are zero by definition. For example, the enthalpy of formation of water in liquid state at 298.15 K can be represented as

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta_f H^\circ = -285.8 \text{ kJ mol}^{-1} \quad \text{...(3.26)}$$

Here, the superscript, ^{o} is indicative of the standard state and the subscript; $_f$ represents 'formation'. The expression implies that one mole of hydrogen gas reacts with half a mole of oxygen gas to give one mole of liquid water in their standard states at 298.15 K and 1 bar. Similarly, for carbon dioxide gas at 298.15 K we can write,

$$C\text{ (s, graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta_f H^0 = +393.5\text{ kJ mol}^{-1} \quad \ldots(3.27)$$

The standard enthalpy of formation of some of the compounds is given in Table 3.1.

Table 3.1: Standard molar enthalpies (in kJ mol^{-1}) of formation for some common compounds

Compound	**Standard molar enthalpy / kJ mol^{-1}**	**Compound**	**Standard molar enthalpy / kJ mol^{-1}**
$CO(g)$	– 110.5	$HBr(g)$	– 36.40
$CO_2(g)$	– 393.5	$HI(g)$	26.48
$CH_4(g)$	– 74.81	$H_2O(g)$	– 241.8
$C_2H_2(g)$	226.7	$H_2O(l)$	– 285.8
$C_2H_4(g)$	52.26	$H_2S(g)$	– 20.63
$C_2H_6(g)$	– 84.68	$NH_3(g)$	– 46.11
$C_3H_8(g)$	– 103.8	$NO(g)$	90.25
$C_4H_{10}(g)$	– 125.6	$N_2O(g)$	82.05
$CH_3OH(l)$	– 238.7	$NO_2(g)$	33.18
$C_2H_5OH(l)$	– 277.7	$N_2O_4(g)$	9.16
$HF(g)$	– 271.1	$SO_2(g)$	– 296.8
$HCl(g)$	– 92.31	$SO_3(g)$	– 395.7
$HCHO(g)$	– 117.00	CH_3CHO (l)	– 192.30

3.3.1 Enthalpy of Formation and Enthalpy of Reaction

An important consequence of defining the enthalpy of formation is that the enthalpy of a reaction can be expressed in terms of the difference in the enthalpies of formation of the products minus those of the reactants. Let us reconsider the formation of carbon dioxide from C (graphite) and oxygen as given below.

$$C\text{ (s, graphite)} + O_2(g) \rightarrow CO_2(g) \qquad \Delta_f H^0 = +\ 393.5\text{ kJ mol}^{-1} \quad \ldots(3.28)$$

Let us represent the enthalpy of the reaction in terms of the enthalpy of formation of the products and reactants as given below.

$$\Delta_r H^0 = \Delta_f H^0(CO_2) - \Delta_f H^0(O_2) - \Delta_f H^0(\text{C, graphite}) \quad \ldots(3.29)$$

Since the enthalpies of formation for the elemental oxygen and carbon are zero by definition, we get

$$\Delta_r H^o = \Delta_f H^o(CO_2) - 0 - 0 = \Delta_f H^o(CO_2) \quad \ldots(3.30)$$

This equation is quite important as it allows us to calculate the enthalpy change for any reaction weather feasible or not.

This fact can be generalised and we can write that

$$\Delta_r H^o = \sum_{\text{Products}} \nu\Delta_f H^o - \sum_{\text{Reactants}} \nu\Delta_f H^o \qquad \ldots (3.31)$$

Where, ν refers to the stoichiometric coefficients for the reactants and products in the balanced chemical equation. Let us take an example to calculate the enthalpy of a reaction using Eq. 3.31.

Example 3.3: The combustion of methane is given by the following expression.

$$CH_4(g) + 2O_2(g) \rightarrow CO_2 + 2H_2O(l)$$

Calculate the enthalpy of the combustion of methane in terms of enthalpies of formation of the reactants and the products. Use data from Table 3.1.

Solution: As per Eq.(3.31) the enthalpy of the combustion of methane, can be written as

$$\Delta_r H^o = \Delta_f H^o\ (CO_2(g)) + 2\Delta_f H^o\ (H_2O(l)) - \Delta_f H^o\ (CH_4(g)) - 2\Delta_f H^o\ (O_2(g))$$

Substituting the values from the Table 3.1, we get,

$$\Delta_r H^o = -393.5 - (2 \times 285.8) - (-74.74) - 0.0$$

$$= -890.36\,\text{kJ mol}^{-1}$$

Thus, you can note that Eq. (3.31) is quite useful in calculating the enthalpies of reactions. Let us learn about the methods for the determination of standard enthalpies of formation. However, before that answer the following SAQ

SAQ 4

The thermochemical equation for the combustion of benzene is given below,

$$2C_6H_6(l) + 15\ O_2(g) \rightarrow 12\ CO_2(g) + 6H_2O(l) \qquad \Delta_{comb}H = -6535\,\text{kJ mol}^{-1}$$

Calculate the enthalpy of formation of benzene. (You may use the data from Table 3.1 as required).

3.3.2 Direct Determination of Enthalpy of Formation

The direct determination of the standard enthalpies of formation $\Delta_f H^o$ is possible only for those compounds that can be readily synthesized from their elements. In such cases the formation of a compound from its elements is carried out in a calorimeter and the enthalpy change for the reaction is directly measured. For example, the enthalpy of formation of carbon dioxide can be readily determined by measuring the enthalpy of the reaction between carbon (graphite) and molecular oxygen in their standard states to give carbon dioxide in its standard state as given by the following equation.

$$C\ (\text{s, graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_f H^o = +393.5\ \text{kJmol}^{-1} \qquad \ldots(3.32)$$

Similarly, measuring the enthalpy of reaction between sulphur and fluorine in their standard states can provide the standard enthalpy of formation of SF_6 as given below.

$$S\ (\text{rhombic}) + 3F_2(g) \rightarrow SF_6(g) \qquad \Delta_f H^o = -1209\ \text{kJ mol}^{-1} \qquad \ldots(3.33)$$

You may note here that the rhombic form is the standard state of elemental sulphur. Though this method of determination of standard enthalpy of formation is quite straight forward, it is generally not used because there are not many compounds that can directly prepared from their elements in the standard state. In such cases, $\Delta_f H^o$ is determined by an indirect method based on Hess's law of constant heat summation. Let us learn about the indirect method

3.3.3 Indirect Determination of Enthalpy of Formation

The indirect method for the determination of the enthalpy of formation is based on an important empirical law of thermochemistry discovered by G. H. Hess in 1840. The law states that, *"the enthalpy change associated with a given chemical reaction is the same whether it occurs in a single stage or in many stages"*. The law is commonly known as the law of constant heat summation and implies that the net enthalpy change for a reaction depends only on the initial and final states, and not on the intermediate states through which the system passes. An important consequence of the Hess's law is that the thermochemical equations can be added and subtracted, like algebraic equations. Let us take an example,

The Hess's law of constant heat summation follows directly from the first law of thermodynamics. We know that enthalpy, H is a state function and ΔH depends only on the initial and final state (that is, only on the nature of reactants and the products).

The partial oxidation of graphite to carbon monoxide can be represented by the following thermochemical equation,

$$C\ (\text{s, graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g) \qquad \Delta_f H^o = -110.5\ \text{kJ mol}^{-1} \qquad \ldots(3.34)$$

and the oxidation of carbon monoxide to carbon dioxide is given as

$$CO(g) + \frac{1}{2}O_2(g) \rightarrow CO_2(g) \qquad \Delta_f H^o = -283.0\ \text{kJ mol}^{-1} \qquad \ldots(3.35)$$

Let us add these two equations Eq. (3.35) and Eq. (3.36), to get

$$C\ (\text{s, graphite}) + \frac{1}{2}O_2(g) + CO\ (g) + \frac{1}{2}O_2(g) \rightarrow CO(g) + CO_2(g) \qquad \ldots(3.36)$$

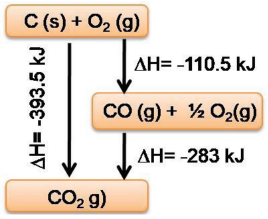
The corresponding enthalpies add as

$$\Delta_f H^o = (-110.5\ \text{kJ mol}^{-1}) + (-283.0\ \text{kJ mol}^{-1}) = -393.5\ \text{kJ mol}^{-1} \qquad \ldots(3.37)$$

The resulting thermochemical equation can be written as

$$C\ (\text{s, graphite}) + O_2(g) \rightarrow CO_2(g) \qquad \Delta_f H^o = -393.5\ \text{kJ mol}^{-1} \qquad \ldots(3.38)$$

This equation is the same as Eq.(3.32), representing the formation of CO_2 from its elements in the standard states.



This consequence of the Hess's law forms the basis for the indirect determination of the enthalpies of formation. In order to apply Hess's law the first step is to identify a set of chemical reactions such that their equations can be arranged in such a way that, when added together, all species other than the reactants and products of the desired reaction cancel out. This may involve multiplying certain equations with suitable coefficients or reversing some reactions.

3.4 ENTHALPY CHANGES IN DIFFERENT TYPES OF REACTIONS

The enthalpies of some of the types of reactions havebeenassigned special names and are quite important. Let us learn about these enthalpies.

3.4.1 Enthalpy Changes in Combustion Reaction

You may note here that the reactants and the products are in their standard states.

As you are aware, combustion refers to the reaction of a compound with an oxidant (usually oxygen) to produce oxidized products accompanied by energy. The standard enthalpy of combustion of a compound is defined as the enthalpy change accompanying the complete combustion of one mole of the compound in presence of sufficient oxygen under standard conditions. All the reactants and the products are in their standard states. For example the combustion of carbon and ethanol are represented as:

$$\mathrm{C\,(s,\,graphite) + O_2(g) \rightarrow CO_2\,(g)} \qquad \ldots(3.32)$$

$$\mathrm{C_2H_5OH\,(l) + 3O_2(g) \rightarrow 2CO_2\,(g) + 3H_2O\,(l)} \qquad \ldots(3.39)$$

The products of combustion for the compounds containing C, H and O are carbon dioxide in the gaseous state and water in the liquid state. In case the compound also contains N, the nitrogen gas is obtained in the products and the compounds containing halogens produce aqueous solutions of halogen acids at infinite dilution.

$$\mathrm{CO(NH_2)_2(s) + \frac{3}{2}\,O_2(g) \rightarrow CO_2\,(g) + 2H_2O\,(l) + N_2(g)} \qquad \ldots(3.40)$$

$$\mathrm{CH_3Cl\,(g) + \frac{3}{2}\,O_2(g) \rightarrow CO_2(g) + H_2O\,(l) + HCl(aq)} \qquad \ldots(3.41)$$

One of the applications of the values of the enthalpies of combustion is in the determination of the standard enthalpy of formation of compounds, which cannot be measured directly. Let us take an example to learn how do we use enthalpy of combustion to get standard enthalpy of formation? We make use of the Hess's law for this purpose.

Example 3.4: Determine the enthalpy of formation of methane from its elements using Hess's law.

Solution: You know that the enthalpy of formation of methane corresponds to the enthalpy change for the following reaction

$$C\ \mathrm{(s,\,graphite) + 2H_2(g) \rightarrow CH_4(g)} \qquad \ldots(3.42)$$

You would recall from above that the direct determination of enthalpy of formation of methane is not possible. We identify the following equations involving the combustion of the reactants and the products

$$C\ (\text{s, graphite}) + O_2(g) \rightarrow CO_2\ (g) \qquad \Delta_f H^o = -393.5\ \text{kJ mol}^{-1} \qquad \ldots(3.32)$$

$$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l) \qquad \Delta_f H^o = -285.8\ \text{kJ mol}^{-1} \qquad \ldots(3.43)$$

$$CH_4(g) + 2O_2(g) \rightarrow CO_2 + 2H_2O(l) \quad \Delta_f H^o = -890.36\ \text{kJ mol}^{-1} \qquad \ldots(3.44)$$

The formation reaction involves one mole of carbon and two moles of hydrogen therefore we multiply Eq. (3.43) by two to get

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta_f H^o = -571.6\ \text{kJ mol}^{-1} \qquad \ldots(3.45)$$

Further, as we need to get one mole of methane as the product we reverse Eq.3.44 i.e.,

$$CO_2 + 2H_2O(l) \rightarrow CH_4(g) + 2O_2(g) \quad \Delta_f H^o = 890.36\ \text{kJ mol}^{-1} \qquad \ldots(3.46)$$

Now adding, Eq. (3.32), (3.45) and (3.46) we get,

$$\begin{gathered} C(\text{s,graphite}) + O_2 + 2H_2 + O_2 + CO_2 + 2H_2O(l) \rightarrow \\ CH_4(g) + 2O_2(g) + CO_2(g) + 2H_2O\ (l) \end{gathered} \qquad \ldots(3.47)$$

You must recall from above that when a thermochemical equation is multiplied by a number 'n' then the enthalpy change, ΔH, for the reaction must also change by the same factor and secondly, if we reverse the equation, then the sign of enthalpy change also changes and the magnitude remains the same.

Cancelling the common terms on the two sides we get, the desired expression for the formation of methane,

$$C\ (\text{s, graphite}) + 2H_2(g) \rightarrow CH_4(g) \qquad \ldots(3.42)$$

The corresponding enthalpy change can be calculated as

$$\Delta_f H^o = -393.5\ \text{kJ mol}^{-1} - 571.6 + 890.36 = -74.74\text{kJ mol}^{-1}$$

3.4.2 Enthalpy Changes in Dissolution and Dilution

The enthalpy of dissolution refers to the enthalpy change accompanying the dissolution of a solute in a solvent or the process of solution formation. The enthalpy of solution formation depends on the composition of solution besides the nature of solute and solvent. In the context of composition of solution, we define **integral enthalpy of solution**, as *the enthalpy change associated with the addition of a specified amount of solute to a specified amount of solvent under standard conditions.* For example, the following thermochemical equation,

$$HCl\ (g) + 5\ aq \rightarrow HCl.5aq \qquad \Delta H = -63.47\ \text{kJ mol}^{-1} \quad \ldots(3.48)$$

represents the dissolution of 1 mole of HCl in 5 moles of water. Here, 'HCl.5aq' represents a solution of 1 mole of HCl in 5 moles of H_2O. In other words, the enthalpy change accompanying the process (Eq. 3.48) is called integral enthalpy of solution for the dissolution of 1 mole of HCl in 5 moles of water. The integral enthalpy of solution depends on the molar ratio of the solute and the solvent as shown in the following equations.

$$\text{HCl (g)} + 10\text{ aq} \rightarrow \text{HCl.10aq} \qquad \Delta H = -69.01\text{ kJ mol}^{-1} \qquad \ldots(3.49)$$

$$\text{HCl (g)} + 25\text{ aq} \rightarrow \text{HCl. 25aq} \qquad \Delta H = -72.03\text{ kJ mol}^{-1} \qquad \ldots(3.50)$$

$$\text{HCl (g)} + 40\text{ aq} \rightarrow \text{HCl.40aq} \qquad \Delta H = -72.79\text{ kJ mol}^{-1} \qquad \ldots(3.51)$$

$$\text{HCl (g)} + 100\text{ aq} \rightarrow \text{HCl.100aq} \qquad \Delta H = -73.61\text{ kJ mol}^{-1} \qquad \ldots(3.52)$$

$$\text{HCl (g)} + 200\text{ aq} \rightarrow \text{HCl. 200 aq} \qquad \Delta H = -73.96\text{ kJ mol}^{-1} \qquad \ldots(3.53)$$

$$\text{HCl (g)} + \infty\text{ aq} \rightarrow \text{HCl. }\infty\text{ aq} \qquad \Delta H = -74.85\text{ kJ mol}^{-1} \qquad \ldots(3.54)$$

Thus, the integral enthalpy of solution can be seen as the enthalpy change accompanying the dissolution of 1 mole of the solute in a definite quantity of solvent to get a solution of the desired concentration. A look at the Eq. (3.49) to Eq. (3.54) shows that as we add more and more solvent to a given amount of the solute the integral enthalpy of solution reaches a limiting value. This limiting value is called the **integral enthalpy of solution at infinite dilution,** $\Delta_{\infty}H^{o}$. Any further addition of solvent does not alter the enthalpy change value.

