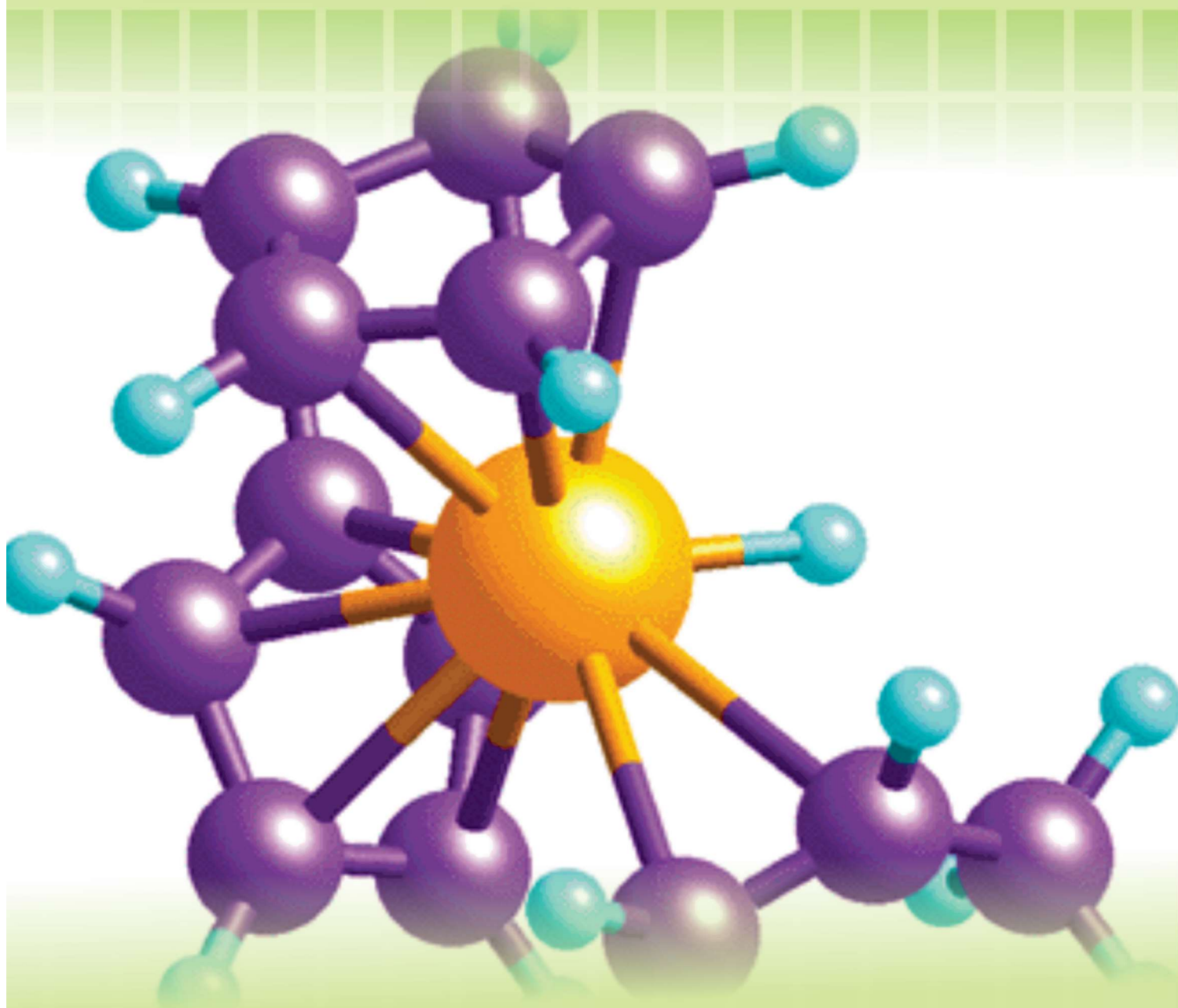


Physical Chemistry

CHM 111



CODeL

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA
CENTRE FOR OPEN DISTANCE AND e-LEARNING

**FEDERAL UNIVERSITY OF TECHNOLOGY MINNA,
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**CENTRE FOR OPEN DISTANCE AND
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**B.TECH. COMPUTER SCIENCE
PROGRAMME**

COURSE TITLE
PHYSICAL CHEMISTRY

COURSE CODE
CHM 111

Module 2

Chemical Thermodynamics

- Unit 1: The first Law of Thermodynamics
- Unit 2: Thermochemistry
- Unit 3: The Second Law of Thermodynamics

Unit 1

The First Law Of Thermodynamics

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1.0 Introduction

In this unit, we shall introduce you to some of the terms used in thermodynamics; The definitions of work, heat and heat capacity will be stated. The first law of thermodynamics will be explained with particular reference to isothermal and adiabatic processes. The calculation of work, internal energy change and heat absorbed or evolved in reversible and irreversible processes will be outlined. The significance of enthalpy and enthalpy change of a system will be stated. We shall study the applications of the first law of thermodynamics in making thermochemical calculations.

2.0 Learning Outcomes

After studying this unit, you should be able to

- i. explain the terms-system, surroundings and thermodynamic variables
- ii. state the zeroth law of thermodynamics
- iii. differentiate between extensive and intensive variables
- iv. define isothermal, adiabatic and cyclic processes
- v. explain the terms-work, heat and heat capacity
- vi. state the first law of thermodynamics
- vii. explain the term, internal energy of a system
- viii. calculate the work done on an ideal gas in isothermal and adiabatic processes
- ix. state the significance of enthalpy and enthalpy change of a system,

3.0 Learning Content

3.1 Thermodynamic Terminology

In this section, a number of commonly used terms in thermodynamics are defined and explained. These terms should be understood clearly before you proceed further.

System

Any part of the universe which is under study is called a system. It can be as simple as a gas contained in a closed vessel or as complicated as a rocket shooting towards moon. A system may be homogeneous or heterogeneous depending on its contents and conditions. A system is homogeneous if physical properties and chemical composition are identical throughout the system. Such a system is also called a single phase system.

Surroundings

The rest of the universe around the system is considered its surroundings. A system and its surroundings are always separated by boundaries across which matter and energy may be exchanged. The boundaries can be real (fixed or moveable) or

imaginary. Based on the exchange of matter and energy between the system and the surroundings, a system can be classified into the following three types:

1. Isolated system
2. Closed system
3. Open system

Let us explain these terms.

Isolated system is one which exchanges neither energy nor matter with its surroundings. There is no perfectly isolated system; but, a system which is thermally well insulated (i.e., does not allow heat flow) and is sealed to inflow or outflow of matter can be considered as an isolated system. A sealed thermos flask having some matter thus approximates to an isolated system.

Closed system allows exchange of energy (heat or work) with the surroundings but, matter is not allowed to enter or leave it. A properly sealed system (to prevent the passage of matter across its boundary) can be considered as a closed system.

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

Let us now explain the terms, state variables and state of the system.

State Variables

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

For example, if you write ideal gas equation as

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

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

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

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

State of a System

The state of a system is defined when the state variables have definite values. It is not necessary to specify all the state variables since these are interdependent. For example, if the system is an ideal gas, then its pressure, volume, temperature, and the amount of the gas (number of moles) are related by the gas equation. Thus, if we specify three of these, the fourth variable is automatically fixed. Similarly many of its other properties like density, heat capacity etc. are also fixed although through more complicated relations.

Self-Assessment Exercise 1

Identify the type of system in each of the following cases:

- i) A beaker covered with a lid
- ii) A closed thermos flask
- iii) A beaker without lid.

3.2 The Zeroth Law of Thermodynamics

The zeroth law of thermodynamics is based on the concept of thermal equilibrium. It helps us in defining temperature. If two closed systems are brought together so that these are in thermal contact, changes take place in the properties of both the systems, but, eventually a state is reached when there is no further change in any of the systems. This is the state of thermal equilibrium. Both the systems are at the same temperature..

In order to find whether two systems are at the same temperature, the two can be brought into thermal contact; then the changes in the properties of either of these are to be observed. If no change occurs, they are at the same temperature.

The zeroth law of thermodynamics states that if a system A is in thermal equilibrium with system C. and, system B is also in thermal equilibrium with C, then A and B are also in thermal equilibrium with each other.

This is an experimental fact and may be illustrated by assuming that systems A and B are two vessels containing different liquids, and C is an ordinary mercury thermometer. If A is in thermal equilibrium with C, then mercury level in the thermometer will show a constant reading: This indicates the temperature of system A as well as that of C. Now if A is also in thermal equilibrium with B, then the height of mercury level in the thermometer (in contact with B) is the same as before; B also has the same temperature as A. There is thermal equilibrium in both A and B or these are at the same temperature. Here we have only explained the concept of temperature; the temperature scale will be discussed in Unit 3.

3.3 Extensive and Intensive Variables

We have defined homogeneous and heterogeneous systems in Sec. 3.1.2. Let us now discuss the difference between the two with respect to the value of some variables. In this connection, we must first define extensive and intensive variables.

Self-Assessment Exercise 2

1. What is extensive property of a homogenous system ?

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

$$\begin{aligned}\text{Volume of 0.100 kg of ice} &= \frac{\text{Mass of ice}}{\text{Density of ice}} = \frac{0.100 \text{ kg}}{917 \text{ kg m}^{-3}} \\ &= 1.09 \times 10^{-4} \text{ m}^3\end{aligned}$$

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

$$\begin{aligned}\text{Total volume} &= (1.09 + 1.00) \times 10^{-4} \text{ m}^3 \\ &= 2.09 \times 10^{-4} \text{ m}^3\end{aligned}$$

An intensive property of a phase is independent of the amount of the phase. Thus refractive index, density and pressure are intensive properties. However, if a system consists of several phases, then some of the intensive properties may be different. For example, density is an intensive property but its value is different for ice and liquid water in equilibrium at 273.15 K. For thermal equilibrium, the intensive property, temperature, has to be same throughout the system. Otherwise heat will flow from one point of the system to another. Similarly, for mechanical equilibrium, the intensive property, pressure, has to be the same throughout the system. An extensive property when divided by mass or molar mass of the system becomes an intensive property.

Self-Assessment Exercise 3

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

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

3.4 Types of Processes

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

Self-Assessment Exercise 4

1. What is isothermal process ?
2. What is adiabatic process ?
3. What is an isochoric process?
4. When is a process cyclic?

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

In An Adiabatic Process, no heat is allowed to enter or leave the system. Systems in which such processes occur are thermally insulated from the surroundings. An adiabatic process may involve increase or decrease in the temperature of the system. We shall discuss these two processes in detail in Secs. 3.7 and 3.11.