We may take a solution of known concentration (solute-solvent ratio) and add a definite amount of solvent to get a solution of a lower concentration. This process is called dilution and the enthalpy change accompanying this process is called **enthalpy of dilution**. Let us take an example wherein a solution of HCl(g) in water having solute-solvent mole ratio of 1:10 and we add 15 moles of water to it. The process will be represented as

$$\text{HCl .10aq (g)} + 15\text{ aq} \rightarrow \text{HCl . 25aq} \qquad \ldots(3.55)$$

The enthalpy change for this process can be obtained with the help of Hess's law. Let us rewrite Eq.(3.49) and Eq. (3.50),

$$\text{HCl (g)} + 10\text{ aq} \rightarrow \text{HCl.10aq} \qquad \Delta H = -69.01\text{ kJ mol}^{-1} \quad \ldots(3.49)$$

$$\text{HCl (g)} + 25\text{ aq} \rightarrow \text{HCl. 25aq} \qquad \Delta H = -72.03\text{ kJ mol}^{-1} \quad \ldots(3.50)$$

Subtracting Eq. (3.49) from Eq.(3.50) and rearranging we get the reaction given in Eq. (3.55) and the associated enthalpy change.

$$\text{HCl . 10aq (g)} + 15\text{ aq} \rightarrow \text{HCl . 25aq} \qquad \Delta H = -3.02\text{ kJ mol}^{-1} \quad \ldots(3.56)$$

Thus, we can define the enthalpy of dilution as the enthalpy change accompanying the dilution of a solution containing 1 mole of solute from a given concentration to a lower concentration.

SAQ 5

An aqueous solution of HCl in water having solute-solvent mole ratio of 1:25, is diluted by adding sufficient solvent such that any further addition of solvent does not change its enthalpy. Represent the process in the form of an equation and compute the enthalpy change for the process. [You may use data from Eq.(3.49) to Eq. (3.54) as required].

3.5 TEMPERATURE DEPENDENCE OF $\Delta_r H$: KIRCHHOFF'S EQUATION

You have learnt that the enthalpy of different types of reactions can be computed with the help of enthalpy of formation of different compounds. However, most of the data available on enthalpy of reaction or enthalpy of formation of compounds are at 298 K. If the enthalpy of reaction is required at some other temperature, we need to know the temperature dependence of the enthalpy of reaction. The enthalpy of reaction at a desired temperature can be obtained from the enthalpy of reaction at some other temperature with the help of Kirchhoff's equation. Let us derive Kirchhoff's equation.

We know that: $\Delta_r H^o = H^o(\text{products}) - H^o(\text{reactants})$

Differentiating with respect to temperature we get,

$$\frac{d}{dT}(\Delta_r H^o) = \frac{d}{dT}H^o(\text{products}) - \frac{d}{dT}H^o(\text{reactants}) \qquad \ldots(3.57)$$

As $\frac{d}{dT}H^o = C_p^o$ we can write

$$\frac{d}{dT}(\Delta_r H^o) = C_p^o(\text{products}) - C_p^o(\text{reactants}) \qquad \ldots(3.58)$$

$$\frac{d}{dT}(\Delta_r H^o) = \Delta C_p^o \qquad \ldots(3.59)$$

Writing the equation in the differential form

$$d(\Delta_r H^o) = \Delta C_p^o\, dT \qquad \ldots(3.60)$$

Integrating the equation between temperatures T_1 and T_2,

$$\int_{T_1}^{T_2} d(\Delta_r H^o) = \int_{T_1}^{T_2} \Delta C_p^o\, dT \qquad \ldots(3.61)$$

$$\Delta_r H^o(T_2) - \Delta_r H^o(T_1) + \Delta C_p^o\ (T_2 - T_1) \qquad \ldots(3.62)$$

Rearranging,

$$\Delta_r H^o(T_2) = \Delta_r H^o(T_1) + \Delta C_p^o\ (T_2 - T_1) \qquad \ldots(3.63)$$

This is the Kirchhoff's equation that gives the temperature dependence of enthalpy change for a reaction. Let us take up an example to learn about the application of Kirchhoff's equation.

Example 3.5: The enthalpy change for the following reaction is determined to be131.28 kJ mol^{-1} at 298 K.

$$C(\text{graphite}) + H_2O(g) \rightarrow CO(g) + H_2(g) \qquad \ldots(3.64)$$

Calculate the enthalpy change for the reaction at 100°C.The C_p^o ($\text{J K}^{-1}\text{mol}^{-1}$) values are given as: C (graphite) = 8.53; H_2O (g) = 33.58; CO (g)= 29.12; H_2 (g)= 28.82. Assume the heat capacity values to be temperature independent in the range.

Solution: As per Eq. (3.63):

$$\Delta H^o(T_2) = H^o(T_1) + \Delta C_p^o\ (T_2 - T_1)$$

We begin by calculating the C_p^o values

$$\Delta C_p^o = C_p^o[\text{CO(g)}] + C_p^o[\text{H}_2\text{(g)}] - C_p^o[\text{C(graphite)}] - C_p^o\ [\text{H}_2\text{O(g)}] \qquad \ldots(3.59)$$

Substituting the values

$$\Delta C_p^o = 29.12 + 28.82 - 8.53 - 33.58 = 15.83\,\text{J K}^{-1}\text{mol}^{-1}$$

Substituting in Eq. (3.63)

$$\Delta H^o(373.15) = 131.28\ \text{kJ mol}^{-1} + 15.83\ \text{J K}^{-1}\ (373.15 - 298)\ \text{K}$$

Solving, we get, $\Delta H^o(373.15) = 130.09\ \text{kJ mol}^{-1}$

3.6 BOND ENTHALPIES AND ESTIMATION OF ENTHALPIES OF REACTION

You know that a chemical reaction involves breaking and making of bonds. We may ask, “Can we determine the enthalpy of a reaction in terms of bond enthalpies?”. The answer is yes, let us learn about the meaning of bond enthalpies and how can these be used to determine the enthalpy of reaction.

3.6.1 Bond Enthalpies

Let us consider the following thermochemical reactions

$$\text{H}_2\text{(g)} \rightarrow 2\ \text{H (g)} \qquad \Delta H^o = 436.4\ \text{kJ mol}^{-1} \qquad \ldots(3.65)$$

$$\text{O}_2\text{(g)} \rightarrow 2\ \text{O (g)} \qquad \Delta H^o = 498.34\ \text{kJ mol}^{-1} \qquad \ldots(3.66)$$

$$\text{N}_2\text{(g)} \rightarrow 2\ \text{N (g)} \qquad \Delta H^o = 941.4\ \text{kJ mol}^{-1} \qquad \ldots(3.67)$$

$$\text{Cl}_2\text{(g)} \rightarrow 2\ \text{Cl (g)} \qquad \Delta H^o = 242.7\ \text{kJ mol}^{-1} \qquad \ldots(3.68)$$

The bond enthalpies for diatomic (homonuclear and heteronuclear) molecules simply are the bond dissociation energies and are directly measurable.

The enthalpy changes in these reactions indicate the amount of energy required to break the covalent bonds in 1 mole of the respective gaseous diatomic molecules. These numbers are in fact a measure of the strengths of the bonds. These energies are called **bond enthalpies** and are directly measurable in case of homonuclear diatomic molecules. The bond enthalpies for heteronuclear diatomic molecules can also be directly measured. For example,

$$\text{HCl(g)} \rightarrow \text{H(g)} + \text{Cl (g)} \qquad \Delta H^o = 441.9\ \text{kJ mol}^{-1} \qquad \ldots(3.69)$$

However, for larger molecules the same is not true. Let us take the successive dissociation of C-H bonds in methane.

$$CH_4(g) \rightarrow CH_3(g) + H(g) \qquad \Delta H^o = 431.8 \text{ kJ mol}^{-1} \qquad \ldots(3.70)$$

$$CH_3(g) \rightarrow CH_2(g) + H(g) \qquad \Delta H^o = 471.1 \text{ kJ mol}^{-1} \qquad \ldots(3.71)$$

$$CH_2(g) \rightarrow CH(g) + H(g) \qquad \Delta H^o = 421.7 \text{ kJ mol}^{-1} \qquad \ldots(3.72)$$

$$CH(g) \rightarrow C(g) + H(g) \qquad \Delta H^o = 338.8 \text{ kJ mol}^{-1} \qquad \ldots(3.73)$$

You can observe here that each of these equations represent the dissociation of a C-H bond but the energies required for them are different. Though all the C-H bonds in methane are equivalent the dissociation energies are not the same. This is due to the fact that once a C-H bond is dissociated; the remaining species has different electronic distributions.

We can add these four equations to get,

$$CH_4(g) \rightarrow C(g) + 4\,H(g) \qquad \Delta H^o = 1663.4 \text{ kJ mol}^{-1} \qquad \ldots(3.74)$$

In this reaction the methane molecule has got converted into its constituent atoms therefore the enthalpy change is called the enthalpy of atomization of methane. If we divide the enthalpy of atomization of methane by 4 (the number of C-H bonds broken), we get an average value (1663.4 / 4 = 415.9 kJ mol^{-1}) for the bond enthalpy for C-H bond.

Similarly, we can take up the case of the dissociation of O-H bonds in water.

$$H_2O(g) \rightarrow OH(g) + H(g) \qquad \Delta H^o = 502 \text{ kJ mol}^{-1} \qquad \ldots(3.75)$$

$$OH(g) \rightarrow O(g) + H(g) \qquad \Delta H^o = 427 \text{ kJ mol}^{-1} \qquad \ldots(3.76)$$

Adding the two, we get

$$H_2O(g) \rightarrow O(g) + 2\,H(g) \qquad \Delta H^o = 929 \text{ kJ mol}^{-1} \qquad \ldots(3.77)$$

Here again the two bond dissociation energies are different and their average value (464.5 kJ mol^{-1}) is the bond enthalpy for the O-H bond. Another example could be the dissociation of N-H bonds of ammonia. In all these molecules we have equivalent bonds.

If we extend the argument further and try to determine the bond enthalpy for the molecule like ethane. In such a case two different types of bonds exist, e.g., C-H and C-C bonds. In order to determine bond enthalpies we need to introduce some assumption, as we cannot get the value of two unknowns from one data (i.e., enthalpy of atomization of ethane).

We assume that the bond enthalpy for a given bond (say C-H) in ethane is same as that in methane. The atomization of ethane is given by the following expression.

$$C_2H_6(g) \rightarrow 2\,C(g) + 6\,H(g) \qquad \Delta H^o = 2842.4 \text{ kJ mol}^{-1} \qquad \ldots(3.78)$$

The enthalpy of atomization of ethane would equal the bond enthalpies of six C-H bonds and one C-C bond. If we subtract the bond enthalpies of six C-H bonds from the enthalpy of atomization we can get the bond enthalpy for C-C bond. Thus, the bond enthalpy for a given bond refers to the average bond dissociation energy for the same bond in a number of related molecules having the said bond. This way the bond enthalpies for different bonds are determined and are compiled. Table 3.2 gives the bond enthalpies of different types of bonds.

Table 3.2: Bond Enthalpies of Common Bonds

Bond	**Bond Enthalpy (kJ mol^{-1})**	**Bond**	**Bond Enthalpy (kJ mol^{-1})**
H — H	436.4	C — S	255
H — N	393	C = S	477
H — O	460	N — N	193
H — S	368	N = N	418
H — P	326	N ≡ N	941.4
H — F	568.2	N — O	176
H — Cl	431.9	N = O	607
H — Br	366.1	O — O	142
H — I	298.3	O = O	498.7
C — H	415.9	O — P	502
C — C	347	O = S	469
C = C	620	P — P	197
C ≡ C	812	P = P	489
C — N	276	S — S	268
C = N	615	S = S	352
C ≡ N	891	F — F	156.9
C — O	351	Cl — Cl	242.7
C = O[†]	745	Br — Br	192.5
C — P	263	I — I	151.0
C-Br	234		

3.6.2 Enthalpy of Reaction from Bond Enthalpies

As you know that any chemical reaction can be seen in terms of breaking and making of chemical bonds. That is we need energy to break chemical bonds and formation of new chemical bonds is accompanied by a release of energy. Therefore, it is possible to predict the approximate enthalpy of reaction by using the average bond enthalpies. This is done by counting the number of bonds being broken and the new bonds being formed in the reaction and accounting for the energy changes involved. The enthalpy of reaction in the gas phase is given simply by the following expression.

$$\Delta H^{o} = \text{Total energy input} - \text{total energy output} \qquad \ldots(3.79)$$

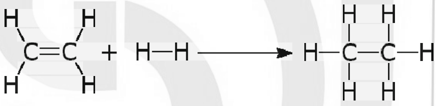
As the energy input is to break the bonds and energy output is in the process of bond making, we can write

$$\Delta_r H^{o} = \sum \text{Bond Enthalpy (Reactants)} - \sum \text{Bond Enthalpy (Products)} \qquad \ldots(3.80)$$

If the sum of bond enthalpies of all the reactants (energy input) is greater than the sum of bond enthalpies of all the products (energy output), $\Delta H°$ is positive and the reaction is endothermic. On the other hand, if the reverse is true, $\Delta H°$ is negative and the reaction is exothermic. Let us take an example to understand the determination of enthalpy of a reaction using bond enthalpies.

Example 3.6: Predict the enthalpy of hydrogenation of ethene to ethane using the bond enthalpy data from Table 3.2. Compare it with the same calculated on the basis of standard enthalpy of formation values from Table 3.1.

Solution: The hydrogenation of ethene is given by the following equation.



…(3.81)

As explained above, to calculate the enthalpy of the reaction we first need to list the bonds being broken and the bonds being formed.

The bonds being broken: 1 C=C, 4 C-H and 1 H-H

The bonds being formed: 1 C-C and 6 C-H

The energy spent on breaking the bonds, Σ Bond Enthalpy (Reactants)

Substituting the values from Table 3.2,

$= 1\ (620\ \text{kJ mol}^{-1}) + 4\ (415.9\ \text{kJ mol}^{-1}) + 1\ (436.4\ \text{kJ mol}^{-1}) = 2720\ \text{kJ mol}^{-1}$

The energy released in formation the bonds, Σ Bond Enthalpy (Products)

Substituting the values from Table 3.2,

$= 1\ (347\ \text{kJ mol}^{-1}) + 6\ (415.9\ \text{kJ mol}^{-1}) = 2842.4\ \text{kJ mol}^{-1}$

The enthalpy of reaction:

$$\Delta_r H^{o} = \Sigma \text{ Bond Enthalpy (Reactants)} - \Sigma \text{ Bond Enthalpy (Products)}$$

Substituting the values from Table 3.1

$$\Delta_r H^{\circ} = 2720 - 2842.4 = -122.4\ \text{kJ mol}^{-1}$$

Thus, the enthalpy of hydrogenation of ethene as calculated above on the basis of bond enthalpies is found to be = -122.4 kJ mol^{-1}.

Let us calculate the same by using the standard enthalpies of formation of the reactants and the products. For the given reaction we can write,

$$\Delta_r H^{o} = \Delta_f H^{o}(C_2H_6) - \Delta_f H^{o}(C_2H_4) - \Delta_f H^{o}(H_2) \qquad \ldots(3.82)$$

Substituting the values from Table 3.1,

$$\Delta_r H^{o} = -84.68 \; -52.26 \; -0 \; = -136.94 \text{ kJ mol}^{-1}$$

The discrepancy in the two values is due to the fact that some of the bond enthalpies used are average values.

Why don't you practice the method for calculation of enthalpy of reaction from bond enthalpies by solving the following SAQ

SAQ 6

Predict the enthalpy change for the addition of HBr to ethene on the basis of bond enthalpies. Use Table 3.2

3.7 SUMMARY

In this unit we continued our discussion on the applications of the first law of thermodynamics and focused on thermochemistry-the study of the heat changes associated with chemical reactions. We began by discussing the energy changes accompanying chemical reactions under the conditions of constant volume and constant pressure and learnt about their experimental determination by calorimetry. Since vast majority of the chemical reactions are performed under the conditions of constant pressure, we introduced the concept of enthalpy of reaction as the heat change accompanying a chemical reaction. It was shown that the enthalpy change for a reaction equals the sum of enthalpies of the products minus the sum of enthalpies of the reactants.

In order to highlight the energy changes accompanying the chemical reaction, the concept of thermochemical equations was introduced. In thermochemical equations the energy changes are integrated with the chemical equation. The meaning of thermochemical equations was explained and their characteristics and significance was discussed. As the enthalpy change for a reaction depends on variety of parameters like, pressure, temperature, concentration, and the physical state of the reactants and the products, etc. we argued for and defined standard enthalpy change. This refers to the enthalpy change associated with a reaction in which the reactants and the products are in their standard states. This in turn necessitated the need for a standard state, which was defined.

We then defined the standard enthalpy of formation as the enthalpy of reaction for the formation of the compound from its elements in their standard or reference states. The importance of standard enthalpies of formation was demonstrated in terms of their ability to give enthalpy of a reaction. The enthalpy of reaction is equal to the difference in the sum of enthalpies of formation of the products minus the sum of enthalpies of formation of the reactants. Owing to their importance we discussed about the direct and indirect determination of the enthalpies of formation of compounds. In the context of indirect determination, we introduced a very important empirical law, called Hess's law of constant heat summation and discussed about its importance and applications.

Then we took up the enthalpy changes associated with different types of chemical reactions. Herein we defined standard enthalpies of combustion, dissolution and dilution. We demonstrated how we could use enthalpies of combustion for the determination of enthalpies of formation of compounds. Since temperature is one of the important variables in thermodynamics; we took up the variation in the enthalpy changes with temperature. In this context we formulated the Kirchhoff's equation and discussed its importance. We showed with the help of examples that if we know the enthalpy of reaction at a given temperature, the same at some other temperature can be calculated if we know the heat capacities of the reactants and the products. Towards the end of the unit we introduced the concept of bond enthalpy and demonstrated how the bond enthalpies can be used to predict enthalpy of reaction.

3.8 TERMINAL QUESTIONS

1. Why is the bomb calorimeter so called?

2. Enlist salient features of thermochemical equations.

3. What is meant by standard state? Why do we need to define standard state?

4. Two molecules of α-D-glucose condense in an enzyme catalysed reaction to give a molecule of disaccharide, maltose. The reaction is as under

   $$2\alpha-\mathrm{D}-\text{glucose} \quad \rightarrow \quad \text{maltose}$$

   Calculate the enthalpy of the reaction. The enthalpies of combustion for crystalline α-D-glucose and maltose at 298 K are -2809.1 kJ mol^{-1} and -5645.5 kJ mol^{-1} respectively.

5. The thermochemical equation for the combustion of ethanol is given below,

   $$C_2H_5OH(l)+3\ O_2(g)\rightarrow 2\ CO_2(g)+3\ H_2O(l) \quad \Delta_{comb}H = -1368.82\ \text{kJ mol}^{-1}$$

   Calculate the enthalpy of formation of ethanol. (You may use the data from Table 3.2 as required)

6. The standard enthalpy of formation of NO_2 (g) is found to be -33.18 kJ mol^{-1}. Calculate the enthalpy of formation of NO_2 at 100^{oC}. The C_p values are:

$O_2(g) = 29.36$; $NO_2(g) = 37.20$; $N_2(g) = 29.13$. Assume the heat capacity values to be temperature independent in the range of the temperature.

3.9 ANSWERS

Self-Assessment Questions

1. As per the Eq. (3.1) and (3.2) we can write,

   $q_{\text{rexn.}} = -C_{\text{calorimeter}}\,\Delta T$

   Given: $\Delta T = 3.9$ K $C_{\text{calorimeter}} = 9.4$ k J K^{-1}

   Substituting the values in the equation,

   $q_{\text{rexn.}} = -9.4 \text{ kJ K}^{-1} \times 3.9 \text{ K} = -36.66 \text{ kJ}$

   Thus, the combustion of 1.75 g of ethanol with an excess of oxygen is associated with the release of 36.66 kJ of energy as heat. In order to obtain the heat change expected for 1 mole of ethanol we calculate the change per gram and then per mole as given below.

   Heat change per g of ethanol

   $$q_{\text{rexn.}} = \frac{-36.66\text{kJ}}{1.75\text{g}} = -20.95\text{k J g}^{-1}$$

   Heat change per mole of ethanol =

   $$q_{\text{rexn.}} = -20.95\,\text{kJg}^{-1} \times 46\ \text{gmol}^{-1} = -963.7\,\text{kJ mol}^{-1}$$

2. $\Delta n_g = n_g(\text{products}) - n_g(\text{reactants}) = 2-1=1$

   We know: $\Delta_r U = \Delta_r H - \Delta n_g RT$

   Substituting the values,

   $$\Delta_r U = 46.11\text{kJ mol}^{-1} - (1 \times 8.314\,\text{J K}^{-1}\text{mol}^{-1} \times 298\text{K})$$

   $$= 46.11\text{ kJ mol}^{-1} - 2.48\text{ kJ mol}^{-1} = 43.63\text{ kJ mol}^{-1}$$

3. As per example 3.3,

   $$H_2(g) + Cl_2 \rightarrow 2HCl(g) \qquad \Delta_r H = -184.6\text{ kJmol}^{-1}$$

   The given expression can be obtained by dividing this equation by 2 therefore the enthalpy change also would be half of the value in the example. That is we can write,

   $$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow HCl(g)\ \Delta_r H = \frac{-184.6}{2} = -92.3\text{ kJmol}^{-1}$$

4. As per Eq.(3.28) the enthalpy of the combustion for the given reaction can be written as

   $$\Delta_{\text{Comb}}H^\circ = 12\Delta_f H^\circ(CO_2(g)) + 6\Delta_f H^\circ(H_2O(l)) - 2\Delta_f H^\circ(C_6H_6(l)) - 15\Delta_f H^\circ(O_2(g))$$

Substituting the values from the Table 3.1, we get,

$$-(12\times 393.5)-(6\times 285.8)-2\Delta_f H^\circ(C_6H_6(l))-0.0=-6535\ \text{kJmol}^{-1}$$

Solving, $-2\Delta_f H^\circ(C_6H_6(l))=-98.2\ \text{kJmol}^{-1}$

$$\Rightarrow \Delta_f H^\circ(C_6H_6(l))=-49.1\ \text{kJmol}^{-1}$$

5. The process can be represented by the following equation,

$$\text{HCl 25(aq)} + \infty\text{(aq)} \rightarrow \text{HCl}\infty\text{(aq)}$$

In order to calculate the enthalpy change for the process we use the thermochemical Eq. (3.50) and Eq. (3.54)

$$\text{HCl(g)} + 25\text{(aq)} \rightarrow \text{HCl 25(aq)} \qquad \Delta H = -72.03\ \text{kJ mol}^{-1} \qquad \ldots(3.50)$$

$$\text{HCl(g)} + \infty\text{(aq)} \rightarrow \text{HCl}\ \infty\text{(aq)} \qquad \Delta H = -74.85\ \text{kJ mol}^{-1} \qquad \ldots(3.54)$$

Subtracting Eq. (3.50) from Eq. (3.54) we get

$$\text{HCl 25(aq)} + \infty\text{(aq)} \rightarrow \text{HCl}\ \infty\text{(aq)} \qquad \Delta H = -2.82\ \text{kJ mol}^{-1}$$

6. The reaction can be represented as

In order calculate the enthalpy of the reaction we first need to list the bonds being broken and the bonds being formed.

The bonds being broken: 1 C=C, 4 C-H and 1 H-Br

The bonds being made: 1 C-C , 5 C-H and 1 C-Br

The energy spent on breaking the bonds,ΣBond Enthalpy (Reactants)

= 1 (620 kJ mol^{-1}) + 4 (415.9 kJ mol^{-1}) + 1 (366.1 kJ mol^{-1})

= 2649.7 kJ mol^{-1}

The energy released on making the bonds, ΣBond Enthalpy (Products)

= 1 (347 kJ mol^{-1}) + 5 (415.9 kJ mol^{-1}) + 1 (234)

= 2660 kJ mol^{-1}

The enthalpy of reaction:

$\Delta_r H^\circ$ = ΣBond Enthalpy (Reactants) –ΣBond Enthalpy (Products)

Substituting the values,

$$\Delta_r H^\circ = 2649.17 - 2660.5 = -10.8\ \text{kJmol}^{-1}$$

Thus, the enthalpy of addition of HBr to ethene as calculated above on the basis of bond enthalpies is found to be = -10.8 kJ mol^{-1}.

Terminal Questions

1. In constant volume calorimetry a known quantity of the reactant and oxygen gas under pressure is placed in the container and combusted with the help of an electrical ignition. The reaction is accompanied with a minor explosion. It is because of this the reaction vessel is called a bomb.

2. A thermochemical equation is an equation that is a combination of the chemical equation and the associated enthalpy change. It consists of the chemical formulae of the reactants and the products along with their stoichiometric coefficients, physical state and enthalpy change.

   The salient features of the thermochemical equations are as under:

   - The enthalpy change refers to the reaction as written i.e., it corresponds to one mole of the reaction. If a thermochemical equation is multiplied by a factor ‘n’ on both sides, then the enthalpy change, $\Delta_r H$, for the reaction must also change by the same factor.
   - It is mandatory to specify the state of the reactants and the products in the thermochemical equation
   - In case the chemical equation is reversed, the sign of enthalpy change would change; magnitude remaining the same.

3. The standard state of a substance at a specified temperature is defined as its pure form at a pressure of 1 bar. We need to define a standard state so as to be able to define the standard enthalpy change, which is the enthalpy change for a reaction in which the reactants and products are in their standard states. This facilitates the compilation and comparison of the enthalpy change data.

4. On the basis of given data we can write the following thermochemical equations:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O(l) \quad \Delta_{comb.}H = -2809.1 \text{ kJ mol}^{-1}$$

$$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O(l) \quad \Delta_{comb.}H = -5645.5 \text{ kJ mol}^{-1}$$

Multiply Eq.1 by 2

$$2C_6H_{12}O_6 + 12O_2 \rightarrow 12CO_2 + 12H_2O(l) \quad \Delta_{comb.}H = -5618.2 \text{ kJmol}^{-1}$$

Subtracting Eq.2 from the above equation, we get

$$2C_6H_{12}O_6 \rightarrow C_{12}H_{22}O_{11} + H_2O(l) \qquad \Delta_r H = -27.3 \text{ kJ mol}^{-1}$$

5. On the basis of given thermochemical equation we can write,

$$\Delta_{comb.}H^o = -1368.82 \text{ kJ mol}^{-1}$$

$$= 3\Delta_{f.}H^o (H_2O(l) + 2\Delta_{f.}H^o (CO_2(g)) - \Delta_{f.}H^o (C_2H_5OH(l) - 3\Delta_{f.}H^o (O_2(g))$$

Substituting the values,

$$-1368.82 \text{ kJ mol}^{-1} = 3\ (-285.8) + 2\ (-393.5) - \Delta_f H^o\ (C_2H_5OH(l)) - 3\ (0.0)$$

Solving we get

$$\Delta_f H^o\ (C_2H_5OH(l)) = -275.58 \text{ kJ mol}^{-1}$$

6. The formation of NO_2 can be given as

$$\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \quad \Delta_f H = -33.18 \text{ kJmol}^{-1}$$

As per Eq. (3.63): $\Delta_r H^o(T_2) = \Delta_r H^o(T_1) + \Delta C_p^o\ (T_2 - T_1)$

We begin by calculating the ΔC_p^o values

$$\Delta C_p^o = C_p^o[NO_2(g)] - C_p^o[O_2(g)] - \frac{1}{2}C_p^o[N_2(g)]$$

Substituting the values

$$\Delta C_p^o = 37.20 - 29.36 - \frac{1}{2}(29.13) \text{ J K}^{-1}\text{mol}^{-1}$$

Solving

$$\Delta C_p^o = 6.725 \text{ J K}^{-1}\text{mol}^{-1}$$

Substituting in Eq. (3.63)

$$\Delta H^o(373.15) = -33.18 \text{kJ}^{-1}\text{mol}^{-1} - 6.725 \text{J K}^{-1}(373.15 - 298) \text{ K}$$

Solving, we get

$$\Delta H^o(373.15) = -33.685 \text{kJ}^{-1}\text{mol}^{-1}$$

UNIT 4

SECOND AND THIRD LAWS OF THERMODYNAMICS

Structure

4.1 INTRODUCTION

In the previous unit you have learnt about thermochemistry i.e., application of the First Law of thermodynamics to the study of heat changes associated with chemical reactions. In the last unit of this block we would take up Second and the Third Laws of thermodynamics. You would recall that the First Law of thermodynamics concerns about the conservation of energy. However, it does not say anything about the direction in which thermodynamic processes may proceed. The direction of thermodynamic processes is the subject matter of the Second Law of thermodynamics.

To learn about the Second Law we would begin by a initiating a discussion on spontaneity and the need for a criterion for the same. For this we would take up spontaneous and non-spontaneous processes and check whether the internal energy and enthalpy, the two thermodynamic properties related to the first law, could serve as criterion for spontaneity? This will be followed by introduction of the concept of entropy-another state function. This would also be put to test as a criterion for spontaneity. Then we would take up different statements of the Second Law of thermodynamics.

Having learnt about the Second Law of thermodynamics we would briefly discuss about an important thermodynamic parameter viz., Gibbs energy and outline its significance and properties. Thereafter, we would move to the Third Law of thermodynamics. After stating the law we would introduce absolute entropy and take up its determination for a system. Towards the end of the unit we would explain the concept of residual entropy. In the next block you would learn about the chemical and ionic equilibrium.

Expected Learning Outcomes

After studying this unit, you should be able to:

- explain spontaneous and non-spontaneous processes giving suitable examples;
- establish the inadequacy of enthalpy as a criteria for spontaneity using suitable examples;
- explain the concept of entropy as a measure of dispersal of energy and matter;
- give the thermodynamic and statistical definitions of entropy;
- explain the statistical viewpoint of entropy;
- demonstrate that entropy can act as a thermodynamic criteria for spontaneity of a reaction;
- give different statements of the Second Law of thermodynamics;
- define Gibbs energy and outline its significance;
- explain the difference between enthalpy driven and entropy driven reactions;
- ascertain using the data whether a given reaction is enthalpy driven or entropy driven;
- state and give significance of the Third Law of thermodynamics;
- determine the absolute entropy for a given system using the provided data;
- define and explain the concept of residual entropy for a system; and
- explain the meaning of the Third Law entropy for a system.

4.2 SPONTANEITY

One of the most significant considerations for a practicing Chemist when s/he is planning a new chemical reaction is that whether or not would the reaction occur under given set of conditions−say at room temperature and pressure? In other words, would the reaction be spontaneous? A criterion to determine the spontaneity of a reaction is provided by the Second Law of thermodynamics in terms of the thermodynamic property called entropy (S). Let's first learn about the spontaneous and non-spontaneous processes to understand about entropy and its suitability as a criterion for spontaneity.