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

In An Isochoric Process, the volume of the system remains constant. Thus, a chemical reaction in a sealed flask of constant volume is an isochoric process.

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

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

Consider a gas at pressure P in a cylinder fitted with an air-tight piston. If the external pressure on the gas is equal to the pressure of the gas, then there is neither expansion nor compression and the piston remains at its position. However, on increasing the

external pressure (P_{ext}) infinitesimally, the gas can be compressed. On the other hand by slightly decreasing the external pressure, the gas may be expanded. Thus

If $P_{\text{ext}} = P$; the system is static and piston does not move.

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

If $P_{\text{ext}} = P - dp$; the gas expands and the piston moves outwards infinitesimally slowly

Hence you can see that in a reversible process, the direction of a process is changed by changing the magnitude of the driving force by a small amount. In Module 4, you will study how reversible condition is used in constructing electrochemical cells. Any process which is not reversible is termed as irreversible. All natural processes are irreversible. The flow of heat from a high temperature body to a low temperature body is a natural process and hence, irreversible. So is the expansion of a gas against vacuum, known as free expansion. Irreversible processes are also called spontaneous processes: We will be studying reversible and irreversible processes in detail in Secs. 3.7 and 3.11.

3.5 Work, Heat and Heat Capacity

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

Heat is a form of energy. Heat is not the property of a system but is exchanged between a system and the surroundings during a process, when there is a temperature difference between the two.

Self-Assessment Exercise 5

Explain the term : work, and its different kinds.

Let us now explain the term, work, and its different kinds.

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

$$W = F \cdot X \dots\dots\dots (1)$$

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

1. Gravitational Work: When a body of mass m is moved through a height h against gravity, then force is equal to mg and the gravitational work done is mgh.
2. Electrical work: If an electric potential E is applied across a resistance R so that current i flows through it, then work done per second is Ei and in t seconds it is equal to Eit.

3. Pressure- volume work: This is a type of mechanical work performed when a system changes its volume against an opposing pressure. This also is known as work of expansion or compression. We will study this in detail in later sections. The energy gained or lost during heat exchange between the system and the surroundings can be stated in terms of heat capacity values. Let us now define the term heat capacity.

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

For changing the temperature of a particular system by dT , if the heat required is dq_v (at constant volume) or dq_p (at constant pressure), then we have

$$C_v = nC_v = \frac{dq_v}{dT} \dots\dots\dots(2)$$

$$C_p = nC_p = \frac{dq_p}{dT} \dots\dots\dots(3)$$

where n is the amount (i.e., number of moles) of the substance constituting-the system.

From these equations, it is possible to determine the heat required for a process, by integration over the temperature range T_1 and T_2 . Hence,

$$q_v = \int_{T_1}^{T_2} C_v dT = \int_{T_1}^{T_2} nC_v dT \dots\dots\dots(4)$$

$$q_p = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} nC_p dT \dots\dots\dots(5)$$

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

Example 1

The equation for the molar heat capacity of butane is $C_p = (19.41 + 0.233 T) \text{ J mol}^{-1} \text{ K}^{-1}$. Calculate the heat necessary to raise the temperature of 3.00 mol of butane from 2 to 573 K at constant pressure. We have to calculate q_p as per Eq. 5.

$$q_p = \int_{T_1}^{T_2} nC_p dT \quad (T_1 = 298, T_2 = 573\text{K}, n = 3.00\text{mol}, C_p = (19.41 + 0.233 T) \text{ J mol}^{-1})$$

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

$$\begin{aligned}
&= 3.00 \times 19.41 \int_{298}^{573} dT + 3.00 \times 0.233 \int_{298}^{573} T dT \\
&= [3.00 \times 19.41 (573 - 298) + \frac{3.00 \times 0.233(573^2 - 298^2)}{2}] \text{ J} \\
&= 9.97 \times 10^4 \text{ J} = 99.7 \text{ kJ}
\end{aligned}$$

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

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

Self-Assessment Exercise 6

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

3.6 The First Law of Thermodynamics

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

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

The energy of an isolated system remains constant.

Energy can neither be created nor destroyed although it can be changed from one form to another.

It is not possible to construct a perpetual motion machine which can work endlessly without the expenditure of energy. (Such a machine is known as perpetual motion machine of the first kind.)

All the above statements are equivalent to the principle of conservation of energy. These statements point out that energy of a system will remain constant if it is left undisturbed. If, on the other hand, the system interacts with the surroundings, then its energy may change; but then, there will also be equal and opposite change in the energy of the surroundings. Since work is a form of energy, it is not possible for a machine to keep on doing work indefinitely. As soon as its own energy is exhausted, it will require a source of energy to continue, doing work. The first law of thermodynamics has no theoretical proof. It is a law based on observation. Since the law has never been contradicted, its truth is taken for granted.

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

$$E = mc^2 \dots\dots\dots(6)$$

This means that if mass m is destroyed, then energy E is produced; c is the velocity of light. This is not a contradiction since mass can also be considered as a form of energy. We shall shortly arrive at the mathematical forms of the first law of thermodynamics. Before that let us first introduce the term, internal energy.

3.6.1 Internal Energy

The internal energy U of a system is the entire energy of its constituent atoms or molecules including all forms of kinetic energy (due to translation, vibration and rotation) as well as energy due to all types of interactions between the molecules and subparticles. It is a state variable and an extensive property and its absolute value cannot be determined. However, in thermodynamics we are interested in the changes in internal energy which accompany any process, but not in the absolute value of U . These changes in internal energy can be brought about only by interaction of the system with its surroundings. The change in internal energy (ΔU) depends only on the initial and final states and is independent of the path adopted.

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

The heat change, dq , and the work done, dw , contribute towards the change in the internal energy of the system. We adopt the convention that the change in the internal energy is equal to the sum of the heat absorbed by the system and the work done on it. If dq is positive (heat absorbed by the system is positive), this leads to an increase in the internal energy of the system. A negative dq implies loss of heat from the system and denotes a decrease in internal energy.

If the work done on the system (dw) is positive, this increases the internal energy of the system. A negative value of dw implies that work has been done by the system at the expense of its internal energy.

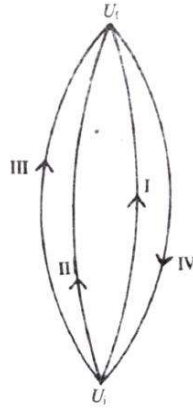


Fig. 1: Energy change through different onward paths, I, II and III and return path, IV.

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

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

3.6.2 Mathematical Forms of the First Law of Thermodynamics

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

$$dU = dq + dw \dots\dots\dots(7)$$

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

$$\Delta U = U_f - U_i = q + w \dots\dots\dots(8)$$

where U_f and U_i are the initial and final internal energies of the system, and ΔU , the net change. It is obvious that ΔU can have either negative or positive value depending on q and w . But once the initial and final states of a system are fixed, ΔU is automatically fixed, no matter what path is adopted in carrying out the process. In other words, internal energy is a state function while heat and work are not.

As an example, consider a system being taken from the initial state where it has energy U_i to the final state having energy U_f along different paths I, II and III (Fig.1). Then in all these cases, ΔU is same. If this were not so, then it would have been possible to construct a perpetual motion machine by reaching the final state via a high energy change path (say, III) and coming back via a low energy change path (IV) thereby releasing the energy difference for work. Eqs. 7 and 8 are mathematical expressions of the first law of thermodynamics.

Self-Assessment Exercise 7

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

3.7 Isothermal Expansion

In this section, we are going to calculate the work done on the gas in an isothermal process. For this we must first arrive at a general expression for pressure-volume work done in an infinitesimal process. Suppose that a gas is enclosed in a cylinder fitted with an air tight piston of area A . Assume that pressure of the gas is P and the external pressure is P_{ext} which is slightly less than the gas pressure. The gas will, hence, expand against an opposing force which is given by .

$$F = P_{\text{ext}}A \dots\dots\dots(9)$$

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

$$dw' = Fdx = P_{\text{ext}}Adx \dots\dots\dots(10)$$

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

$$dw' = P_{\text{ext}}dV \dots\dots\dots(11)$$

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

$$dw = -P_{\text{ext}}dV \dots\dots\dots(12)$$

Eq. 12 is a general expression useful in calculating pressure-volume work whether it is isothermal or adiabatic process. It can be seen that dw is negative when the gas expands and it is positive when the gas contracts. [$dv = +ve$ in expansion and $dv = -ve$ in compression].

We shall now calculate the work of expansion (as also of compression) under isothermal conditions. First let us take up the work done under isothermal irreversible conditions.

3.7.1 Isothermal Irreversible Process

Let us assume that the gas kept in a cylinder expands isothermally and irreversibly against a constant pressure. This means that (i) the gas expands against a constant external pressure ($P_{\text{ext}} = \text{constant}$) (ii) there is considerable difference between the gas 'pressure (inside the cylinder) and the external pressure (iii) that the temperature does not change during the process.

Let the initial and final volumes be V_1 and V_2 , respectively. The total work, W , done on the system is obtained by integrating Eq. 12.

$$W = -\int_{v_1}^{v_2} P_{ext} dV = -P_{ext} \int_{v_1}^{v_2} dV$$

$$= -P_{ext} (V_2 - V_1) = -P_{ext} \Delta V \dots\dots\dots(13)$$

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

Let us work out an example to illustrate the use of Eq. 13. .

Example 2

A gas expands from 10 m³ to 12 m³ against a constant pressure of 1 bar at 298 K. What is the work done on the gas?

We have to calculate work done under constant pressure using Eq. 13.

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

$$= -2 \times 10^5 \text{ Pa m}^3$$

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

[because 1 bar = 1 x 10⁵ Pa and 1 Pa m³ = 1 J.]

It can be seen that the work done on the system is negative, this means, actually system has done work equal to 2 x 10⁵ J during expansion.

It is also possible to calculate the work done under irreversible isothermal conditions, when the external pressure changes continuously. But then, the concerned equation is more complex than Eq. 13. Let us now calculate the work done under isothermal reversible process.