4.2.1 Spontaneous and Non-Spontaneous Processes

You must have seen and enjoyed a waterfall from a hill either in person or in a movie / picture. The water always flows downhill and never in the reverse direction on its own. Have you ever wondered why? It is an example of a **spontaneous process**−*a process that occurs on its own under a given set of conditions without the aid of any external agency*. That is once the process is started, no action from outside the system is necessary to make it to continue. We have a number of examples of spontaneous processes. Some of these being

- Hot water kept in a bucket cools down to the room temperature over a period of time,
- Water kept in a refrigerator maintained at −5°C freezes spontaneously,
- Ice melts spontaneously at room temperature of say 298 K,
- A ball bouncing on the floor gradually comes to rest on the floor,
- An iron nail kept in open spontaneously gets rusted,
- A cube of sugar added to a glass of water dissolves spontaneously,
- A drop of ink added to a beaker of water spreads till the water is uniformly coloured,
- A puff of scent anywhere in the room spreads all over the room

You can visualise that, none of these processes occur in the reverse direction on their own. Water at room temperature (say 298 K) would not become hot or freeze on its own; the dissolved sugar would not come out of solution; the rusted nail would not get converted into clean nail on its own; a ball kept on the floor will not start bouncing by itself. Such processes are called **non-spontaneous processes**. We need to supply energy in some form or the other for such non-spontaneous processes to occur. A book kept at the edge of a table may fall down spontaneously but someone would have to pick up and keep it back; it won't happen on its own. You may note here that *if a physical or a chemical change is spontaneous in one direction, it is not spontaneous in the opposite direction*. Secondly, *both spontaneous and non-spontaneous processes are possible, but only spontaneous processes occur on their own; the non-spontaneous processes require the help of an external agent to occur*.

Spontaneous does not mean instantaneous and has nothing to do with how long a process takes to occur. It means that if enough time is given, the process will happen by itself. There are many processes that are spontaneous but very slow for example, rusting of iron, ripening of fruits and aging.

You should keep in mind that thermodynamic spontaneity is not related to the speed of the reaction or the process. A reaction being spontaneous does not mean that it would occur very fast or at a measurable rate. For example, the reaction between hydrogen and oxygen gas to give water is a spontaneous reaction but under ordinary conditions we can keep hydrogen and oxygen together for any length of time without getting even a trace of water. The rate of the reaction comes in the domain of Chemical Kinetics about which you would learn in a later course. For now, let's raise a question, "Can the First Law of thermodynamics explain spontaneity of physical and chemical processes"?

To answer this question we take the example of the water in a river flowing down a hill. As the water flows down it loses its potential energy, which is converted into the kinetic energy of the molecules. If we account for the frictional losses during its flow we can find that the loss in potential energy of water is exactly equal to the gain in its kinetic energy. This is as expected from the First Law of thermodynamics according to which the total energy remains constant. On the other hand, though we have never seen rivers flowing upwards, if the river could flow upwards the kinetic energy of the flowing water would be converted into its potential energy such that the total energy remains constant. That is, in principle such a process is not ruled out according to the First Law. In other words, we can say that according to the First Law of thermodynamics the water in river may flow downhill or uphill. However, our experience tells us that the river flows *only* downhill on its own. This is a serious limitation of the First Law that it does not say anything about the directionality or spontaneity of a process.

Let's see whether energy (enthalpy) change for a process can act as criterion for spontaneity?

4.2.2 Enthalpy and Spontaneity

Let's revisit the examples of waterfall and the book falling from the table. We note here that in both of these cases the potential energy of the system decreases. Internal energy or the related thermodynamic property, enthalpy is analogous to the energy of a mechanical system. Then, can we say that 'decrease in internal energy or enthalpy' makes a process spontaneous? In fact P. Berthelot and J. Thomsen proposed in 1870s that the spontaneous processes occur in the direction in which the enthalpy of the system decreases. This proposal got support from the fact that a number of spontaneous chemical reactions were found to be exothermic, i.e., accompanied by a decrease in enthalpy. Some of the common examples of spontaneous exothermic reactions are

Combustion of methane

$$\mathrm{CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)} \qquad \Delta_r H = -890.4\ \mathrm{kJ\ mol^{-1}} \quad \ldots (4.1)$$

Acid-base neutralization

$$\mathrm{H^+(aq) + OH^-(aq) \rightarrow H_2O(l)} \qquad \Delta_r H = -56.2\ \mathrm{kJ\ mol^{-1}} \quad \ldots (4.2)$$

Rusting of iron

$$\mathrm{2Fe(g) + \frac{3}{2}O_2(g) \rightarrow Fe_2O_3(s)} \qquad \Delta_r H = -826\ \mathrm{kJ\ mol^{-1}} \quad \ldots (4.3)$$

On the other hand, there are a number of spontaneous chemical reactions and physical processes that are endothermic, i.e., accompanied by an increase in enthalpy. Some examples being,

Dissolution of ammonium nitrate

$$NH_4NO_3(s) + H_2O \rightarrow NH_4^+(aq) + NO_3^-(aq) \qquad \Delta_r H = +25 \text{kJ mol}^{-1} \qquad \ldots(4.4)$$

Decomposition of nitrogen pentaoxide

$$N_2O_5(s) \rightarrow 2NO_2(g) + \frac{1}{2}O_2(g) \qquad \Delta_r H = +109.5 \text{ kJ mol}^{-1} \qquad \ldots(4.5)$$

Evaporation of water at room temperature

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta_r H = +44 \text{kJ mol}^{-1} \qquad \ldots(4.6)$$

Decomposition mercury(II) oxide at high temperature

$$2HgO(s) \rightarrow 2Hg(l) + O_2(g) \qquad \Delta_r H = +90.7 \text{kJmol}^{-1} \qquad \ldots(4.7)$$

From these examples we can infer that the exothermic nature of a reaction or process favours its spontaneity however it does not guarantee the same. In other words, we **cannot** use enthalpy (or internal energy) as a criterion for spontaneity.

The natural direction of spontaneous processes in the examples stated above can be easily judged by observing the initial and final states of the system. This in turn suggests that we may have a new *state function* that could predict the directionality of spontaneous processes. That is, in order to predict the spontaneity of a chemical reaction we need a yet another thermodynamic property that happens to be a state function. This property is entropy about you would learn in the next subsection. However, before that answer the following simple self assessment question.

SAQ 1

What are spontaneous reactions? Can internal energy serve as a criterion for spontaneity of a chemical reaction?

4.2.3 Entropy

In order to explain the direction of spontaneous change, German physicist and mathematician Rudolf Clausius introduced the concept of entropy−a new thermodynamic quantity in 1865. More than two decades later Austrian physicist and philosopher, Ludwig Boltzmann proposed a statistical view of entropy. The two views were later shown to be equivalent. In order to understand about entropy let's take some of the examples of spontaneous processes given above and analyse them.

- The first example we take is, "hot water kept in a bucket cools down to the room temperature over a period of time". In this case to begin with the molecules of hot water and the molecules constituting the bucket have high kinetic energy (you know that the kinetic energy is proportional to the absolute temperature). This energy is dissipated (or is dispersed) to the molecules of air in the immediate vicinity and the floor where the bucket is kept. Over a period of time, due to the random motion of the molecules of the air and the floor this energy is further spread out to infinite surroundings. The process is spontaneous and continues till the temperatures of the water in bucket and the surroundings become equal. The reverse of all this is improbable. It can never happen that the molecules of air surrounding the bucket or the floor, at the same temperature as the bucket and the water in it, transfer their energy to the water in the bucket and it becomes hot. From this we can conclude that the energy of a system spontaneously “spreads out” or “disperses”.

- As the second example let’s consider another spontaneous process, viz., “puff of scent anywhere in the room spreads all over the room”. When we open a bottle of scent anywhere in the room the molecules of scent spontaneously spread out to the whole room. The reverse never happens i.e., the perfume spread in a room does not on its own accumulate and get back into the bottle (it is like running a film in the reverse direction). Here what we observe is that like energy, matter also spontaneously “spreads out or disperses”.

- We can also consider the example of spontaneous evaporation of water though it is an endothermic process. This phase change involves going from a state (liquid) with water molecules having limited freedom to move around each other, to a state (gas) with much greater freedom of particle motion.

- Similarly, in the case of another endothermic process viz., dissolution of ammonium nitrate involves a change from initial state of an ordered crystalline solid and relatively less ordered pure liquid to final state of highly disordered ions and solvent molecules moving and interacting throughout the solution. Here again, the energy of motion of particles is much more dispersed in the spontaneous process.

In addition to the examples discussed above, let’s perform an experiment to understand entropy. Let’s consider two glass flasks having equal volumes (*V*) interconnected by a stopcock as shown in the Fig. 4.1. One of these flasks (say A) contains a certain amount of an ideal gas at a certain pressure (say 1 bar) while the other flask (B) is fully evacuated. The whole apparatus is immersed in a thermostat so that the temperature remains constant throughout the process. Now, when we open the stopcock, the gas in flask A spontaneously expands into the evacuated flask B. The molecules get dispersed throughout the apparatus, such that both the flasks have equal numbers of gas molecules. As after expansion the ideal gas occupies double its initial volume the pressure becomes half i.e., 0.5 bar.

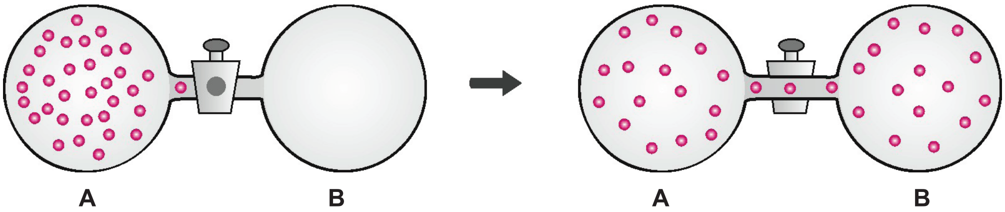


Fig. 4.1: Demonstrating that spontaneous expansion of a gas against vacuum leads to dispersal of energy.

In this spontaneous process, the change in internal energy (ΔU) would be zero as the temperature of the system does not change and for an ideal gas the internal energy depends on the temperature.

Further, as the gas expands into vacuum i.e., against zero opposing pressure, the work of expansion ($p\mathrm{d}V$) is also zero. Therefore, as a result, the enthalpy change ($\Delta H = \Delta U + p\mathrm{d}V$) for the process is zero. Now, neither the internal energy is changed nor the enthalpy, then what causes this process to happen on its own? Since the volume available to the gas has increased there is much greater freedom of particle motion. In other words, the energy of motion is much more dispersed. It is this dispersal of energy that is the 'driving force' behind the spontaneous process.

The dispersal of matter leads to more disorder. Therefore, entropy can be taken as a measure of disorder. As we heat a solid to its melting point the particles in the liquid so obtained are more disordered. Similarly when we heat a liquid to convert it to a gas then there is much more disorder. Hence, the entropy varies as g > l > s

On the basis of the examples considered above, we can conclude that a change in the freedom of motion of particles in a system and the dispersal of their energy of motion is important in determining the direction of a spontaneous process. The dispersal of energy is measured in terms of a thermodynamic property called **entropy**; greater the dispersal, greater is the entropy. Like internal energy and enthalpy, entropy is also a state function; that is it depends on the initial and final states of the system and does not depend on how (the path taken) the final state has been achieved. Having got some kinds of a mental picture of entropy now let's give a thermodynamic definition to it.

Thermodynamic Definition of Entropy

The thermodynamic property identified with this dispersal of energy in spontaneous processes as discussed above is called entropy. It is denoted as *S* and defined as per the following equation

$$\mathrm{d}S = \frac{\mathrm{d}q_{rev}}{T} \qquad \ldots (4.8)$$

Where, $\mathrm{d}q_{rev}$ is the infinitesimal heat exchange between the system and the surroundings at temperature, T K. The importance of Eq. (4.8) is that it relates a small change in entropy, $\mathrm{d}S$ to quantities that are easily interpreted i.e., heat and temperature of the system. Further, since entropy is defined as a ratio of q to T (q/T) its units are J K^{-1}. However, to calculate the entropy change for a system using this expression, we must devise a way to accomplish a given change in a reversible way i.e., the one occurring in an infinite number of infinitesimal steps. So the finite change in entropy $S_f - S_i$ of the system during a process that takes the system from an initial state *i* into a final state *f* can be obtained by integrating Eq. (4.8) i.e.,

$$\Delta S = S_f - S_i = \int_i^f \frac{\mathrm{d}q_{rev}}{T} \qquad \ldots (4.9)$$

Entropy being state function implies that the entropy change ΔS for an irreversible process that takes a system from an initial state i to a final state f is exactly equal to the entropy change ΔS for any reversible process that takes the system between those same two states

You must remember that the entropy change in a system is calculated by assuming the process to be reversible, irrespective of the fact that whether the process is reversible or not. We would calculate the entropy changes associated with different processes. However, before that let us learn about the statistical definition of entropy.

Statistical definition of entropy

We have so far talked qualitatively about entropy as a measure of more disorderly distribution of matter and a greater dispersal of energy. Austrian mathematician and physicist **Ludwig Boltzmann** in 1877 provided a quantitative interpretation of these in terms of number of microstates i.e., *the number of ways in which the molecules of a system can be arranged while keeping the total energy of the system constant.* He proposed that the entropy of a system is given by the following expression.

$$S = k \ln W \qquad \ldots (4.10)$$

Where, k is the Boltzmann constant (=1.381 x 10^{-23}J K^{-1}) and W is the number of microstates. It is obvious that a state with more microstates has greater entropy. In order to understand the concept let us consider a hypothetical system with four molecules in a container, which is divided (by an imaginary partition) into two equal parts as shown in Fig. 4.2. Let us label these parts as part A and part B. Now we try to think of different possibilities of the distribution of the molecules in the box. In one of the ways, all the molecules can be in the part A and none in part B. There is only one way to arrange the molecules like this. Now suppose we distribute the molecules in such a way that the part A has three molecules and part B has only one molecule. There are four different possible arrangements as shown in the figure.

Boltzmann constant can be seen as universal gas constant divided by Avogadro's number, i.e., gas constant per molecule; R / N_A

If we continue and distribute the molecules equally in the two parts such that each part has two molecules then there are six different possible arrangements as shown. Similarly we can show that there are four different ways of arranging one molecule in the part A and three molecules in part B. Once again there is only one way of arranging molecules such that all the four molecules are in part B and none in part A. Thus, there are a total of sixteen different ways of arranging 4 molecules in two parts of the box.

For N molecules there are 2^N different possibilities

The sixteen possible different ways of distributing the molecules shown in the figure are called microscopic states or *microstates*. Further, each set of similar microstates is called a *distribution* or a *state*. The probability of a particular distribution depends on the number of microstates in it. In this example, we have five different states or distributions (I-V). You can note that of the possible distributions, the distribution III is the most probable as this can be achieved in six possible ways or has six microstates. On the other hand, the distributions I and V are least probable with only one microstate each. Thus, we can see that the state with even (equal) distribution of molecules in the two parts is most probable.

The entropy change for a process in which the system goes from an initial state i to final state f can be given as

$$\Delta S = S_f - S_i = k \ln W_f - k \ln W_i \qquad \ldots (4.11)$$

$$\Delta S = k \ln \frac{W_f}{W_i} \qquad \ldots (4.12)$$

Where S_i and S_f are the entropies of the system in the initial and final states and W_i and W_f are the corresponding numbers of microstates.