3.7.2 Isothermal Reversible Process

We have already mentioned that a reversible process can be carried out when external pressure (P_{ext}) is only infinitesimally different from the gas pressure inside a cylinder (P). . In such a case, $P_{ext} = P$ and hence, Eq. 12 can be written as,

$$dw = -pdV \dots\dots\dots(14)$$

The total work *done*, W , as the gas expands isothermally and reversibly from a volume V_1 to a volume V_2 is then given by integrating Eq. 14 within limits V_1 and V_2

$$W = - \int_{v_1}^{v_2} P dV \dots\dots\dots(15)$$

Let us assume that the gas behaves ideally. Hence,

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

Using this in Eq. 15,

$$W = - \int_{v_1}^{v_2} nRT/V dV$$

$$= - nRT \int_{v_1}^{v_2} 1/V dV \dots\dots\dots(16)$$

$$= -nRT \ln V_2/V_1 = nRT \ln V_1/V_2 \dots\dots\dots(17)$$

$$\text{Hence, } W = -2.303nRT \log V_2/V_1 = 2.303nRT \log V_1/V_2 \dots\dots\dots(18)$$

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

Similarly, if V_2 is greater than V_1 then the gas undergoes expansion and W is negative. This means, work is done by the gas; $-W$ represents the maximum work available through expansion.

Eq. 18 can also be given in terms of initial and final pressures (P_1 and P_2) of the ideal gas.

For an ideal gas at constant temperature,

$$P_1V_1 = P_2V_2 \dots\dots\dots(19)$$

$$V_2/V_1 = P_1/P_2 \dots\dots\dots(20)$$

$$W = -2.303 nRT \log P_1/P_2$$

$$W = 2.303 nRT \log P_2/P_1 \dots\dots\dots(21)$$

Let us illustrate the use of Eq. 21.

Example 3

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

$$P_1 = 3.00 \times 10^5 \text{ Pa}; P_2 = 6.00 \times 10^6 \text{ Pa}$$

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

We have to calculate the value of n (the amount of the gas) in order to use Eq. 21; the value of n can be found out from the initial conditions using ideal gas equation.

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

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

Substituting the values in Eq. 21.

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

$$= 2.303 \times 1.00 \times 10^2 \times 8.314 \times 3.00 \times 10^2 \times (6.7782 - 5.4771) \text{ J}$$

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

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

Using the principles studied above, answer the following **SAE**.

Self-Assessment Exercise 8

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

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

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

Note that the difference between Eqs. 13 and 15 is that P depends on volume in the latter; whereas, P_{ext} in Eq. 13 is constant throughout. As a result of this, P_{ext} is taken out of integration sign in Eq. 13 whereas P in Eq 15 is to be expressed as a function of volume. Note that n , R and T are constants and are taken out of the integration sign in Eq. 16. Note that formula 2 of Sec. 3.5 is used here].

[Note that Eqs 18 and 21 are applicable only for an ideal gas undergoing isothermal reversible expansion or compression. If the gas does not have ideal behaviour, suitable equation of state must be used. . Using Eqs. 18 and 2

3.8 Heat Change Under Constant Volume

The reactions are carried out under constant volume or under constant pressure conditions. Let us now arrive at an expression useful in calculating the heat change in a system under constant volume conditions. In the next section, we shall discuss heat change under constant pressure conditions.

Let us examine Eq. 7. Let us assume that the work done on the system is only pressure-volume work, whereas electrical, magnetic or other types of work are not involved. Then from Eqs. 7 and 14,

$$dU = dq - pdV \dots\dots\dots(22)$$

$$\text{or } dq = dU + pdV \dots\dots\dots(23)$$

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

$$dV = pdV = 0$$

$$\text{Hence, } dq_v = dU \dots\dots\dots(24)$$

For finite changes in internal energy Eq. 24 becomes,

$$q_v = \Delta U \dots\dots\dots(25)$$

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

Let us try to correlate internal energy change with heat capacity at constant volume, assuming that there is no phase change or chemical reaction. From Eqs. 2 and 24,

$$dU = C_v dT = nC_v dT \dots\dots\dots(26)$$

This holds good for n mol of an ideal gas.

Eq. 26 can be rewritten as

$$C_v = (\partial U / \partial T)_v \dots\dots\dots(27)$$

i.e., heat capacity at constant volume is equal to change in internal energy per 1K rise in temperature at constant volume. $(\partial U / \partial T)_v$ = *partial differentiation of internal energy with respect to temperature, at constant volume.*

In order to obtain ΔU when an ideal gas is heated from temperature T_1 to T_2 at constant volume, the integrated form of Eq. 26 is to be used

$$\Delta U = \int_{T_1}^{T_2} C_v dT = \int_{T_1}^{T_2} n C_v dT \dots\dots\dots(28)$$

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

We have defined C_v through Eq. 27. What about C_p ? Is there some thermodynamic property to which C_p can be related in a similar way? For this purpose, we define the term, enthalpy, in the next section.

Using the ideas developed in this section, answer the following **SAE**.

3.9 Enthalpy and Enthalpy Changes

Enthalpy of a system is defined by the relation,

$$H = U + pV \dots\dots\dots(29)$$

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

$$\Delta H = H_2 - H_1 \dots\dots\dots(30)$$

$$= (U_2 + P_2 V_2) - (U_1 + P_1 V_1)$$

$$= \Delta U + (P_2 V_2 - P_1 V_1) \dots\dots\dots(31)$$

In case of a constant pressure process ($P_1 = P_2 = P$), Eq. 31 can be written as,

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

$$\Delta H = \Delta U + P \Delta V \dots\dots\dots(32)$$

Rewriting Eq. 23 for a finite change, we get

$$q_p = \Delta U + P \Delta V \dots\dots\dots(33)$$

Using this equation in Eq. 32, $q_p = \Delta H$

The subscript p in q_p stands for the constant pressure condition. In other words, the enthalpy change is equal to the heat absorbed by the system at constant pressure .

For a small change in enthalpy, we can write

$$dq_p = dH \dots\dots\dots(34)$$

Using Eq. 3 and assuming that there is no phase change or chemical reaction we have

$$dH = C_p dT = nC_p dT \dots\dots\dots(31)$$

In order to obtain ΔH value when an ideal gas is heated from temperature T_1 to T_2 at constant pressure, the integrated form of Eq. 36 is to be used.

$$\Delta H = \int_{T_1}^{T_2} C_p dT = \int_{T_1}^{T_2} nC_p dT$$

[heat capacity at constant pressure is equal to the partial differential, of H with respect to temperature at constant pressure].

Since many laboratory processes are carried out at constant pressure (atmospheric pressure), the enthalpy change of a system is of great significance. It may be noted that since the absolute value of the internal energy of a system is not known, it is also impossible to know the absolute enthalpy of the system. Fortunately, for most processes we are only concerned with the changes in enthalpy which may be measured by taking any suitable reference states of elements.

Those processes in which heat is supplied to the system are called endothermic and, ΔH is given a positive sign; in exothermic processes (in which heat is evolved), ΔH negative. Enthalpy changes connected with certain typical processes are given special names.

For example, enthalpy of vaporization or evaporation is the enthalpy change accompanying the conversion of one mole of a liquid to its vapour. Similarly, enthalpy of fusion and sublimation are the enthalpy changes accompanying fusion or sublimation of one mole of a substance. For a chemical reaction, the enthalpy of reaction is the difference in the enthalpies of the products and the reactants as per the stoichiometry given in the chemical equation. We shall study enthalpy changes in detail in the next unit. In the next section we shall study the relationship between C_p and C_v ; values of an ideal gas.

4.0 Conclusion

We have discussed the, terms used in thermodynamics and defined work, heat and heat capacity. We have also explained the the first law of thermodynamics and looked at the calculation of work, internal energy change and heat absorbed or evolved in reversible and irreversible processes. The significance of enthalpy and enthalpy change of a system and Joule-Thompson effect.

5.0 Summary

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

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

The extensive and intensive variables are explained with examples.

The terms heat capacity, internal energy and enthalpy have been defined and discussed.

The formulae for the calculation of work, heat exchange and internal energy change in isothermal and adiabatic processes are derived. Examples are also worked out to explain the use of these formulae.

Joule-Thomson effect is explained and its importance in the liquefaction of gases is indicated.

6.0 Tutor-Marked Assignment

1. A gas is expanded from $4.00 \times 10^{-3} \text{ m}^3$ to $8.00 \times 10^{-3} \text{ m}^3$ against a constant pressure of $1.00 \times 10^5 \text{ Pa}$ and it has been used to heat 0.010 kg of water. Calculate the final temperature of water. Given: Initial temperature of water = 296.2 K and C_p for water = $75.2 \text{ J mol}^{-1} \text{ K}^{-1}$

2. A sample of 0.200 mol of argon expands adiabatically and reversibly such that temperature drops from 298 K to 188 K . If molar heat capacity for argon at constant volume is 12.48 J/mol/K , calculate the change in internal energy and the work done on the gas.

3. Calculate the heat required to increase the temperature of 1.00 mol of methane from 298 K to 398 K at constant pressure. C_p for methane = $35.3 \text{ J mol K}^{-1}$.

4. 1.00 mol of an ideal gas at $3.00 \times 10^2 \text{ K}$ and $2.00 \times 10^6 \text{ Pa}$ pressure is expanded reversibly and isothermally till its pressure is $2.00 \times 10^5 \text{ Pa}$. Calculate, ΔU , q and W .

7.0 References/Further Reading

Principles of Physical Chemistry, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.

Physical Chemistry, Gilbert W. Castellan, Narosa Publishing House, Addison-Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.

Physical Chemistry, P.c. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.

Physical-Chemistry through Problems, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.

Physical Chemistry-Principles and Problems, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi. 1990.

Unit 2

Thermochemistry

Content

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1.0 Introduction

The branch of science dealing with heat changes during a chemical reaction is known as Thermochemistry. In this unit, we shall deal with heat change accompanying a chemical reaction when it is carried out under constant volume or constant pressure. We shall define standard enthalpy of formation and enthalpy changes in different chemical reactions.

We shall also discuss the experimental method of determination of enthalpy changes. We will list some of the applications of Hess's Law of constant heat summation. Finally, we shall derive Kirchhoff's equation and discuss its importance.

2.0 Objectives

After studying this unit, you should be able to:

- i. derive the relationship between ΔU and ΔH and make calculations based on this relationship
- ii. define standard enthalpy of formation
- iii. state Hess's law of constant heat summation and explain its significance
- iv. calculate the enthalpy of a reaction using enthalpies of formation of compounds
- v. describe an experimental method for the determination of enthalpy of combustion
- vi. derive Kirchhoff's equation and state its significance
- vii. define bond enthalpy and
- viii. calculate enthalpies of reactions from bond enthalpies.

3.0 Learning Content

3.1 Relationship Between ΔU and ΔH

A chemical reaction can be carried out in two ways:

- i) In a closed vessel, so that there is no volume change.
- ii) In a pressure regulated vessel, so that there is no pressure change.