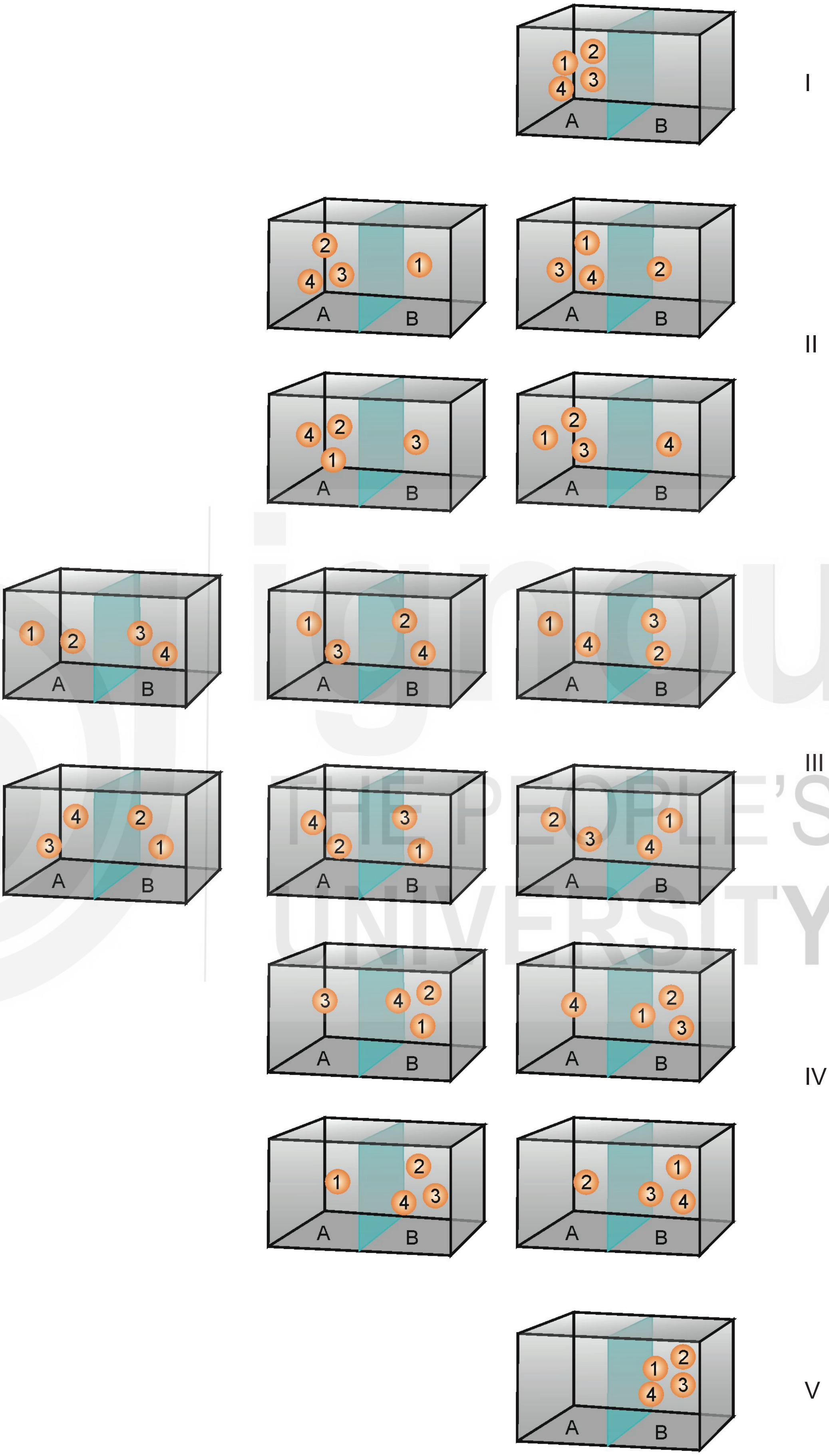


Fig. 4.2: Different possible ways of distributing four molecules in two equal parts of a box.

If the number of microstates in the final state (W_f) is greater than that in the initial state (W_i) then ΔS is positive i.e., entropy increases. On the other hand, if the number of microstates in the final state is lesser the entropy decreases. On the basis of what you have learnt about entropy answer the following simple question.

SAQ 2

State whether the entropy of the system would increase or decrease in the following processes.

i) Condensation of a gas to form a liquid

ii) Crystallisation from a saturated solution

iii) Sublimation of a solid

iv) Dissolution of sucrose in water

4.2.4 Entropy Changes in Some Simple Processes

Having learnt about the thermodynamic and statistical definitions of entropy let's calculate the entropy changes associated with some simple processes. We start with the isothermal expansion of an ideal gas.

a) Reversible Isothermal Expansion of an Ideal Gas

Let's take 1 mole of an ideal gas having a volume of V_1 at a pressure p_1 and expand it reversibly to a volume V_2 under isothermal conditions i.e., the temperature is maintained at T K. For such a process the Eq. (4.9) becomes

$$\Delta S = \frac{1}{T}\int_i^f \mathrm{d}q_{rev} = \frac{q_{rev}}{T} \qquad \text{…(4.13)}$$

Further, you would recall again that in such an isothermal process the change in internal energy would be zero (ΔU=0) as for an ideal gas the internal energy depends on temperature of the system and here the temperature does not change. Also, from the First Law of thermodynamics, we can write

$$\Delta U = q + w \qquad \text{…(2.1)}$$

In the present context (reversible expansion) we can write,

$$\Delta U = q_{\text{rev}} + w_{\text{rev}} \qquad \text{…(4.14)}$$

Now, since ΔU=0 we can write

$$0 = q_{\text{rev}} + w_{\text{rev}} \;=>\; q_{\text{rev}} = -\,w_{\text{rev}} \qquad \text{…(4.15)}$$

From Unit 2 you would recall that the expression for work for isothermal reversible expansion of an ideal gas is given by Eq. (2.66),

$$w_{rev} = -2.303\,nRT\log\frac{V_2}{V_1} \qquad \text{…(2.66)}$$

Substituting in Eq. (4.15) we get,

$$q_{rev} = -w_{rev} = -(-2.303\ nRT\log\frac{V_2}{V_1}) = 2.303\ nRT\log\frac{V_2}{V_1} \qquad \text{…(4.16)}$$

Substituting Eq. (4.16) in Eq. (4.13) we get

$$\Delta S = \frac{q_{rev}}{T} = \frac{1}{T}(2.303\ nRT\log\frac{V_2}{V_1})$$

$$\Rightarrow \qquad \Delta S = 2.303\ nR\log\frac{V_2}{V_1} \qquad \text{…(4.17)}$$

We know that for an ideal gas $p_1V_1 = p_2V_2,$ so we can replace $\frac{V_2}{V_1}$ in Eq. (4.17) by $\frac{p_1}{p_2}$ to get,

$$\Rightarrow \qquad \Delta S = 2.303\ nR\log\frac{p_1}{p_2} \qquad \text{…(4.18)}$$

Thus, Eq. (4.17) and Eq. (4.18) are the desired expressions to compute entropy change for reversible isothermal expansion of an ideal gas. The corresponding expressions for one mole of an ideal gas (or molar entropy changes) would be:

$$\Rightarrow \qquad \Delta S_m = 2.303\ R\log\frac{V_2}{V_1} \qquad \text{…(4.19)}$$

$$\Rightarrow \qquad \Delta S_m = 2.303\ R\log\frac{p_1}{p_2} \qquad \text{…(4.20)}$$

As per Eq. (4.17) for reversible isothermal expansion of an ideal gas the entropy change would be positive, i.e., the entropy would increase. From the same expression we can conclude that in case of isothermal compression since V_2 will be less than V_1 the entropy would decrease. Let us take an example to see the application of the expression derived above.

Example 4.1: 1 mole of neon gas behaving ideally is taken in a cylinder fitted with massless and frictionless piston and occupies a volume of 10 dm^3. If the gas is reversibly expanded to double its volume at 298 K, calculate the entropy change for the process.

Solution: The entropy change for reversible isothermal expansion of a gas is given by the following expression; Eq. (4.17).

$$\Rightarrow \qquad \Delta S = 2.303\ nR\log\frac{V_2}{V_1}$$

The data provided is as under

n = 1.00 mol $\qquad$ V_1= 10 dm^3 $\qquad$ V_2= 20 dm^3

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

Substituting the values in the equation we get

$$\Rightarrow \qquad \Delta S = 2.303 \times 1.0\,\text{mol} \times 8.314\,\text{J K}^{-1}\,\text{mol}^{-1} \log \frac{20}{10}$$

$$\Rightarrow \qquad \Delta S = 19.147\,\text{J K}^{-1} \log 2 = 5.76\,\text{J K}^{-1}$$

b) Adiabatic Expansion of an Ideal Gas

As you know that in an adiabatic process, there is no associated heat change i.e., $q = 0$ therefore, the entropy change would be

$$\Delta S = \frac{q_{rev}}{T} = 0$$

c) Isothermal Mixing of Ideal Gases

Let us take n_A moles of an ideal gases A and n_B moles of ideal gas B at same pressure in two glass flasks (A and B) of respective volumes of V_A and $V_B$connected by a stopcock as shown in Fig. 4.3 (a). The whole system is placed in a thermostat to keep the temperature constant. On opening the stopcock the two gases mix spontaneously Fig. 4.3 (b). The process can be represented as

$$\text{A(g)} \quad + \quad \text{B(g)} \quad \rightarrow \quad \text{Mixture of A(g) and B(g)} \qquad \ldots(4.21)$$

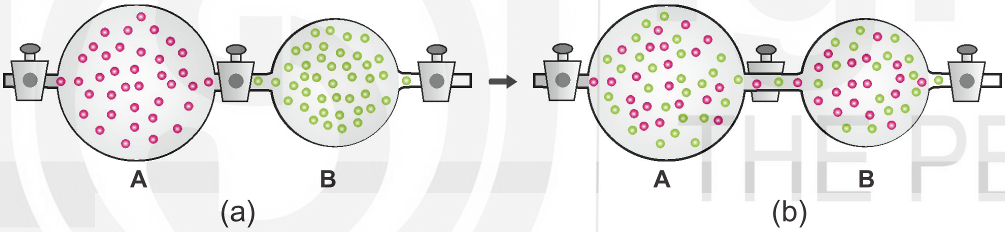


Fig. 4.3: Isothermal mixing of ideal gases.

After mixing both the gases occupy a final total volume (= $V_A + V_B$). Therefore, the mixing process can be assumed to be equal to combined effect of A(g) and B(g) expanding to a final volume of $V_A + V_B$ from their respective initial volumes of V_A and V_B respectively. We can write the corresponding isothermal entropy changes by using Eq. (4.17), as below

For expansion of A(g) $\quad \Rightarrow \Delta S_{A(g)} = 2.303\; n_A\; R \log \frac{V_A + V_B}{V_A} \qquad \ldots(4.22)$

For expansion of B(g) $\quad \Rightarrow \Delta S_{B(g)} = 2.303\; n_B\; R \log \frac{V_A + V_B}{V_B} \qquad \ldots(4.23)$

The total entropy change for the mixing process is equal to the sum of the entropy changes of expansion of A(g) and B(g):

$$\Delta S_{mixing} = \Delta S_{A(g)} \; + \; \Delta S_{B(g)} \qquad \ldots(4.24)$$

$$\Delta S_{mixing} = 2.303R \left[n_A \log \frac{V_A + V_B}{V_A} + \; n_B \log \frac{V_A + V_B}{V_B} \right] \qquad \ldots(4.25)$$

We know that for an ideal gas

$pV = nRT$

$\Rightarrow V = nRT / p$

If p, R and T are const.

$n \propto V$

$n_A \propto V_A; n_B \propto V_B$

$n_T \propto V_A + V_B$

$X_A = \frac{n_A}{n_A + n_B} = \frac{V_A}{V_A + V_B}$

$X_B = \frac{n_B}{n_A + n_B} = \frac{V_B}{V_A + V_B}$

In the mixture of gases the mole fractions of the gases would be

$$\text{Mole fraction of A(g)= } X_A = \frac{V_A}{V_A + V_B} \qquad \ldots(4.26)$$

$$\text{Mole fraction of B(g)= } X_B = \frac{V_B}{V_A + V_B} \qquad \ldots(4.27)$$

Substituting Eq. (4.26) and Eq. (4.27) in Eq. (4.25), we get

$$\Delta S_{mixing} = 2.303R\left[n_A \log\left(\frac{1}{X_A}\right) + n_B \log\left(\frac{1}{X_B}\right)\right] \qquad \ldots(4.28)$$

$$\Delta S_{mixing} = 2.303\ R\ [\ -n_A \log(X_A) - n_B \log(X_B)] \qquad \ldots(4.29)$$

$$\Delta S_{mixing} = -\ 2.303\ R\ [\ n_A \log(X_A) + n_B \log(X_B)] \qquad \ldots(4.30)$$

As the values of mole fractions of the two gases are less than 1; their logs will be negative so both the terms in the bracket would be negative. This implies that ΔS_{mixing} of the gases would be positive.

d) Expansion and Heating of an Ideal Gas

In the cases considered above we have taken systems where only one parameter viz., the volume is allowed to change during the process. We may have thermodynamic processes wherein more than one of the thermodynamic parameters of the system can change. Such processes are called *composite processes*. Let us consider one such process wherein a gaseous system at initial state characterised by (V_1, T_1) changes to final state (V_2, T_2). That is in this case both the volume and the temperature of the gas is different in the initial and final states.

In order to compute the associated entropy change, we make use of the fact that the entropy is a state function. Since entropy is a state function, we can choose any convenient path to go from the initial state to the final state. We can achieve the given changes in the thermodynamic parameters of the system by first considering reversible isothermal expansion of the gas from volume V_1 to volume V_2 at temperature T_1, followed by reversible heating of the gas at constant volume (V_2) to the final temperature T_2. The total entropy change would be the sum of the two contributions.

$$(V_1, T_1) \xrightarrow{\mathrm{I}} (V_2, T_1) \xrightarrow{\mathrm{II}} (V_2, T_2) \qquad \ldots(4.31)$$

For the first step we can write the entropy change by using Eq. (4.17)

$$\Rightarrow \qquad \Delta S_{\mathrm{I}} = 2.303\ nR \log\frac{V_2}{V_1}$$

For second step, as the process involves reversibly heating the gas at constant volume (i.e., ΔV=0) which means that w=0. In such a case we can write from the First Law expression (Eq. 2.1)

$$\Delta U = q_{\text{rev}}$$

From Eq. (2.21) we know that

$$\Delta U = C_v \mathrm{d}T$$

Therefore, we can write

$$\Delta S_{\mathrm{II}} = \frac{q_{rev}}{T} = \int_{T_1}^{T_2} \frac{C_V \mathrm{d}T}{T} \qquad \ldots(4.32)$$

Taking C_V out of the integration sign and integrating the equation, we get

$$\Delta S_{\mathrm{II}} = C_V \int_{T_1}^{T_2} \frac{\mathrm{d}T}{T} = C_V \Big[\ln T\Big]_{T_1}^{T_2} \qquad \ldots(4.33)$$

$$\Delta S_{\mathrm{II}} = C_V \ln\frac{T_2}{T_1} = 2.303 \log\frac{T_2}{T_1} \qquad \ldots(4.34)$$

Thus, the overall entropy change for the process would be

$$\Rightarrow \quad \Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} = 2.303\left[nR\log\frac{V_2}{V_1} + C_V\log\frac{T_2}{T_1}\right] \qquad \ldots(4.35)$$

Let us take an example to see the application of this expression:

Example 4.2: One mole of an ideal gas is taken in a cylinder fitted with massless and frictionless piston and occupies volume of 2 dm^3 at 298 K. The gas is isothermally and reversibly expanded to ten times its initial volume at 298 K. After this the gas is reversibly heated at constant volume to 323 K. Calculate the entropy change for the overall process. The heat capacity of the gas at constant volume in the range of temperature is given as 12.47 J K^{-1} mol^{-1}.

Solution: As stated there are two stages in the process i.e., isothermal reversible expansion of the ideal gas and isochoric reversible heating of the gas. Let's compute the entropy changes for the two stages one by one.

Stage 1: From Eq. (4.17) the entropy change for isothermal reversible expansion of the ideal gas is given as

$$\Rightarrow \quad \Delta S_{\mathrm{I}} = 2.303\ nR\log\frac{V_2}{V_1}$$

We are given n= 1 mol; V_1= 2 dm^3; V_2= 20 dm^3

We know R= 8.314 J $\mathrm{K}^{-1}\mathrm{mol}^{-1}$

Substituting the values in the equation, we get

$$\Rightarrow \quad \Delta S_{\mathrm{I}} = 2.303 \times 1.0\,\mathrm{mol} \times (8.314\,\mathrm{J\,K^{-1}mol^{-1}})\log\frac{20}{2}$$

Solving, we get,

$$\Rightarrow \qquad \Delta S_{\mathrm{I}} = 19.15\,\mathrm{J\,K^{-1}}$$

Stage 2: For isochoric reversible heating of an ideal gas the molar entropy change can be calculated by using Eq. (4.34)

$$\Delta S_{\mathrm{II}} = C_V \ln\frac{T_2}{T_1} = 2.303\ C_V \log\frac{T_2}{T_1}$$

We are given $C_{V,\mathrm{m}}$= 12.47 J $\mathrm{K^{-1}mol^{-1}}$ T_1 = 298 K T_2 = 323 K

Substituting the values in the expression, we get

$$\Delta S_{\mathrm{II}} = 2.303(12.47\ \mathrm{J\,K^{-1}\ mol^{-1}})\log\frac{323}{298}$$

Solving, we get

$$\Delta S_{\mathrm{II}} = 1.005\ \mathrm{J\,K^{-1}mol^{-1}}$$

Total entropy change for the overall process would be

$$\Rightarrow \qquad \Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} = 19.15\,\mathrm{J\,K^{-1}mol^{-1}} + 1.005\,\mathrm{J\,K^{-1}mol^{-1}} = 20.155\,\mathrm{J\,K^{-1}mol^{-1}}$$

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e) Phase Transformation

We know that matter exists in different physical states (solid, liquid, gas, crystalline forms) called phases. The matter in a given phase can change into another phase under appropriate conditions, for example, a solid transforms into a liquid at its melting point. The change of matter from one phase into another phase is called *phase transition* and the temperature at which these occur are called *transition temperatures* at a given pressure. The change of entropy accompanying the transformation of one mole of a substance from one physical state into another physical state at its transition temperature is called *entropy of phase transformation*. It is denoted as $\Delta_{\mathrm{tr}}S$ and is defined as

$$\Delta_{\mathrm{tr}}S = \frac{q_{tr}}{T_{tr}} = \frac{q_{rev}}{T_{tr}} \qquad \ldots(4.36)$$

The Eq. (4.36) is valid only when the two phases are in equilibrium. Further, as we know that for a process at constant pressure $q_{\mathrm{p}} = \Delta H$, therefore, we can write,

$$\Delta_{\mathrm{tr}}S = \frac{\Delta_{tr}H}{T_{tr}} \qquad \ldots(4.37)$$

Different phase transitions are identified in terms of the process is involved. For example, when one mole of a liquid vaporises to gaseous phase the entropy change is given as under

$$\Delta_{vap}S = \frac{\Delta_{\mathrm{vap}}H}{T_b} \qquad \ldots(4.38)$$

Where, $\Delta_{vap}H$ is the enthalpy of vaporization of the liquid; T_b is the boiling point of the liquid and $\Delta_{vap}S$ is the entropy of vaporisation. Similarly, when one mole of a solid melts to give liquid the entropy change is given by the following expression

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_f} \qquad \ldots(4.39)$$

$\Delta_{fus}H$ is the enthalpy of fusion of the liquid; T_f is the melting point of the liquid and $\Delta_{fus}S$ is the entropy of fusion. It is important to note that the entropy of the reverse processes would be negative of the given process. For example, the entropy of condensation of vapors to liquid phase would be $-\Delta_{vap}S$. Let us take an example for the calculation of entropy change associated with phase transition.

Example 4.3: Elemental sulphur undergoes a phase transition from orthorhombic form to monoclinic form at 363 K. If the molar enthalpy of transition is −402 J mol^{-1}, calculate the entropy of transition.

Solution: The entropy change for phase transition is given by Eq. (4.37)

$$\Delta_{tr}S = \frac{\Delta_{tr}H}{T_{tr}}$$

We are provided with the enthalpy change and the temperature for the transition of elemental sulphur from orthorhombic to monoclinic form. The calculation of the entropy change is quite straightforward.

Substituting the values in the expression, we get

$$\Delta_{tr}S = \frac{-402 \text{ J mol}^{-1}}{363 \text{ K}} = -1.107 \text{ J K}^{-1}\text{mol}^{-1}$$

Having learnt about entropy and entropy changes in different types of processes, let's now check whether it can serve as a criterion for spontaneity?. However, before that answer the following simple questions

SAQ 3

One mole each of two ideal gases at same pressure are taken in two separate containers interconnected with a valve and having volumes of 5 dm^3 and 10 dm^3 respectively at 298 K. On opening the interconnecting valve the gases are allowed to mix. Calculate the entropy of mixing of the gases at 298 K.

SAQ 4

At a pressure of 1 bar, water undergoes fusion at 273.1 K. Write the equation for the process. Calculate the entropy of fusion of water if the molar enthalpy of fusion of water is found to be 6.02 kJ mol^{-1}.

4.2.5 Entropy and Spontaneity

We had demonstrated above that the internal energy and enthalpy do not serve as a criterion to determine the spontaneity of a thermodynamic process. Now, having learnt about a new state function viz., entropy let us evaluate it as a criterion for spontaneity. For this we take up entropy changes in isolated systems. We begin with an isolated system involving a cyclic process of isothermal expansion and compression.

a) Cyclic Isothermal Reversible Expansion and Isothermal Reversible Compression in an Isolated System

Let's take a certain amount of an ideal gas occupying a volume V_1 in a cylinder fitted with a massless and frictionless piston. The system is maintained at temperature T in a thermostat. Now if the gas expands reversibly fromthe initial volume V_1 to V_2, the system would absorb heat equal to q_{rev} from the surroundings and the associated entropy change of the system would be

$$\Delta S_{\text{sys}} = \frac{q_{rev}}{T} \qquad \ldots(4.8)$$

Since the surroundings also loses heat equal to $-q_{\text{rev}}$ in a reversible way, the entropy change, for the surroundings would be

$$\Delta S_{\text{surr}} = -\frac{q_{rev}}{T} \qquad \ldots(4.40)$$

The total entropy change for the isothermal reversible expansion process in the isolated system would be

$$\Delta S_{\text{isoth exp}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{q_{rev}}{T} + \left(-\frac{q_{rev}}{T}\right) = 0 \qquad \ldots(4.41)$$

Once the gas has been reversibly expanded to a volume V_2 under isothermal conditions, we reversibly compress it back to volume V_1 again under isothermal conditions. In such a case the system would lose heat equal to $-q_{\text{rev}}$ to the surroundings and the corresponding entropy change for the system would be

$$\Delta S_{\text{sys}} = -\frac{q_{rev}}{T} \qquad \ldots(4.42)$$

As the surrounding would gain heat equal to q_{rev}, the associated entropy change would be

$$\Delta S_{\text{surr}} = \frac{q_{rev}}{T} \qquad \ldots(4.43)$$

The total entropy change in the isolated system for the isothermal reversible compression process would be

$$\Delta S_{\text{isoth comp}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -\frac{q_{rev}}{T} + \frac{q_{rev}}{T} = 0 \qquad \ldots(4.44)$$

The entropy change for the overall reversible cyclic process in the isolated system would be

$$\Delta S_{\text{cyclic}} = \Delta S_{\text{isoth exp}} + \Delta S_{\text{isoth comp}} = 0 + 0 = 0 \qquad \ldots(4.45)$$

Thus, we see that overall entropy change in a reversible cyclic process in an isolated system is zero. Let us now calculate the entropy changes in a cyclic process having an irreversible step.

b) Cyclic Isothermal Irreversible Expansion and Isothermal Reversible Compression in an Isolated System

Let's again take a certain amount of an ideal gas occupying a volume V_1 in a cylinder fitted with a massless and frictionless piston. The system is maintained at temperature T in a thermostat. Let us assume that the gas expands against zero opposing pressure (free expansion; irreversible process) from the initial volume V_1 to V_2. In this case, as we have discussed before the change in internal energy, ΔU=0 and also work, $p\mathrm{d}V$=0 [the opposing pressure is zero] so according to the First Law of thermodynamics

$$\Delta U = q + w \quad \Rightarrow 0 = q + 0 \qquad \Rightarrow q = 0 \qquad \ldots(4.46)$$

The heat absorbed by the system from the surrounding, q=0. However as per the definition the entropy change for the system would be

$$\Delta S_{\text{sys}} = \frac{q_{rev}}{T} \qquad \ldots(4.8)$$

Now, since the surroundings lost no heat the entropy change, for the surroundings would be

$$\Delta S_{\text{surr}} = 0 \qquad \ldots(4.47)$$

The total entropy change in the isolated system for the irreversible expansion process would be

$$\Delta S_{\text{isoth irr exp}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = \frac{q_{rev}}{T} + 0 = \frac{q_{rev}}{T} \qquad \ldots(4.48)$$

Once the gas has been irreversibly expanded to a volume V_2 under isothermal conditions, we reversibly compress it back to volume V_1 under similar conditions. In such a case the system would lose heat equal to $-q_{\text{rev}}$ to the surroundings and the corresponding entropy change would be

$$\Delta S_{\text{sys}} = -\frac{q_{rev}}{T} \qquad \ldots(4.49)$$

As the surrounding would gain heat equal to q_{rev} the associated entropy change would be

$$\Delta S_{\text{surr}} = \frac{q_{rev}}{T} \qquad \ldots(4.50)$$

The total entropy change in the isolated system for the isothermal reversible compression process would be

The energy of a closed system is conserved; it always remains constant. For irreversible processes, the entropy of a closed system always increases. Therefore, the change in entropy is sometimes called "the arrow of time."

$$\Delta S_{\text{isoth rev comp}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -\frac{q_{rev}}{T} + \frac{q_{rev}}{T} = 0 \qquad \ldots(4.51)$$

The overall entropy change for the cyclic process would be

$$\Delta S_{\text{cyclic}} = \Delta S_{\text{isoth irr exp}} + \Delta S_{\text{isoth rev comp}} = \frac{q_{rev}}{T} + 0 = \frac{q_{rev}}{T} > 0 \qquad \ldots(4.52)$$

Thus, we see that overall entropy change in a cyclic process involving an irreversible step in an isolated system is positive.

All real processes occur spontaneously in the direction that increases the entropy of the universe (system plus surroundings)

On the basis of the two cases of cyclic processes in isolated systems discussed here we can say that the entropy of the system plus the surroundings increases in case of a spontaneous (irreversible) process. In other words, we can say that for an isolated system the total entropy of the universe *increases in an irreversible process* and remains *constant for reversible processes*. However, it never decreases. Mathematically,

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} = \Delta S_{\text{total}} \geq 0 \qquad \ldots(4.53)$$

Thus, we see that entropy does provide a criterion for establishing the spontaneity of a process. This, infact paves way for stating the Second Law of thermodynamics.

4.3 THE SECOND LAW OF THERMODYNAMICS

According to the second law if a system is at equilibrium, then any infinitesimally small perturbation of the system will not change its total entropy i.e., $\Delta S=0$. However, if the system is not at equilibrium, then a spontaneous change in the system will occur in such a way that the total entropy of the system and surroundings increases.

You would recall that in the beginning of the unit we discussed and showed that the First Law of thermodynamics concerns the conservation of energy, however, it does not tell anything about the 'directionality' of the process. In other words, according to the First Law of thermodynamics a system can in principle undergo any process as long as the energy is conserved. However, as we have just shown above that the natural (spontaneous) direction of a process i.e., of the possible processes, the one, which happens on its own, or the directionality of a process can be ascertained in terms of entropy. This leads us to state the Second Law of thermodynamics as

Sum of the entropy of a system and its surroundings increases for a spontaneous process, $\Delta S_{\text{total}} > 0$.

Freezing is an exothermic process; the heat transferred from the system to the surroundings increases disorder in the surroundings thereby increasing the entropy of surroundings.

Further, we have shown that for non-spontaneous processes, $\Delta S_{\text{total}} = 0$. Thus, according to the Second Law of thermodynamics, a spontaneous process will be accompanied by an increase in ΔS_{total} or ($\Delta S_{\text{sys}} + \Delta S_{\text{surr}}$). However, you may note here that the Second Law places no limitations on the individual entropy changes of the system or the surroundings. The only requirement from the law is that the total entropy change of the system and the surroundings put together *must be positive*. The entropy change for either the system or the surroundings may even be negative. Thus, for a spontaneous process if the entropy of the system decreases, the entropy of the surroundings increases even more so as to offset the decrease in system's entropy, such that the sum of their entropies is positive. For example, for spontaneous freezing of a liquid (or condensation of a gas) the entropy of the system decreases. However, this decrease in entropy is more than compensated by the increase in the entropy of the surroundings. The total entropy change for the system and the surroundings becomes positive and these processes are spontaneous.

Thus, we have a criterion for spontaneity of a process in terms of its entropy change. However there is a limitation in applying this criterion to different systems. This is so because it requires calculating the entropy changes for the system as well as for the surroundings. Calculation of the entropy change for the system is relatively straightforward, but it is quite tedious (sometimes not practical) to calculate the entropy change for the surroundings. Therefore, we need a criterion for spontaneity that depends only on the properties of the 'system'. We would introduce such a criterion in the next section. For now let us share different statements of the Second Law of thermodynamicsThese statements are equivalent; though these may not appear to have much connection with each other. The significant statements of the Second Law of thermodynamics and their authors are as under.

Clausius (1850)

"*Heat can never pass from a colder to a warmer body without some other change, connected therewith, occurring at the same time*". In simple words, "it is impossible to transfer heat from a colder body to hotter body without doing some work."

Kelvin (1851)

It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.

Planck

It is impossible to construct an engine, which will work in a complete cycle, and produce no effect except the raising of a weight and cooling of a heat reservoir.

Lewis

"In any irreversible process the total entropy of all the bodies concerned (system and surroundings) is increased."

Kelvin-Plank

"The thermal efficiency of a cyclic heat engine must be less than one, or less than 100 percent."

When we say that the efficiency of a heat engine can never be hundred per cent it means that no heat engine can completely convert heat into work in a cyclic process even if the process is reversible. As you have learnt above that all real processes are irreversible therefore, their efficiency is even lesser than that of a reversible engine.

In case of a reversible engine the entire amount of heat absorbed is converted into kinetic energy of gas molecules and they start moving faster. If all the heat absorbed had to be converted to work (i.e., 100 % efficiency) then it would be necessary that all the molecules of the gas move in the same direction simultaneously and hit the piston of the engine perpendicularly as shown in Fig 4.4 (a). This you know is highly improbable because the molecules are in random motion. Thus, only a certain fraction of them would hit the piston and push it Fig. 4.4 (b), and the efficiency would be less than 100%.

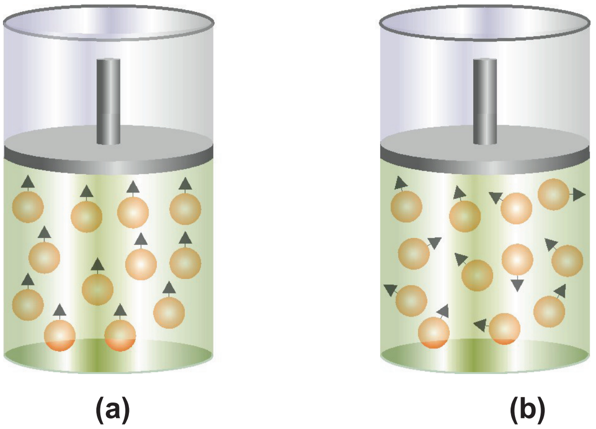

Fig. 4.4: (a) All the molecules of the gas need to simultaneously strike the piston in same direction to completely convert heat into work b) In real systems due to random motion of the molecules only a fraction of the molecules hit the piston and efficiency is less than 100%.