Accordingly, the heat change accompanying a chemical reaction can also be measured in two ways, viz., heat change at constant volume (q_v) and at constant pressure (q_p). From Eqs. 25 and 34, $q_v = \Delta U$ and $q_p = \Delta H$. In thermochemistry, the enthalpy change accompanying a chemical reaction is called the reaction enthalpy and is denoted by the symbol ΔH . Similarly, the internal energy change accompanying a chemical reaction is given the symbol ΔU . To denote formation, combustion and vaporization processes, subscripts used are *f*, *c* and *vap*, respectively. As in the case of Eqs. 25 and 34 we can write,

$$q_v = \Delta U \dots\dots\dots(1)$$

$$\text{and } q_p = \Delta H \dots\dots\dots(2)$$

Self-Assessment Exercise 1

1. In which two ways chemical reactions can be carried out?

The significance of ΔU and ΔH can be explained by the following equations:

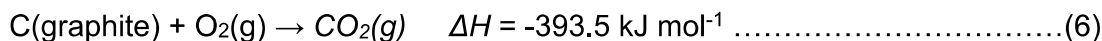
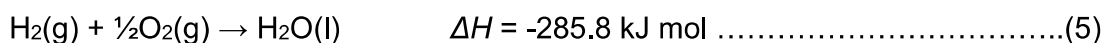
$$\Delta U = U_{\text{Products}} - U_{\text{Reactants}} \dots\dots\dots(3)$$

$$\Delta H = H_{\text{Products}} - H_{\text{Reactants}} \dots\dots\dots(4)$$

Since most reactions are carried out at constant pressure ΔH is more commonly used than ΔU .

3.1.2 Thermochemical Equations

In a thermochemical equation, in addition to the chemical reaction, the physical state of the various chemical species and the energy change are also specified. For example,



are thermochemical equations. In such equations, s, l and g, refer to solid, liquid and gaseous states, respectively. If a substance can exist in various allotropic forms, the particular form must be mentioned.

Relation between

ΔU and ΔH

If in a chemical reaction, the enthalpy of the system changes from H_1 to H_2 and if U_1 , P_1 , V_1 and U_2 , P_2 , V_2 are the corresponding internal energies, pressures and volumes, then

$$H_1 = U_1 + P_1V_1 \dots\dots\dots(7)$$

$$\text{and } H_2 = U_2 + P_2V_2 \dots\dots\dots(8)$$

$$\Delta H = H_2 - H_1 = U_2 + P_2V_2 - (U_1 + P_1V_1) = U_2 - U_1 + (P_2V_2 - P_1V_1)$$

$$\text{Hence, } \Delta H = \Delta U + (P_2V_2 - P_1V_1) \dots\dots\dots(9)$$

At constant pressure ($P_1 = P_2 = P$)

$$\Delta H = \Delta U + (PV_2 - PV_1) = \Delta U + P(V_2 - V_1)$$

$$\Delta H = \Delta U + P\Delta V \dots\dots\dots(10)$$

Using Eqs. 1 and 2,

$$q_p = q_v + P\Delta V \dots\dots\dots(11)$$

If we assume that (i) all gaseous reactants and products are ideal and (ii) there are n_1 and n_2 moles of gaseous reactants and products, respectively, then,

$$P_1V_1 = n_1RT \quad \text{and} \quad P_2V_2 = n_2RT$$

$$\text{Hence, } P_2V_2 - P_1V_1 = (n_2 - n_1)RT$$

Since pressure is constant,

$$P(V_2 - V_1) = P\Delta V = (n_2 - n_1)RT \dots\dots\dots (12)$$

Replacing $(n_2 - n_1)$ by Δn to represent the change in the number of moles of gaseous species in Eq. 12,

$$P\Delta V = \Delta nRT \dots\dots\dots (13)$$

Using this in Eq. 11,

$$q_p = q_v + \Delta nRT \dots\dots\dots(14)$$

$$\Delta H = \Delta U + \Delta nRT \dots\dots\dots (15)$$

or

Note that only the gaseous reactants and products are considered in the calculation of Δn . It may be noted that Δn can be

(i) positive, if the number of moles of gaseous products is more than those of gaseous reactants

(ii) negative, if the number of moles of gaseous reactants is more than those of gaseous products

(iii) zero, if $n_1 = n_2$

For example, consider the following reactions:

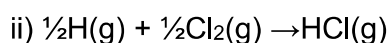
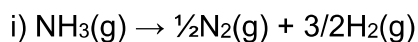


In Eq. 16, $\Delta n = (0 - (1 + \frac{1}{2})) = -\frac{3}{2}$; there are no gaseous products, but one mole of hydrogen and half a mole of oxygen are present as gaseous reactants. In Eq. 17, $\Delta n = (1 - 1) = 0$, since there is one mole each of gaseous reactant and product.

Using the above ideas, answer the following **SAE**.

Self-Assessment Exercise 2

1. Calculate $\Delta H^\circ_{\text{rxn}}$ for the following reactions:



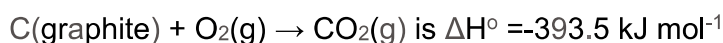
3.2 Standard Enthalpy of Formation

The standard enthalpy of formation of a compound is the enthalpy change accompanying the formation of one mole of the compound from its elements in their most stable state, all substances being in their standard state (1 bar pressure and any specified temperature). The standard enthalpy of formation is denoted by ΔH_f° .

The superscript $^\circ$ indicates the standard state and the subscript 'f' denotes formation reaction. Although we do not know the absolute enthalpy of the compound, we know its relative enthalpy with respect to the elements from which it is formed. Therefore, we adopt an arbitrary convention that the standard enthalpies of formation of all elements is zero at any specific temperature at 1 bar. If an element shows allotropy or exists in different phases, then the enthalpy is taken as zero for the most stable allotrope or phase. Phosphorus is an exception (yellow phosphorus is taken as standard).

As a result of this, the enthalpy of any substance in its standard state is equal to ΔH° , the enthalpy change of the reaction in which one mole of the substance is formed from the elements in their standard state.

For example, the enthalpy of the reaction:



Thus, we have

$$\begin{aligned} \Delta H^\circ &= \Delta H^\circ(\text{CO}_2) - \Delta H^\circ(\text{graphite}) - \Delta H^\circ(\text{O}_2) \\ &= \Delta H^\circ(\text{CO}_2) - 0 - 0 = \Delta H^\circ(\text{CO}_2) \end{aligned}$$

Therefore, the standard enthalpy of formation for CO_2 is equal to ΔH° which in turn is equal to $-393.5 \text{ kJ mol}^{-1}$. If temperature has also to be indicated, then it is shown in the parenthesis. Thus, $\Delta H_f^\circ(298.15\text{K})$ means standard enthalpy of formation at 1 bar and 298.15 K. Most of the data are available at 298.15 K in thermodynamic tables. Standard enthalpy of formation of some substances are given in Table 1.

Table 1: Standard Enthalpy of Formation of Some Selected Substances at 298.15 K

Substance	$\frac{\Delta_f H^\circ(298.15 \text{ K})}{\text{kJ mol}^{-1}}$	Substance	$\frac{\Delta_f H^\circ(298.15 \text{ K})}{\text{kJ mol}^{-1}}$
$\text{H}_2\text{O}(l)$	-285.8	$\text{H}_2\text{O}_2(l)$	-187.8
$\text{H}_2\text{O}(g)$	-241.6	$\text{N}_2\text{H}_4(l)$	+50.6
$\text{CO}_2(g)$	-393.5	$\text{NO}_2(g)$	+33.2
$\text{NH}_3(g)$	-46.1	$\text{N}_2\text{O}_4(g)$	+9.2
$\text{CH}_4(g)$	-74.81	$\text{NaCl}(s)$	-411.2
$\text{C}_2\text{H}_6(g)$	-84.68	$\text{KCl}(s)$	-436.8
$\text{CH}_3\text{OH}(l)$	-238.7	$\text{Glucose}(s)$	-1268.0
$\text{C}_6\text{H}_6(l)$	+49.0		

3.3 Calculation of Reaction Enthalpies

It is possible to calculate standard reaction enthalpies using thermodynamic tables such as Table 1. The principle is that,

$$\Delta H = (\text{Sum of } \Delta H \text{ values of products}) - (\text{sum of } \Delta H \text{ values of reactants}) \dots\dots\dots(18)$$

This relationship can be explained using general reaction of the following type:



where p, q, r and s are the stoichiometric coefficients and A, B, C and D are reactants and products. Let the standard enthalpies of formation of A, B, C and D be represented by $\Delta H^\circ(A)$, $\Delta H^\circ(B)$, $\Delta H^\circ(C)$, and $\Delta H^\circ(D)$, respectively: The standard reaction enthalpy for the reaction mentioned in Eq. 19 is given by,

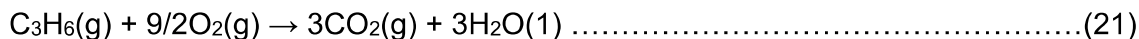
$$\Delta H^\circ = (r\Delta H^\circ(C) + s\Delta H^\circ(D)) - (p\Delta H^\circ(A) + q\Delta H^\circ(B)) \dots\dots\dots(20)$$

[Earlier the standard state was defined as 1 atmosphere and any specified temperature but IUPAC has now adopted the standard state as 1 bar at any specified temperature. Since 1 atm. is equal to 1.01325 bar, it does not cause much change in ΔH° , specially for substances in liquid and solid states]

Let us illustrate the calculation of ΔH° using an example.

Example 1

For the reaction given in Eq. 21, let us calculate ΔH° at 298.15 K.



Given that: ΔH° values of propene, carbon dioxide and water at 298.15 K are 20.42, -393.5 and

-285.8 kJ mol⁻¹, respectively.

From Eqs. 18 and 21,

$$\Delta H^\circ = (3 \Delta H^\circ(CO_2) + 3 \Delta H^\circ(H_2O)) - (\Delta H^\circ(C_3H_6) + 9/2\Delta H^\circ(O_2))$$

$$= 3 \times (-393.5) + 3 \times (-285.8) - (1 \times 20.42)$$

(since the standard enthalpy of formation of oxygen is zero.)

$$\Delta H^\circ = -2058 \text{ kJ}$$

Hence, we are in a position to calculate ΔH° for a reaction using ΔH° values.

Enthalpy is a state property; its value changes by the same amount irrespective of the path from the reactants to the products. Hence, it is possible to calculate ΔH° of a reaction from a sequence of reactions. This is generalised as Hess's law of constant heat summation; we shall study this law in the next section.

Self-Assessment Exercise 3

1. Express the standard reaction enthalpy of the reaction,

$C_2H_6(g) + 7/2O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$ in terms of the standard enthalpies of formation of the components.

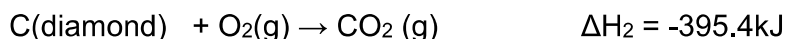
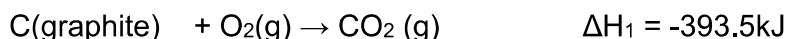
3.4 Hess's Law of Constant Heat Summation

Hess's law can be stated as follows:

The standard enthalpy change for a reaction is the sum of standard enthalpies of a sequence of reactions (at the same temperature and pressure); the overall reaction should be capable of being represented by the given sequence of reactions.

Hess's law is a direct consequence of the law of conservation of energy. It is not necessary that every reaction in the given sequence should be conducted in a laboratory. A particular reaction can also be imaginary. The only requirement is that the individual chemical reactions in the sequence must balance and add up to the equation for a particular reaction. Also Hess's law enables arithmetic operations of chemical equations. This law is helpful in calculating enthalpies of reactions which cannot be experimentally determined; what is required is to select a correct sequence of reactions. We give below the use of Hess's law in calculating the enthalpy of conversion of graphite to diamond which is very difficult to determine.

Example 2



Then subtracting, we get

$$C(\text{graphite}) - C(\text{diamond}) = 0 \quad \text{and} \quad \Delta H = \Delta H_1 - \Delta H_2 = -393.5 \text{ kJ} - (-395.4 \text{ kJ}) = 1.9 \text{ kJ}$$

Hence, we can write

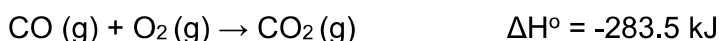
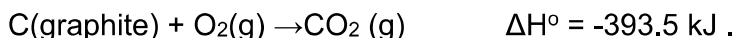


We shall consider many examples of the use of Hess's Law in the next section. Before proceeding to the next section, answer the following **SAE**.

Self-Assessment Exercise 4

Calculate ΔH° for the reaction,

$C(\text{graphite}) + \frac{1}{2}O_2(g) \rightarrow CO(g)$ at 298 K, using the following thermochemical equations:

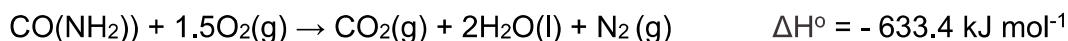
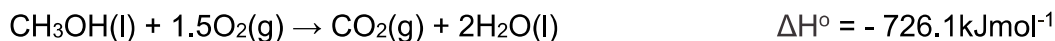


3.5 Enthalpy Changes in Different Processes and Reactions

Enthalpy changes take place in almost all physical and chemical processes. Due to their importance in science and engineering, special names have been assigned to enthalpy changes of some such processes. We define below the enthalpy changes for some of these processes.

3.5.1 Enthalpy of Combustion

The change in enthalpy during the complete combustion of one mole of a substance in oxygen is called its enthalpy of combustion (ΔH°_c). The final oxidation products for a compound containing only C, H, and N are $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{l})$ and $\text{N}_2(\text{g})$; its compound also contains Cl, Br, I, F, S, P, the final products include the aqueous solutions of HCl, HBr, HI, HF, H_2SO_4 and H_3PO_4 at infinite dilution. Thus, the enthalpies of combustion for methanol and urea are represented by the reactions:

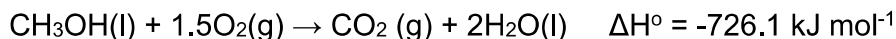


The enthalpy of combustion is quite useful to determine the enthalpies of formation of those substances which are difficult to measure experimentally. Here again we make use of Hess's law.

Example 3

The enthalpy of combustion for methanol at 298.15 K is $-726.1 \text{ kJ mol}^{-1}$. What is its enthalpy of formation? Given: $\Delta H^{\circ}_f(\text{CO}_2) = -393.5 \text{ kJ mol}^{-1}$ and $\Delta H^{\circ}_f(\text{H}_2\text{O}) = -285.8 \text{ kJ mol}^{-1}$.

The combustion reaction of methanol can be written as,



Using Eq. 18,

$$\Delta H^{\circ} = \Delta H^{\circ}_c(\text{CH}_3\text{OH}) = \Delta H^{\circ}_f(\text{CO}_2) + 2\Delta H^{\circ}_f(\text{H}_2\text{O}) - \Delta H^{\circ}_f(\text{CH}_3\text{OH})$$

(since $\Delta H^{\circ}_f(\text{O}_2) = 0$)

$$\text{Hence, } \Delta H^{\circ}_f(\text{CH}_3\text{OH}) = \Delta H^{\circ}_f(\text{CO}_2) + 2\Delta H^{\circ}_f(\text{H}_2\text{O}) - \Delta H^{\circ}_c(\text{CH}_3\text{OH})$$

$$= ((-393.5) + (2 \times (-285.8) + 726.1)) \text{ kJ mol}^{-1}$$

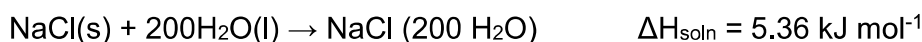
$$= -239.0 \text{ kJ mol}^{-1}$$

It can be seen that it agrees with the value given in Table 1.

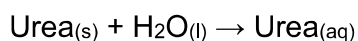
3.5.2 Enthalpy of Solution

The formation of solution (by dissolution of a solute in a solvent) is also accompanied by heat changes, but these heat changes are dependent not only on the nature of the solute and solvent but also on the composition of the solution. Therefore, the enthalpy change accompanying the complete dissolution of one mole of solute in a definite

amount of the solvent so as to give a solution of a specified concentration is defined as the integral enthalpy of solution (or integral heat of solution). As an example, consider the dissolution of 1 mol of NaCl in 200 mol (water as represented by the equation,



Where $\Delta H_{\text{soln}} = 5.36 \text{ kJ mol}^{-1}$ represents the integral enthalpy of solution. In general, it can be positive or negative depending on the nature of the solute and solvent. A special case of enthalpy of solution arises when a sufficiently large amount of solvent is used so that further dilution does not bring any heat changes. This is defined as the enthalpy of solution at infinite dilution. For aqueous solution, this reaction is represented by,



The symbol (*aq*) is used to represent an aqueous solution which is so dilute that additional dilution is not accompanied by any heat changes. In contrast to integral enthalpy of solution, we define a quantity called differential enthalpy of solution. This is the enthalpy change when 1 mol of solute is dissolved in a sufficiently large volume of solution of concentration, *c*, so that the final concentration remains almost unchanged. The differential enthalpy of solution depends on the concentration of the solution. It can be calculated from the integral enthalpy of solution.

Another type of enthalpy term often used in solutions is the enthalpy of dilution, ΔH_{dil} . This is defined as the enthalpy change when a solution containing one mole of solute at concentration C_1 is diluted by the addition of solvent so that the final concentration is C_2 . It is obvious that the enthalpy of dilution depends on both C_1 and C_2 .

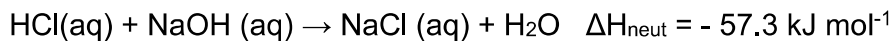
Self-Assessment Exercise 5

1. What is enthalpy of dilution

3.5.3 Enthalpy of Neutralization

The enthalpy of neutralization of an acid is the enthalpy change which accompanies the complete neutralization of a dilute aqueous solution of an acid containing one mole of H^+ ions by a dilute aqueous solution of a base containing one mole of OH^- ions.

An example is given below:



It is observed experimentally that the enthalpy of neutralization of strong acids or bases (with strong bases or acids, respectively) is essentially the same (i.e., -57 kJ/mol). This is because of the fact that strong acids and bases are completely dissociated in their aqueous solutions, and the process of neutralization of strong acids and bases is represented by



Hence, the enthalpy of neutralization of strong acids and bases is the enthalpy of formation of one mole of water from one mole each of H^+ and OH^- ions. When a weak acid or base is neutralised, the enthalpy of neutralisation deviates from the value of $-57.3 \text{ kJ mol}^{-1}$. This is due to the low dissociation of weak acids and bases; a portion of the energy is utilised in the process of dissociation of the weak acids and bases.

So far, we defined enthalpies of some processes; let us now study the experimental determination of enthalpy changes. On the basis of the above material, answer the following **SAE**.

Self-Assessment Exercise 6

At 298 K, the standard enthalpies of formation of $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ are 33.2 and 9.2 kJ mol^{-1} . Calculate the standard enthalpy of the following reaction: $\text{N}_2\text{O}_4(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

3.6 Experimental Determination of Enthalpy of Combustion

Calorimeters are used for determining the enthalpy changes in various processes. As a matter of fact, calorimetry is the most important experimental technique in thermodynamics and a lot of attention has been devoted to make it very sensitive. At present calorimeters are available which can measure heat and temperature changes accurately. Let us explain here the experimental determination of the enthalpy of combustion.

The enthalpy of combustion is determined using a Bomb Calorimeter (Fig. 1).

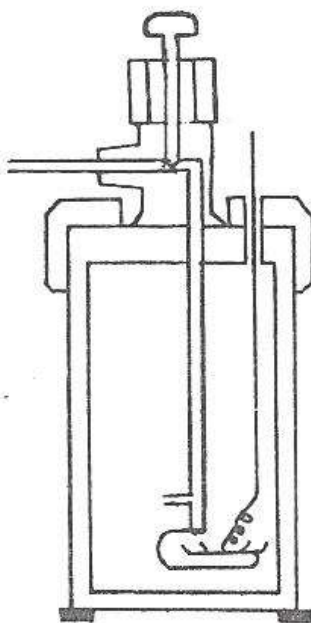


Fig. 1: Bomb Calorimeter.

The method consists of the combustion of a definite amount of the substance in an inner vessel called the 'bomb'. The bomb is placed inside a definite quantity of water taken in an outer vessel. The outer vessel is thoroughly insulated. The temperature readings of the water kept in it are measured before and after the combustion using a sensitive thermometer. From the heat capacity of the calorimeter, the amount of the substance taken and the temperature readings, the enthalpy of combustion can be calculated. In general, using adiabatic calorimeters, the enthalpies of reactions can be determined.