4.4 THE GIBBS ENERGY

As stated above, we need a criterion for spontaneity that depends on the properties of the system only. Such a criterion is 'Gibbs energy'. Let us learn about Gibbs energy and its significance. From Eq. (4.53) we can write that for a spontaneous process,

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$$

For a process at constant pressure, we can substitute ΔS_{surr} by $-\dfrac{\Delta H_{\text{sys}}}{T}$

$$\Rightarrow \quad \Delta S_{\text{total}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T} > 0 \qquad \ldots(4.54)$$

On multiplying the Eq. (4.54) throughout by T we get

$$T\Delta S_{\text{total}} = T\Delta S_{\text{sys}} - \Delta H_{\text{sys}} > 0 \qquad \ldots(4.55)$$

This provides us a criterion for spontaneity in terms of the properties of system only.

Now if we multiply Eq. (4.55) by (–1) throughout, we get

$$-T\Delta S_{\text{total}} = -T\Delta S_{\text{sys}} + \Delta H_{\text{sys}} < 0 \qquad \ldots(4.56)$$

You may note here that the greater than sign in Eq. (4.55) is changed to less than sign on multiplying by (–1). On rearranging Eq. (4.56) we get,

$$\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0 \qquad \ldots(4.57)$$

$q_{sur} = -q_{sys}$

As the surroundings are big in size, therefore the transfer of heat from the surroundings can be considered as a reversible process.

$q_{sur} = -q_{rev(sys)}$

at constant pressure

$q_{rev(sys)} = \Delta H_{sys}$

$q_{sur} = -q_{sys} = -\Delta H_{sys}$

$\Delta S_{sur} = \dfrac{-q_{sys}}{T} = \dfrac{-\Delta H_{sys}}{T}$

This implies that for a thermodynamic process carried at constant pressure (p) and temperature (T), if the changes in enthalpy and entropy of the system are such that $\Delta H_{\text{sys}} - T\Delta S_{\text{sys}} < 0$ then the process must be spontaneous. As this expression involves three properties of the system and gives a condition for spontaneity it prompts us to define a new thermodynamic property called Gibbs energy (G) as

$$G = H - TS \qquad \ldots(4.58)$$

Gibbs energy (earlier called as Gibbs free energy) is denoted by the symbol G and like U, H and S is a state function. We cannot determine its absolute value; however we can determine the change in Gibbs energy for a system and this acts as the criterion for spontaneity. Gibbs energy is an extensive property and the Gibbs energy per mole i.e., molar Gibbs energy (G_{m}) is an intensive property. The SI unit for Gibbs energy is joule (J) and that of molar Gibbs energy, joule per mole (J mol^{-1}). Thus, the condition for spontaneity is that $\Delta G < 0$, i.e., the change in Gibbs energy should be negative for a process to be spontaneous.

At constant temperature and pressure, the chemical reactions are spontaneous in the direction in which the Gibbs energy decreases.

Significance of Gibbs energy

We have defined Gibbs energy as

$$G = H - TS \qquad \ldots(4.58)$$

We know that, $H = U + pV$

Therefore, we can write

$$G = U + pV - TS \qquad \ldots(4.59)$$

For an infinitesimal change, the equation becomes

$$\mathrm{d}G = \mathrm{d}U + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T \qquad \ldots(4.60)$$

From the First Law of thermodynamics

$$\mathrm{d}U = \mathrm{d}q + \mathrm{d}w \qquad \ldots(2.6)$$

For a reversible process, we can write by rearranging Eq. (4.8)

$$\mathrm{d}q_{\text{rev}} = T\mathrm{d}S \qquad \ldots(4.61)$$

Also, $\mathrm{d}w = \mathrm{d}w_{\text{rev}}$

$$\Rightarrow \quad \mathrm{d}U = T\mathrm{d}S + \mathrm{d}w_{\text{rev}} \qquad \ldots(4.62)$$

Substituting in Eq. (4.60)

$$\Rightarrow \quad \mathrm{d}G = T\mathrm{d}S + \mathrm{d}w_{\text{rev}} + p\mathrm{d}V + V\mathrm{d}p - T\mathrm{d}S - S\mathrm{d}T \qquad \ldots(4.63)$$

Simplifying,

$$\Rightarrow \quad \mathrm{d}G = \mathrm{d}w_{\text{rev}} + p\mathrm{d}V + V\mathrm{d}p - S\mathrm{d}T \qquad \ldots(4.64)$$

Under the conditions of constant T and p ($\mathrm{d}T = 0$ and $\mathrm{d}p = 0$), the expression becomes

$$\mathrm{d}G_{\text{p,T}} = \mathrm{d}w_{\text{rev}} + p\mathrm{d}V = \mathrm{d}w_{\text{rev}} - (-p\mathrm{d}V) \qquad \ldots(4.65)$$

At constant pressure and temperature, dG represents non mechanical work.

On the right side of the Eq. (4.65) the first term (dw_{rev}) represents all types of work in the process whereas the second term ($-pdV$) is for the mechanical work. In other words we can say that $dG_{p,T}$ represents the non-mechanical work. This expression finds application in assessing the electrical work produced by fuel cells and electrochemical cells.

Properties of Gibbs energy

Once again from Eq. (4.60)

$$dG = dU + pdV + Vdp - TdS - SdT \quad \ldots(4.60)$$

For a closed system doing only work of expansion, we can write Eq. (4.62) as

$$\Rightarrow \quad dU = TdS - pdV \quad \ldots(4.66)$$

Substituting in Eq. (4.60), we get

$$dG = TdS - pdV + pdV + Vdp - TdS - SdT \quad \ldots(4.67)$$

On simplification we get an important equation

$$dG = Vdp - SdT \quad \ldots(4.68)$$

This implies that for a system with constant composition G is a function of p and T *i.e.,* [G= f (p,T)]

Therefore, we can write total differential of G as

$$dG = \left(\frac{\partial G}{\partial p}\right)_T dp + \left(\frac{\partial G}{\partial T}\right)_p dT \quad \ldots(4.69)$$

The terms in the brackets on right hand side of Eq. (4.69) represent the partial differentials where we take derivative of the property w.r.t one variable while keeping the other variable constant. The first term on right hand side in the Eq. (4.69) represents the rate at which the Gibbs energy changes with pressure at constant temperature multiplied by the change in pressure. Similarly, the second term represents the rate at which the Gibbs energy changes with temperature at constant pressure multiplied by the change in temperature.

Comparing Eq. (4.68) and Eq. (4.69) we get

$$\left(\frac{\partial G}{\partial p}\right)_T = V \quad \ldots(4.70)$$

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \quad \ldots(4.71)$$

These are very important relations. According to Eq. (4.70) for a system with constant composition increase in pressure increases Gibbs energy (as $V > 0$) and according to Eq. (4.71) for a system with constant composition increase in temperature decreases Gibbs energy (as $S > 0$)

Enthalpy and Entropy driven reactions

You would recall that while discussing about decrease in enthalpy as a criterion for spontaneity we found that there are a number of examples of reaction accompanied by an increase in enthalpy ($\Delta H>0$, endothermic process). Therefore, decrease in enthalpy could not serve as the desired criterion. Let's revisit spontaneous endothermic reactions in terms of Gibbs energy change. In such reactions $\Delta H > 0$ but for spontaneity ΔG must be negative. This is possible only when the entropy change for the system is positive (increases) and secondly it is so much positive that $T\Delta S$ term in the expression; $\Delta G = \Delta H - T\Delta S$ is greater than the ΔH term. Such reaction are said to be **'entropy driven'** reactions because in such cases the decrease in Gibbs energy is caused by the entropy term.

Similarly, if for a reaction ΔH as well as ΔS were negative then the value of ΔG would depend on the relative magnitude of ΔH and $-T\Delta S$ terms. The value of ΔG would be negative only if ΔH is highly negative such that it outweighs the $-T\Delta S$ term (which is positive). Since in such a case the Gibbs energy decrease is due to the decrease in enthalpy of the system; such reactions are called **enthalpy driven** reactions.

Chemical potential

For a chemical system with variable composition Gibbs energy is a function of the temperature, pressure and the composition i.e., the number of moles of different components; [$G= f\,(p, T, n_1, n_2, n_3 \ldots . n_i ..)$]

Therefore, we can write total differential of G as

$$\mathrm{d}G = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} \mathrm{d}p + \left(\frac{\partial G}{\partial T}\right)_{p,n_i} \mathrm{d}T + \sum \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \mathrm{d}n_i \qquad \ldots(4.72)$$

The first and second terms are similar to the ones described for Eq. (4.69). The third term in Eq. (4.72) gives the sum of partial derivatives of G, w.r.t to different components (i=1,2,3…) when T, P, and the number of moles of other components is held constant multiplied by the total change in number of moles of component i. This term for a given component (say i) is an important property called chemical potential (μ_i) and is defined as

Chemical potential is the rate of change of Gibbs energy with the number of moles of component i when the temperature, pressure and the number of moles of other components is kept constant.

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j} \qquad \ldots(4.73)$$

A detailed account of the chemical potential is beyond the scope of this course. However, we can state that chemical potential can be seen as 'escaping tendency' of a substance in a mixture. The molecules of a component spontaneously move from regions of high chemical potential to the regions of low chemical potential in a mixture. This continues till the chemical potential of the component becomes same throughout the system. For example, if we add a drop of ink in some water taken in a beaker then the molecules of ink in the region of drop gradually but spontaneously spread out. There is a concentration gradient and the molecules at higher chemical potential move spontaneously to the regions of low chemical potential i.e., they diffuse. Fig. (4.5) gives a schematic representation of a concentration gradient. The species inside the porous membrane (at higher chemical potential) diffuse out to the region of lower chemical potential outside the membrane.

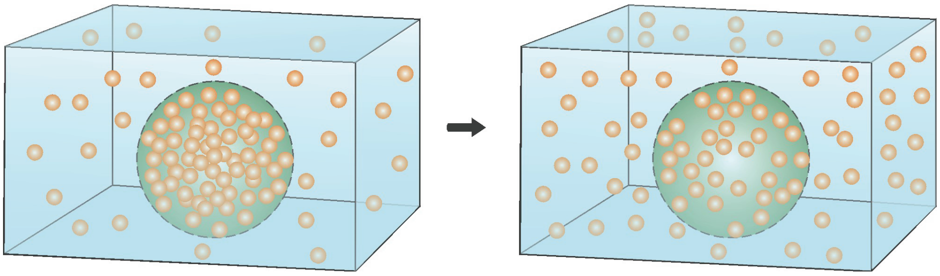

Fig. 4.5: Schematic representation of a concentration gradient.

Having learnt about Gibbs energy and its importance in predicting the spontaneity of a reaction let's now move to the Third Law of Thermodynamics. However, before moving to the Third Law solve the following simple question.

SAQ 5

Crystallisation of a supersaturated solution of sodium acetate is spontaneous and exothermic process. Is the process 'entropy driven' or 'enthalpy driven'? Justify your answer.

4.5 THE THIRD LAW OF THERMODYNAMICS

So far we have introduced four state functions, viz., internal energy, enthalpy entropy and Gibbs energy. You know that the value of state functions for a given system depend on the state and are independent of the path by which the state is achieved. Also we have learnt that we cannot measure the absolute value of a given state function in a given state but can measure the change in the state function for the process. This is so because we do not have a reference point (so called zero). However of these state functions, entropy is different from rest because we can, in principal, determine or estimate the absolute entropy of a system. This is made possible by the Third Law of thermodynamics that provides the 'zero' of the entropy scale. Let's try to understand it.

You know that a substance in gaseous state has greater entropy than that in the liquid state because in gaseous state there is a greater degree of disorder. Liquid state in turn has greater entropy than that of the solid state for the same reason. Further, as you know that when a solid is formed the constituent species pack closely in the lattice. Though the particles do not change their positions they vibrate about their mean positions. Now, if we start cooling a solid the motion of the species would be decreased and at 0 K it would stop completely. In this state since there is no disorder even due to the vibration of particles there would be perfect order so the entropy would be zero. (You know that entropy is a measure of disorder). This fact is stated as the Third Law of thermodynamics, which states that, ***"the entropy of a pure and perfect crystalline solid at 0 K is zero."***

This is in agreement with the statistical view of entropy also in which the entropy is related to the number of microstates; the greater the number of microstates, the larger is the entropy of the system. As in a pure and perfect crystalline solid there can be only one way to arrange constituents. This means that there is only one microstate possible which in turn means that the entropy ($S = k\ln W = k\ln 1 = 0$) is equal to zero.

You have so far learnt about three laws of thermodynamics. Of these, the first and second laws are universally applicable to all types of substances whether they are pure or are mixtures and may be in any physical state. However, the Third Law is different as it is applicable only to substances in solid state and more so they have to be pure and perfectly crystalline in nature. The Third Law is different in a yet another way as contrary to the First and Second Laws; the Third Law has an exception. It has been found that for certain substances the entropy does not become zero even at 0 K. The entropy of a crystalline substance at 0 K temperature is known as residual entropy about which you would learn a little later. Let's first learn how to calculate absolute entropies of substances.

4.5.1 Determination of Absolute Entropy

Once we have defined the 'zero' of the entropy scale it becomes possible to determine the absolute entropy of a substance under a given set of conditions of temperature and pressure. We have seen that at 0 K there is only one possible microstate. If we increase the temperature the freedom of motion of the constituent species increases and so do the number of microstates. This means that the entropy of any substance at a temperature above 0 K is greater than zero and is called its **absolute entropy**. Suppose we heat a pure and perfect crystalline solid at 0 K to a temperature of say 10 K and measure the entropy change for the process it would be

You must remember that it is not possible to define a 'zero' for internal energy, enthalpy and Gibbs energy so we cannot determine their absolute values.

$$\Delta S = S_{10\,\mathrm{K}} - S_{0\,\mathrm{K}} = S_{10\,\mathrm{K}} - 0 = S_{10\,\mathrm{K}} \qquad \ldots(4.74)$$

Thus, the entropy change would provide the absolute entropy of the substance at 10 K. Similarly, we can determine the absolute entropies at any set of temperature and pressure conditions. For this we need to consider different changes occurring in the system as we heat it from 0 K onwards. As we heat the solid at 0 K onwards its entropy would continue to increase till it reaches its melting point. At the melting point there would be a sharp increase in the entropy due to the phase change from solid to liquid. Then on further heating the entropy would continue to increase as the kinetic energy of the molecules of liquid increases leading to more disorder or randomness. Once again, there would be a sharp increase in the entropy at the next phase change from liquid to the vapour phase at the boiling point. Here, the increase in entropy would be much larger than that observed in the phase transition from solid to liquid. In addition to these changes if the substance undergoes some other phase change say from a given crystalline form to the other one there would be corresponding changes in the entropy.

The expression given in Eq. (4.74) is quite simplistic. In order to calculate the absolute entropy of a substance at a given temperature and pressure we can derive the expression as follows.