3.7 Kirchoff's Equation

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

If C_p is the heat capacity of a substance, then for a temperature rise dT , the increase in enthalpy is given by Eq. 36 (of Unit 1) as

$$dH = C_p dT \dots\dots\dots(22)$$

In the case of enthalpy of a reaction (ΔH), we can rewrite Eq. 22 as,

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

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

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

Eq. 23 on integration gives,

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT \dots\dots\dots(24)$$

Where ΔH_2 and ΔH_1 are the enthalpies of reaction at temperatures T_2 and T_1 respectively. Eq. 24 is called Kirchoff's equation. Similarly we can also obtain the expression,

$$\Delta U_2 = \Delta U_1 + \int_{T_1}^{T_2} \Delta C_v dT \dots\dots\dots(25)$$

Where ΔU_1 and ΔU_2 are the changes in internal energy of the reaction at temperatures T_1 and T_2 , and ΔC_v is the difference in heat capacities between products and reactants at constant volume. Let us now consider three of the special cases of Eq. 24:

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

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

$$\Delta H_2 = \Delta H_1 + \Delta C_p(T_2 - T_1) \dots\dots\dots(26)$$

i.e. ΔH either decreases or increases regularly with temperature. For most reactions Eq. 26 is valid for a small range of temperatures.

iii) If ΔC_p changes with temperature, then Eq. 24 has to be integrated by expressing C_p as a function of temperature. The variation in C_p is usually expressed in the following way:

$C_p = a + bT + cT^2 + \dots$; the coefficients a, b, c, \dots etc., are characteristic of a particular substance .

[The heat change measured using a bomb calorimeter is equal to the internal energy change accompanying combustion process, To calculate enthalpy of combustion. use Eq. 15. C_p is usually given in $J\ mol^{-1}\ K^{-1}$ units. You should remember to convert it into $kJ/ mol/K$ (by division by 1000), if ΔH is in kJ/ mol units].

Let us work out an example to show the use of Eq. 26.

Example 4: ΔH for the reaction.

C (graphite) + H_2O (g) \rightarrow CO (g) + H_2 (g) at 298 K is 131.2 kJ. The C_p values are given below in the temperature range, 298 to 348 K.

Substance	CP(J mol ⁻¹ K ⁻¹)
Graphite	15.93
$H_2O(g)$	30.04
$CO(g)$	26.51
$H_2(g)$	29.04

Calculate ΔH at 348 K.

The C_p values given above are independent of temperature; hence, we can find

ΔH at 348 K using Eq. 26.

Let us first calculate ΔC_p

$$\Delta C_p = \{ [1 \times C_p(CO) + 1 \times C_p(H_2)] - [1 \times C_p(\text{graphite}) + 1 \times C_p(H_2O)] \} J.K^{-1}$$

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

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

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

$$= 9.58 \times 10^{-3}\ kJ\ K^{-1}$$

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

Using Eq. 26, .

$$\Delta H \text{ at } 348\ K = \Delta H \text{ at } 298\ K + \Delta C_p(348-298)$$

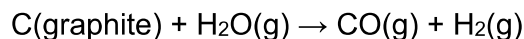
$$= (131.2 + 9.58 \times 10^{-3} \times 50)\ kJ$$

$$= 131.7\ kJ .$$

Using the ideas developed above, work out the following **SAE**.

Self-Assessment Exercise 7

For the reaction,



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

	a	b x 10 ³	c x 10 ³
Graphite	15.93	6.52	0.0
H ₂ O(g)	30.04	9.920	8.71
CO(g)	26.51	7.68	11.71
H ₂ (g)	29.04	-0.836	20.09

3.8 Bond Enthalpies and Estimation of Enthalpies of Formation

Bond enthalpy is a useful concept in thermochemistry. It finds application in the calculation of standard enthalpy of formation and standard enthalpy of reaction of many compounds. In a molecule, atoms are linked through chemical bonds. When a molecule decomposes into atoms, the bonds are broken and the enthalpy increases. This is also defined as the enthalpy of atomization, ΔH_{atm} , and is always positive. For example, the enthalpy of the following reaction is the enthalpy of atomization of ethane gas:



On analysis of ΔH_{atm} for a large number of such reactions, it has been found that specific values of bond enthalpies may be assigned to different types of bonds (Table 2). These bond enthalpies correspond to the decomposition of a molecule in the gaseous state to atoms in the gaseous state. Certain substances in the solid state when sublimed are converted into gaseous atoms. Thus, graphite when heated is converted into gaseous atoms, and the heat required for one mole can be called the molar enthalpy of atomization of graphite which is equal to 717 kJ mol^{-1} . If graphite is considered the reference state for carbon, then the atomisation can be written as follows



[NB: Enthalpy of atomization is the enthalpy change accompanying a reaction in which a molecule is shattered into its component atoms. Enthalpy of atomization of graphite is useful in the calculation of standard enthalpy of formation of organic compounds].

Table 2: Bond Enthalpies (B)

Bond	$\frac{B}{\text{kJmol}^{-1}}$	Bond	$\frac{B}{\text{kJmol}^{-1}}$	Bond	$\frac{B}{\text{kJmol}^{-1}}$
H-H	436	C-F	484	C=C	813
O-H	463	C-Cl	338	N-N	163
C-H	412	C-Br	276	N=N	40
F-F	155	C-I	238	N=N	945
Cl-Cl	242	C-C	348	O-O	146
Br-Br	193	C=C ^a	612	O=O	497
I-I	151	C=C ^b	518	F-H	565
		C-O	358	Cl-H	431
		C=O	745	Br-H	366
				I-H	299

a-in alkenes, b-in aromatic compounds

The enthalpies of atomization of some more elements which become atomized on sublimation are given in Table 3.

Table 3 : Standard enthalpies of Atomization at 208.15 K

Substance	$\frac{\Delta_{atom}H^\circ}{\text{kJ mol}^{-1}}$
C(Graphite)	717
Na(s)	108
K(s)	90
Cu(s)	339

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



[NB: Bond enthalpy is the average amount of energy required to break one mole of similar bonds present in different gaseous compounds into gaseous atoms. Note that in the place of bond enthalpy, the enthalpy of atomization is used for carbon (graphite) and other elements in the solid state]

.The quantities D_1 and D_2 are the first and second bond dissociation energies and are different from the bond enthalpy given for O-H in Table 2. Again, bond enthalpy is some kind of average of a large amounts of experimental data. These are of immense value in estimating the standard enthalpy of formation of a large number of compounds being synthesized and also for estimating the standard enthalpy of reactions involving these new molecules.

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

i) First write the stoichiometric equation; then write (the most acceptable) Lewis structure of each of the reactants and the product.

ii) Use bond enthalpies from Table 2 and enthalpies of atomization from Table 3 to calculate the heat required to break all the bonds in the reactants and the heat released when the atoms form the product. The bond enthalpy of X-X bond can be denoted as $B(X-X)$ in arithmetic expressions.

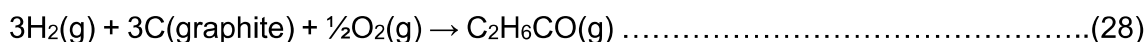
iii) The standard enthalpy of formation

= (Heat required to break all the bonds in the reactants) - (heat released when the atoms form the product).....(27)

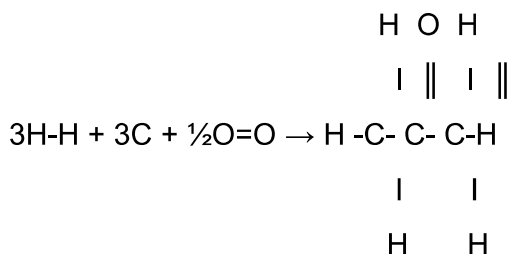
iv) Bond enthalpy values can be applied to compounds only if these are in gaseous if the compounds are in solid or liquid state, molar enthalpies of sublimation or vaporization also must be considered.

Example 5: Estimate the standard enthalpy of formation of acetone vapour and acetone liquid. (Enthalpy of vaporization of liquid acetone = 29 kJ/ mol).

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



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



Step (ii): The heat required to atomize the reactants

$$= 3B(\text{H}-\text{H}) + 3 \Delta H_{\text{atm}}(\text{graphite}) + \frac{1}{2}B(\text{O}=\text{O})$$

$$= [(3 \times 436) + (3 \times 717) + \frac{1}{2}(497)] \text{ kJ}$$

$$= 3708 \text{ kJ}$$

The heat released when the atoms form the product

$$6B(\text{C}-\text{H}) + 2B(\text{C}-\text{C}) + B(\text{C}=\text{O})$$

$$= [(6 \times 412) + (2 \times 348) + 745] \text{ kJ}$$

$$= 3913 \text{ kJ}$$

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

$$= -205 \text{ kJ/mol}$$

Hence the standard enthalpy of formation of acetone vapour is -205 kJ/mol and, the actual value is -216 kJ/mol.

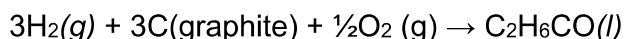
Step (iv): Let us now calculate the standard enthalpy of formation of liquid acetone. The condensation of acetone (l), from acetone (g) can be represented by Eq. 29.

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

$$= -\Delta H^{\circ}_{\text{vap}}(\text{acetone}) = -29 \text{ kJ mol}^{-1}$$



Adding Eqs, 28 and 29,



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

Self-Assessment Exercise 8

1. Calculate the standard enthalpy of formation of hydrogen chloride gas. Use Table
- 2.

4.0 Conclusion

We have discussed the heat change accompanying a chemical reaction when it is carried out under constant volume or constant pressure. We have also defined standard enthalpy of formation and enthalpy changes in different chemical reactions. Experimental method of determining enthalpy changes was also examined. Hess's Law of constant heat summation was defined and some of its applications mentioned. We also derived Kirchhoff's equation and discussed its importance.

5.0 Summary

In this unit, some of the aspects of thermochemistry have been discussed.

The relationship between ΔU and ΔH has been derived and its use in the calculation of internal energy change and enthalpy change has been indicated.

Standard enthalpy of formation has been defined; the relationship between standard enthalpies of formation of substances and standard enthalpies of reactions has been explained with an example.

Hess's law of constant heat summation has been stated and, its use in thermochemical calculations explained.

Kirchhoff's equation has been derived and used in the calculation of ΔH at a given temperature knowing its value at any other temperature.

Bond enthalpy values have been used in the calculation of standard enthalpies of formation.

6.0 Tutor-Marked Assignments

1. For the reaction
$$\text{Fe}_2\text{O}_3 (\text{s}) + 3\text{H}_2 (\text{g}) \rightarrow 2\text{Fe} (\text{s}) + 3\text{H}_2\text{O} (\text{l})$$
 ΔH at 298 K is -35.1 kJ. What will be the enthalpy of reaction at 375 K, if the difference between the sum of the Cps of the products and that of the reactants is 85.7 J/K and, it is independent of temperature?
2. Using Table 1 for the standard enthalpies of formation for $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$, calculate the standard enthalpy of formation for naphthalene, if its standard enthalpy of combustion is $-5153 \text{ kJ mol}^{-1}$.
3. The standard enthalpy of formation of $\text{H}_2\text{O}(\text{l})$ at 298 K is -285.8 kJ/mol . Calculate the standard internal energy change [$\Delta U^\circ(\text{H}_2\text{O})$] for the formation of water at 298 K.
4. Calculate the standard enthalpy of formation of $\text{PCl}_5(\text{s})$, using the following data:
$$\text{P}(\text{s}) + 1.5 \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_3(\text{l}) \quad \Delta H = -318 \text{ kJ}$$
$$\text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \rightarrow \text{PCl}_5(\text{s}) \quad \Delta H = -137 \text{ kJ}$$
5. Using the Cp data given in **SAE5**, calculate ΔH at 1000 K for the reaction:
$$\text{C} (\text{graphite}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO} (\text{g}) + \text{H}_2(\text{g})$$
 ΔH at 298 K is 131.2 kJ. Use the integration formulae given in Sec 3.5 of Unit 1.

7.0 References/Further Reading

- Principles of Physical Chemistry, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.
- Physical Chemistry, Gilbert W. Castellan, Narosa Publishing House, Addison-Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.
- Physical Chemistry, P.c. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.
- Physical-Chemistry through Problems, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.
- Physical Chemistry-Principles and Problems, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi. 1990.

Unit 3

The Second Law Of Thermodynamics

Content

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1.0 Introduction

It was seen in Unit 1 of this module that transfer of energy between a system and its surroundings takes place through heat and work. This is governed by the first law of thermodynamics which says that increase in the energy of a system must be accompanied by an equal decrease in the energy of the surroundings and vice versa. However, it does not tell us anything about the feasibility and direction of flow of energy.

According to the first law of thermodynamics, all processes in which energy is conserved are possible. For example, if a cup of hot tea is left on a table then according to the first law, it may be cooled by transferring energy to the surroundings or be heated by absorbing energy from the surroundings. But we all know from daily experience that the cup of tea will always cool till it acquires the temperature of the surroundings. Similarly, if a bottle of perfume is opened in a room, the perfume spreads throughout the room. The reverse process in which all the perfume vapours are collected in the bottle does not take place.

These are examples of what are known as spontaneous processes which are irreversible and proceed only in one direction. Again, according to the first law, there exists a direct relationship between heat and work. But it does not tell us whether heat can be completely transformed into work and if so, what is the effect on the system and the surroundings. These aspects are discussed in this unit. We shall start this unit with the description of Carnot cycle and calculate the efficiency of Carnot engine. This discussion helps us in arriving at the concept of entropy and thermodynamic scale of temperature.

We will also show how entropy changes can be used to distinguish between reversible and irreversible cyclic processes. Based on this discussion, the statements of the second law of thermodynamics will be given. The expressions useful in calculating the entropy changes under different conditions will then be derived. We shall finally discuss the physical meaning of entropy. Based on this unit, we can conclude that all spontaneous changes must be accompanied by entropy increase.

2.0 Learning Outcomes

After studying this unit, you should be able to

- i. differentiate between reversible and irreversible processes based on the value of q
- ii. describe Carnot cycle and derive an expression useful in calculating the efficiency of a Carnot engine
- iii. discuss thermodynamic temperature scale
- iv. define the term entropy
- v. state the second law of thermodynamics, and

- vi. calculate the entropy changes in chemical reactions

3.0 Learning Outcomes

3.1 Reversible, Irreversible and Cyclic Processes

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

$$\Delta U = q_{rev} + w_{rev} \text{ for reversible process} \dots\dots\dots(1)$$

$$\text{and } \Delta U = q_{irrev} + w_{irrev} \text{ for irreversible process } \dots\dots\dots(2)$$

$$\text{and so } q_{rev} + w_{rev} = q_{irrev} + w_{irrev} \dots\dots\dots(3)$$

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

i.e.,

$$-w_{rev} > -w_{irrev} \dots\dots\dots(4)$$

$$\text{and } w_{rev} < w_{irrev} \dots\dots\dots(5)$$

This is true when we compare the work done on the system under reversible and irreversible conditions. Let us assume that the driving forces under the two conditions mentioned above are fairly different. Also, let us assume that the processes are not adiabatic so that q_{rev} or q_{irrev} is not equal to zero. Using Eqs. 3 and 5, we can write,

$$q_{rev} > q_{irrev} \dots\dots\dots(6)$$

This means that in a nonadiabatic process, heat absorbed by a system from the surroundings is more under reversible conditions than under irreversible conditions. This relationship will be used by us in Sec 3.5 while calculating the entropy changes of isolated systems. Now let us consider ΔU , q and w values of a system in a cyclic process. As defined in Sec. 3.4 of Unit 1, a cyclic process is one in which the system after undergoing any number of processes returns to its initial state. This means that $\Delta U = 0$; hence, the work done by the system during all these processes should be equal to the heat absorbed by the system.

$$\text{i.e., } q = q_1 + q_2 + \dots = -(w_1 + w_2 + \dots) = -w \dots\dots\dots(7)$$

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

Using Example 1 discussed below, you can understand the validity of Eqs. 5 and 6.

Example 1

1.00×10^2 mol of an ideal gas at 3.00×10^2 K temperature and 6.00×10^6 Pa pressure occupies $4.16 \times 10^{-2} \text{ m}^3$ space initially. Calculate the work done on the gas and the heat absorbed by the gas if it undergoes expansion under the following conditions such that the final volume and pressure are 0.832 m^3 and 3.00×10^5 Pa:

(a) Isothermal reversible conditions (b) isothermal irreversible conditions.

Solution

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

Hence, using Eq. 8, $q = -w$ i.e., Heat absorbed by the gas = -(work done on the gas)

This equation is applied for both the processes discussed below.

(a) Let us first calculate q_{rev} and W_{rev} using Eq. 18 for the isothermal reversible expansion,

$$\begin{aligned} q_{\text{rev}} &= -w_{\text{rev}} = -2.303nRT \log V_1/V_2 \\ &= 2.303nRT \log V_2/V_1 \\ &= 2.303 \times 1.00 \times 10^2 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 3.00 \times 10^2 \text{ K} \log(0.832 \text{ m}^3 / 4.16 \times 10^{-2} \text{ m}^3) \\ &= 7.47 \times 10^5 \text{ J} \end{aligned}$$

Hence, the heat absorbed by the gas during isothermal reversible expansion (q_{rev}) = $7.47 \times 10^5 \text{ J}$ and the work done on the gas (w_{rev}) = $-7.47 \times 10^5 \text{ J}$.

(b) Let us calculate q_{irrev} and w_{irrev} for the isothermal irreversible process using Eq. 13 (Unit 1); in this process, the final pressure of the gas is equal to the external pressure (P_{ext}).

Hence, using Eq. 13 (Unit 1),

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

You can compare q and W values in the above two cases to verify the validity of Eqs. 5 and 6. ∴

$$w_{\text{rev}} = -7.47 \times 10^5 \text{ J}; w_{\text{irrev}} = -2.37 \times 10^5 \text{ J}$$

Hence, $w_{\text{rev}} < w_{\text{irrev}}$ as per Eq. 5.

$$q_{rev} = 7.47 \times 10^5 \text{ J}; q_{irrev,,} = 2.37 \times 10^5 \text{ J}$$

Hence, $q_{rev} > q_{irrev}$ as per Eq. 6.

[The work done on the system is given the symbol, w . Since work done by the system is obtained by reversing the sign of the work done on the system, work done by the system = $-w$. Work done by the system under reversible conditions = $-W_{rev}$. Work done by the system under irreversible conditions = $-W_{irrev}$. The transformation of Eq. 4 to Eq. 5 becomes clear once we understand the following relationship between numbers: $-3 > -4$ and $3 < 4$]

3.2 The Carnot Cycle

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

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

Such an engine is known as Carnot engine. The temperature of the source (T_H) is higher than that of the sink (T_C). The source and the sink are assumed to be of infinite heat capacity; that is, the temperatures of the source and the sink are not affected by small amounts of heat exchange. Carnot showed that the entire amount of the heat absorbed cannot be converted into work in a cyclic process, no matter how ideal the heat engine is. He deduced that only a fraction of the total heat absorbed is converted into work and this fraction is known as the efficiency of the Carnot engine. Let us now derive an equation useful in calculating its efficiency.

For the sake of simplicity, let us assume that the engine consists of a cylinder and a piston containing one mole of an ideal gas in between the two. The cylinder has perfectly insulated walls and a perfectly conducting base; the piston is frictionless. It is only for the sake of convenience that we have considered that the engine has ideal gas; actually there can be any suitable fluid. We make use of the following expressions from Unit 6 (for one mole of the gas) in this section.

$$W_{isothermal} = RT \ln \frac{V_{initial}}{V_{final}} \quad (\text{Eq. 17, Unit 1})$$

$$W_{adiabatic} = C_v(T_{final} - T_{initial}) \quad (\text{Eq. 53, Unit 1})$$

where W is the work done on the system and C_v is the molar heat capacity of the gas.

The plot of the pressure-volume data is shown in Fig. 1.

[In our discussion on expansion or contraction process, w is the work done on the system and q is the heat absorbed by the system. The second term on the right hand

side of Eq. 18 and also the right hand side expressions 0; Eqs. 9, 12 and 19 are obtained through the transformation based on the general formula: $\ln \frac{a}{b} = - \ln \frac{b}{a}$]

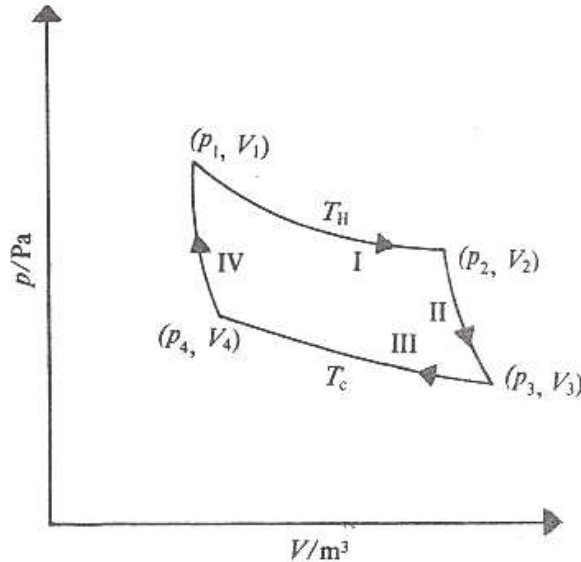


Fig. 1: Carnot cycle.