From Eq. (4.8) we know that

$$\mathrm{d}S = \frac{\mathrm{d}q_{\text{rev}}}{T} \qquad \ldots(4.8)$$

We can write from Eq. (2.45)

$$\mathrm{d}q_p = C_p\mathrm{d}T \qquad \ldots(2.45)$$

Substituting in Eq. (4.8)

$$\mathrm{d}S = \frac{C_p\mathrm{d}T}{T} \qquad \ldots(4.75)$$

To get the value of absolute entropy we need to integrate Eq. (4.75) in the limits of 0 to T K, where the entropy changes from 0 to S we get

$$\int_0^S \mathrm{d}S = \int_0^T C_p \frac{\mathrm{d}T}{T} \qquad \ldots(4.76)$$

Thus, we can calculate the absolute entropy of a substance at temperature T if we know the heat capacity of the solid in the temperature range of 0 K to T K. However, there is a problem that the heat capacities cannot be determined at temperature close to T = 0 K. The heat capacities have been measured to as low a temperature as about 10 K but for temperatures below that we need to depend on empirical expression given by Debye, according to which the heat capacity of a non-metallic solid is proportional to T^3 ($C_p = aT^3$) where T is the temperature at which the entropy value is required. Thus, the expression for computing the entropy of a substance at a temperature T close to 0 K can be given as follows.

$$\int_0^S \mathrm{d}S = \int_0^T aT^3 \frac{\mathrm{d}T}{T} \qquad \ldots(4.77)$$

as 'a' is a constant we can take it out of the integral and write

$$\int_0^S \mathrm{d}S = a\int_0^T T^2\mathrm{d}T \qquad \ldots(4.78)$$

On integrating, we get

$$[S]_0^T = a\left[\frac{T^3}{3}\right]_0^T \qquad \ldots(4.79)$$

On simplification,

$$S(T) - S(0) = \frac{a}{3}T^3 \qquad \ldots(4.80)$$

$$S(T) = S(0) + \frac{a}{3}T^3 \qquad \ldots(4.81)$$

$$S(T) = S(0) + \frac{1}{3}C_{p,m}(T) \qquad \ldots(4.82)$$

This expression can be used to calculate the absolute entropy of a substance at very low temperatures. However, if we wish to calculate the absolute entropy of a substance above the minimum temperature at which entropy can be measured then we need to add more terms. For example if we want to calculate the entropy at a temperature greater than its melting point (T_f) then the expression becomes as follows.

$$\int_0^S \mathrm{d}S = a\int_0^{T_m} T^2\,\mathrm{d}T + \int_{T_m}^{T_f} C_p(\mathrm{s})\frac{\mathrm{d}T}{T} + \frac{\Delta_f H}{T_f} + \int_{T_f}^{T} C_p(\mathrm{l})\frac{\mathrm{d}T}{T} \qquad \ldots(4.83)$$

The first term is for the entropy change upto the minimum temperature (T_m) at which the heat capacity can be determined. The second term is for the entropy change from T_m to T_f .The third term gives the contribution of the phase transition whereas the last term is for the increase in entropy of the liquid from melting point to the temperature of interest. If the temperature of interest happens to be more than the boiling point of the substance then the equation would get further modified. We would need to incorporate another phase change and so on. The desired expression for the calculation of absolute entropy of a substance at a temperature above its boiling point would be

$$\int_0^S \mathrm{d}S = a\int_0^{T_m} T^2\mathrm{d}T + \int_{T_m}^{T_f} C_p(\mathrm{s})\frac{\mathrm{d}T}{T} + \frac{\Delta_f H}{T_f} + \int_{T_f}^{T_b} C_p(\mathrm{l})\frac{\mathrm{d}T}{T} + \frac{\Delta_{vap} H}{T_{vap}} + \int_{T_b}^{T} C_p(\mathrm{g})\frac{\mathrm{d}T}{T} \quad ..(4.84)$$

It is important to note that the entropies calculate on the basis of third law statement, S (0)=0, are called as **third law entropies** or just entropies.

4.5.2 Residual Entropy

As mentioned above, the entropy of some pure and perfectly crystalline solids is found to be non-zero at 0 K and is called as residual entropy. The residual entropies of some substances are given in Table 4.1.

Table 4.1: Residual entropies of some substances

Substance	**Molecular formula**	**Residual entropy / JK^{-1} mol^{-1}**
Hydrogen	H_2	6.2
Carbon monoxide	CO	3.4
Ice	H_2O	5.8

You may note here, that the residual entropy is observed in substances containing molecules, which are either non-polar or have very small dipole moment. The residual entropy of 3.4 J K^{-1} mol^{-1} at 0 K for diatomic carbon monoxide implies that the crystalline carbon monoxide does not have a perfect arrangement of the CO molecules. We can say that in the crystalline state its arrangements like, ..COCOCO..and ..OCCOCO..may not have significant difference in their energies. In other words more than one arrangement are possible for the molecules of carbon monoxide at 0 K, i.e., the number of microstates is more than 1 so the entropy is not zero. The residual entropies can be theoretically calculated using statistical thermodynamics. This is beyond the scope of this course.

Having learnt about the Third Law of thermodynamics, its significance and determination of absolute entropies answer the following simple question to assess your understanding.

SAQ 6

Differentiate between the Third Law entropy and residual entropy of a system.

4.6 SUMMARY

In this last unit of the block we took up the Second and the Third Law of thermodynamics. We began the unit by initiating a discussion on spontaneity and need for a criterion for the same. In this process we examined different spontaneous and non-spontaneous processes and noted that if a physical or a chemical change is spontaneous in one direction, it is not spontaneous in the opposite direction. Secondly, both spontaneous and non-spontaneous processes are possible, but only spontaneous processes occur on their own; the non-spontaneous processes require the help of an external agent to occur. We then examined and showed that internal energy or enthalpy cannot serve as a criterion for spontaneity. In this light we argued for the need of a new thermodynamic parameter that could serve as a criterion for spontaneity.

Thereafter we introduced the concept of entropy as a measure of dispersal of energy and matter by analysing different processes and gave the thermodynamic definition of entropy. It is also a measure of disorder. It was pointed out that in order to calculate the entropy change for a process we need to use the transfer of heat to or from the system in a reversible way irrespective of the fact whether the process is reversible or irreversible. This in fact is a consequence of entropy being a state function. We then took up the statistical viewpoint on entropy according to which the entropy of the system depends on the number of possible ways of distributing the energy of the system. Each of these ways is called a microscopic state or a microstate. Further, each set of similar microstates is called a *distribution* or a *state*. The probability of a particular distribution depends on the number of microstates in it. Greater the number of microstates in a distribution greater is its entropy. We then derived expressions for calculating the entropy changes in some simple processes.

Having introduced the concept of entropy and learning about computing entropy changes in different processes we evaluated entropy as a criterion for spontaneity. We demonstrated that entropy does help in ascertaining whether a process will be spontaneous or not. For this it was shown that the total entropy change in an isolated system i.e., the entropy change for the system and the surroundings must increase for the process to be spontaneous. This in fact formed the basis of stating the Second Law of thermodynamics for which we gave a number of equivalent statements. However, entropy as a criterion for spontaneity is difficult to apply, as it requires calculation of entropy change for the system as well as for the surroundings. This prompted us to introduce Gibbs energy as a criterion for spontaneity as it depends on the properties of the system only. It was shown that for a process to be spontaneous the Gibbs energy must decrease. We then briefly discussed about enthalpy driven and entropy driven reactions.

Thereafter we introduced the Third Law of thermodynamics, which states that at a temperature of 0 K the entropy of a pure and perfect crystalline solid is 0. This provided the reference point for entropy and was used to calculate the absolute entropy of a substance at a given temperature. During the discussion on the Third Law of thermodynamics we introduced the concept of residual entropy as the non-zero entropy of certain substances at 0 K. This in fact is an exception to the Law.

4.7 TERMINAL QUESTIONS

1. The molar enthalpy of fusion of a monoatomic noble gas is found to be 1.3 kJ mol^{-1}. If the melting point of the gas is −190°C calculate the molar entropy of fusion for the gas.
2. 1 mole of argon at 298 K and 1.00 bar taken in a container is confined to a volume of 5.00 dm^3. In a composite process the gas is allowed to expand to double its initial volume and is simultaneously heated to reach a temperature of 323 K. Calculate the entropy change for the process assuming ideal gas behaviour. [Given $C_{v,m}$=12.47 J K^{-1} mol^{-1}].
3. According to Kelvin-Planck statement of the Second Law of thermodynamics, the efficiency of a heat engine cannot be 100%. Justify the statement.
4. Explain enthalpy driven and entropy driven reactions. Melting of ice is an endothermic process. Is the process 'entropy driven' or 'enthalpy driven'? Justify your answer.
5. Define chemical potential and explain its significance.

4.8 ANSWERS

Self-Assessment Questions

1. Spontaneous reactions are the reactions that occur on their own under a given set of conditions without the aid of any external agency. *No*, the internal energy cannot serve as a criterion for spontaneity of a chemical reaction.
2. i) Decrease ii) Decrease iii) Increase iv) Increase
3. The entropy of mixing of n_A moles of gas A occupying a volume V_A with n_B moles of gas B occupying a volume V_B is given by the following expression

$$\Delta S_{mixing} = 2.303\ \mathrm{R}\left[n_A \log\frac{V_A+V_B}{V_A} + \quad n_B \log\frac{V_A+V_B}{V_B}\right]$$

In the present case the given data is as under

n_A= 1.00 mol n_B= 1.00 mol V_A= 5 dm^3 V_B= 10 dm^3

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

Substituting the values in the equation, we get

$$\Delta S_{mixing} = 2.303 \times 8.314\,\text{J K}^{-1}\text{mol}^{-1}\left[1.0\,\text{mol} \times \log\frac{5+10}{5} + 1.0\,\text{mol}\,\log\frac{5+10}{10}\right]$$

Simplifying and solving

$$\Delta S_{mixing} = 2.303 \times 8.314\ \text{J K}^{-1}\left[\log(3.0) + \log(1.5)\right] = 19.147\ \log(4.5)\text{J K}^{-1}$$

$$\Delta S_{mixing} = 12.51\ \text{J K}^{-1}$$

4. The entropy change for fusion of a liquid is given by Eq. (4.39)

$$\Delta_f S = \frac{\Delta_f H}{T_f}$$

We are provided with the enthalpy and the temperature of fusion. Substituting the values in the expression, we get

$$\Delta_f S = \frac{-6.02\ k\text{J mol}^{-1}}{273.1\,\text{K}} = \frac{-602\ \text{J mol}^{-1}}{273.1\,\text{K}} = -\ 2.204\ \text{J K}^{-1}\text{mol}^{-1}$$

5. The process is enthalpy driven. This is so because the crystallisation process is accompanied by a decrease in entropy i.e., ΔS is negative which means $-T\Delta S$ term is positive. On the other, hand the enthalpy change is negative (exothermic). We know that

$$\Delta G = \Delta H - T\Delta S \quad = \quad \Delta H + (-T\Delta S)$$

The first term (ΔH) is negative and the second term ($-T\Delta S$) is positive. As a consequence the change in Gibbs energy can be negative only if the enthalpy change is highly negative so that the sum of two terms becomes negative. As the factor contributing towards making Gibbs energy change negative is the enthalpy change so we say that the process is enthalpy driven.

6. The third law entropy refers to the entropy of a substance at a given temperature w.r.t its entropy in pure and perfect crystalline state at 0 K to be equal to zero. On the other hand, the residual entropy refers to the entropy of a substance at absolute zero (0 K). This is due to imperfections in the crystal at 0 K.

Terminal Questions

1. The entropy change for fusion of a liquid is given by Eq. (4.39)

$$\Delta_f S = \frac{\Delta_f H}{T_f}$$

We are provided with the enthalpy and the temperature of fusion for the substance. Substituting the values in the expression, we get

$$\Delta_f S = \frac{-1.3\ kJ\ mol^{-1}}{83\ K} = \frac{-1300\ J\ mol^{-1}}{83\ K} = -15.66\ J\ K^{-1}mol^{-1}$$

2. The process can be written as

$$(5.0\ dm^3, 298\ K) \rightarrow (10.0\ dm^3, 323\ K)$$

In this process the temperature as well as the volume of the system is changing. Now, since entropy is a state function, the entropy change would remain same irrespective of the path chosen. So for convenience we break this composite process into two steps process as follows.

$$(5.0\ dm^3, 298\ K) \rightarrow (10.0\ dm^3, 298\ K) \rightarrow (10.0\ dm^3, 323\ K)$$

This means that in the first step the gas undergoes isothermal reversible expansion and in the second step the gas is reversibly heated at constant volume. The entropy change for the first step can be calculated by using Eq. (4.19) i.e.,

$$\Rightarrow \quad \Delta S_{\mathrm{I}} = 2.303\, nR \log \frac{V_2}{V_1}$$

We are given n= 1 mol V_1= 5 dm^3 ; V_2= 10 dm^3

Substituting the values in the equation, we get

$$\Rightarrow \quad \Delta S_{\mathrm{I}} = 2.303 \times 1.0\,\mathrm{mol} \times (8.314\,\mathrm{JK^{-1}mol^{-1}}) \log \frac{10}{5}$$

Solving, we get

$$\Rightarrow \quad \Delta S_{\mathrm{I}} = 5.76\ \mathrm{J\ K^{-1}}$$

Stage 2: For the reversible heating of the gas at constant volume the entropy change can be calculated by using Eq. (4.34)

$$\Delta S_{\mathrm{II}} = 2.303\ C_{V,m} \log \frac{T_2}{T_1}$$

We are given:

$C_{V,\mathrm{m}}$= 12.47 J K^{-1}mol^{-1} ; T_1 = 298 K ; T_2 = 323 K

Substituting the values in the expression, we get

$$\Delta S_{\mathrm{II}} = 2.303(12.47\ \mathrm{J\ K^{-1}\ mol^{-1}}) \log \frac{323}{298}$$

Solving, we get

$$\Delta S_{\mathrm{II}} = 1.005\ \mathrm{J\ K^{-1}mol^{-1}}$$

Total entropy change for the overall process would be

$$\Rightarrow \quad \Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} = 5.76\,\mathrm{JK^{-1}mol^{-1}} + 1.005\,\mathrm{JK^{-1}mol^{-1}} = 6.765\,\mathrm{JK^{-1}mol^{-1}}$$

3. It is true that the efficiency of a heat engine cannot be 100 %. It is so because for the efficiency to be 100% all the heat absorbed by the gas should be converted to work. This is possible only if all the gas molecules that absorb heat must simultaneously push the piston while moving in same direction. However, as we know the molecules are in random motion and it is improbable that they push the piston simultaneously in the same direction. Only a few molecules will push the piston in the desired direction and hence the efficiency would be less than 100%.

4. We know that for a reaction to be spontaneous, the Gibbs energy change (ΔG) for the same should be negative. We also know that there are two contributors to the Gibbs energy change ($\Delta G = \Delta H - T\Delta S$) i.e., the enthalpy change (ΔH) and entropy change (as $T\Delta S$). These two factors can work in the same direction or in opposite direction. Accordingly, the Gibbs energy may increase or decrease as a resultant of the two. The process for which the enthalpy change is the main component in making Gibbs energy change negative is called enthalpy driven. In case this job is performed by entropy component then the process is referred to as entropy driven.

   The given process is entropy driven. This is so because the melting of ice is accompanied by an increase in entropy i.e., ΔS is positive which means $-T\Delta S$ term is negative. On the other hand, the enthalpy change is positive, as the process is endothermic. We know that

   $$\Delta G = \Delta H - T\Delta S \quad = \quad \Delta H + (-T\Delta S)$$

   The first term (ΔH) is positive and the second term is negative and large. As a consequence the change in Gibbs energy is negative and the factor contributing for this is the entropy change. Therefore the process is called as entropy driven.

5. The chemical potential is an important thermodynamic parameter and refers to the change in Gibbs energy of a system w.r.t the number of moles of one of its constituents of the system under the conditions of constant temperature, pressure and the number of moles of all other components. Mathematically,

   $$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_j}$$

   As regards the significance the chemical potential can be seen as ‘escaping tendency’ of a substance in a mixture. Molecules move spontaneously from regions of high chemical potential to regions of low chemical potential in a mixture till the chemical potential of the component becomes same throughout the chemical system.