The Carnot cycle operation can be described by the following four steps:

(1) Isothermal expansion (2) Adiabatic expansion (3) Isothermal compression and (4) Adiabatic compression. Let us discuss them one by one.

Step I: Isothermal Expansion

Initially the gas has pressure P_1 and volume V_1 The cylinder is placed on a heat source maintained at the temperature T_H . The gas is isothermally and reversibly expanded-to a volume V_2 and pressure P_2 . Let the work done on the gas be W_1 and the heat absorbed from the source be q_H . In an isothermal process, $\Delta U = 0$.

Hence, using Eqs. 8 and 17

$$W_1 = -q_H = RT_H \ln(V_1/V_2) \dots\dots\dots(8)$$

$$\text{or } q_H = RT_H \ln(V_1/V_2) \dots\dots\dots(9)$$

Step II: Adiabatic Expansion

The cylinder is now placed on a thermally insulated stand and the gas is adiabatically and reversibly expanded till it attains a pressure P_3 , volume V_3 and temperature T_C . During this period, no heat is absorbed by the system. The work done on the gas, W_2 , as the gas gets cooled from T_H to T_C is given by using Eq. 53(Unit 1) as,

$$w_2 = C_V(T_C - T_H) \dots\dots\dots (10)$$

Step III :Isothermal Compression

The cylinder is now placed on a sink at temperature T_c and the gas is isothermally and reversibly compressed to a volume V_4 at pressure P_4 . During the process the work done on the gas is W_3 and the heat evolved to the sink is $-q_c$ (or q_c is the heat absorbed from the sink). Using Eqs. 8 and 17 (Unit 1),

$$W_3 = -q_c = RT_c \ln (V_3/ V_4) \dots\dots\dots(11)$$

$$\text{or } q_c = RT_c \ln (V_4/ V_3) \dots\dots\dots (12)$$

Step IV : Adiabatic Compression

In the last step, the cylinder is again placed on an insulating stand and the gas is adiabatically and reversibly compressed until it reaches its initial state of volume V_1 , pressure P_1 and temperature T_H . Hence the work done on the gas; W_4 is given by Eq. 53 (Unit 1) as,

The net work done on the system

$$W = W_1 + W_2 + W_3 + W_4 \dots\dots\dots (14)$$

$$\text{or } W = RT_H \ln(V_1/V_2) + C_v(T_c - T_H) + RT_c \ln(V_3/V_4) + C_v(T_H - T_c) \dots\dots\dots (15)$$

$$\text{i.e. } W = RT_H \ln V_1/V_2 + RT_c \ln V_3/V_4 \dots\dots\dots(16)$$

Eq. 48 of Unit 1 can be applied to relate the initial and final values of volume and temperature of the two adiabatic processes described in steps II and IV.

Applying Eq. 48 (Unit 1) to Step II we get,

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

Similarly applying Eq. 48 (Unit 1) to Step IV, we get,

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

Hence, $\left(\frac{V_2}{V_3}\right)^{\gamma-1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1}$

i.e., $\frac{V_2}{V_3} = \frac{V_1}{V_4} \dots\dots\dots(17)$

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

Using this in Eq. 16, $w = RT_H \ln V_1/V_2 + RT_c \ln V_2/V_1$

$$w = RT_H \ln V_1/V_2 - RT_c \ln V_1/V_2 \dots\dots\dots(18)$$

Hence, total work done on the system = $w = R(T_H - T_c) \ln V_1/V_2$

or total work done by the system, $w' = -w = R(T_H - T_c) \ln V_2/V_1 \dots\dots\dots(19)$

since work done by the system = $-(\text{work done on the system})$

We know that the heat exchange between the gas and the source or sink takes place only in isothermal processes (steps 1 and 3); in adiabatic processes (steps 2 and 4),

there is no heat exchange. Again, q_H is the heat absorbed from the source in step 1 and q_C is the heat absorbed from the sink in step 3.

The total heat absorbed by the system is,

$$q = q_H + q_C \dots\dots\dots (20)$$

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

$$\text{Hence } q = q_H + q_C = w' = -w = R(T_H - T_C) \ln V_2/V_1 \dots\dots\dots (21)$$

It may however be noted that out of the heat $q_H (=RT_H \ln V_2/V_1)$ as per Eq. 9) absorbed from the source, only some of it is converted into useful work and the rest is lost to the sink. Let us now calculate w'/q_H i.e., the ratio between the total work done by the system during one cycle and the heat absorbed in the first step. This quantity is called the efficiency ' η ' of a Carnot engine.

$$\text{Efficiency}(\eta) = \frac{\text{Total work done by the system}}{\text{Heat absorbed from the source at higher temperature}} = \frac{w'}{q_H} \dots\dots\dots (22)$$

Eqs. 9 and 21,

$$\eta = \frac{q_H + q_C}{q_H} = \frac{R(T_H - T_C) \ln V_2/V_1}{R T_H \ln V_2/V_1} \dots\dots\dots (23)$$

$$\eta = \frac{q_H + q_C}{q_H} = \frac{T_H - T_C}{T_H} \dots\dots\dots (24)$$

Since T_C and T_H are always positive and T_C/T_H is less than one, Eq. 24 can be rearranged as follows :

$$\eta = 1 - \frac{T_C}{T_H} = 1 + \frac{q_C}{q_H} < 1 \dots\dots\dots (25)$$

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

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

This is called Carnot theorem which can also be stated as: In all cyclic engines working between the same temperatures of the source and the sink, the efficiency is same. It must be pointed out that in the Carnot cycle, all processes have been carried out reversibly. Hence, maximum and minimum amount of work are involved in expansion and compression, respectively; this implies that there cannot be any engine more efficient than Carnot engine. In actual engines, there is irreversibility due to sudden expansion and compression and also due to the friction of the piston.

The following example will show the use of Eq. 24.

Example 2

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

Solution

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

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

$$\begin{aligned} \text{Using Eq. 24, } \eta &= \frac{T_H - T_C}{T_H} = \frac{(4.00 \times 10^2 - 3.00 \times 10^2) \text{ K}}{4.00 \times 10^2 \text{ K}} \\ &= 0.250 \end{aligned}$$

Using the data given in this example, answer the following **SAE**.

Self-Assessment Exercise

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

3.3 Thermodynamic Temperature Scale

For an engine of the type discussed above, both the efficiency and the ratio q_C/q_H can be easily calculated by measurement of the work and heat changes involved. The ratio, q_C/q_H , as shown above, depends only on the temperatures T_C and T_H and are completely independent of the properties of any particular substance. Thus, it is possible to establish a scale of temperature (the absolute or thermodynamic scale) which is not dependent on any particular substance. We can see from Eq. 25, that if $T_C = 0$, $\eta = 1$.

We can now define absolute zero as that temperature of the sink at which the efficiency of a Carnot engine will be unity. The size of the degree on this scale is the same as that on the centigrade scale. The kelvin unit is named in honour of Lord Kelvin, who arrived at the thermodynamic scale of temperature based on the properties of reversible heat engines.

3.4 Entropy

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

If in a Carnot engine, heat q_2 is absorbed at the higher temperature T_2 and q_1 is absorbed at the lower temperature T_1 , (actually q_1 will be a negative quantity since heat is rejected) then, according to Eq. 24,

$$\frac{q_2 + q_1}{q_2} = \frac{T_2 - T_1}{T_2} \dots\dots\dots(26)$$

$$\text{or } 1 + q_1/q_2 = 1 - T_1/T_2 \dots\dots\dots(27)$$

i.e., $q_1/T_1 = -q_2/T_2$ (28)

Hence,

$$\frac{q_1}{T_1} = \frac{q_2}{T_2} = 0 \text{ (29)}$$

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

Any reversible cyclic process can be broken into a large number of infinitesimal Carnot cycles (as in Fig. 2). If in each such small Carnot cycle, heat dq_1 is absorbed at temperature T_1' and dq_2 absorbed at T_2' , then for each small Carnot cycle,

$$dq_1/T_1' + dq_2/T_2' = 0 \text{(30)}$$

Summing these over all the cycles we can write in general, sum of dq_i/T_i terms over all the cycles = 0(31)

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

$$\oint dq_{rev}/T=0 \text{ (32)}$$

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

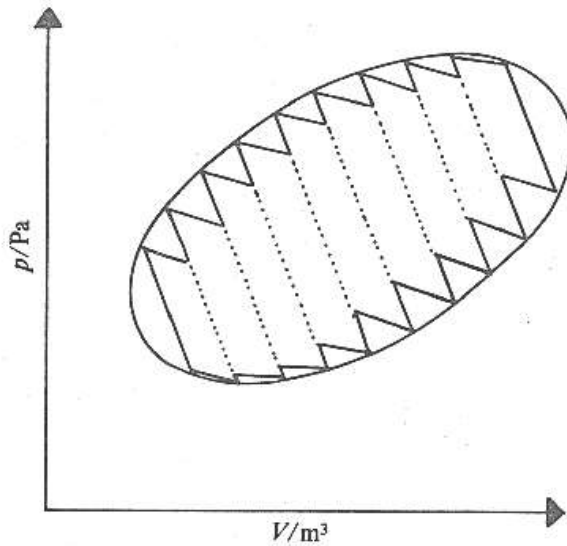


Fig. 2 : Infinitesimal Carnot cycles.

Now consider a system going in a reversible manner from an initial state A to an intermediate state B and then back to A via another path (Fig. 3).

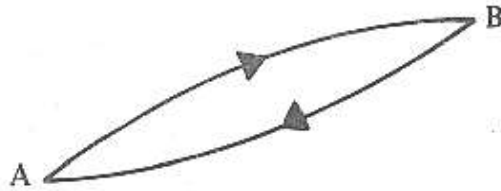


Fig. 3 : The cyclic change ABA.

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

Hence, in the entire cycle,

$$\text{sum of } dq_{rev}/T \text{ terms} = \sum dq_{rev}/T = 0 \dots\dots\dots(33)$$

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

$$\sum_{\text{cycle}} dq_{rev}/T = \sum_{A \rightarrow B} dq_{rev}/T + \sum_{B \rightarrow A} dq_{rev}/T = 0 \dots\dots\dots(34)$$

Or in terms of integrals,

$$\int dq_{rev}/T = \int_B^A dq_{rev}/T + \int_A^B dq_{rev}/T = 0 \dots\dots\dots(35)$$

and so

$$\int_B^A dq_{rev}/T = - \int_A^B dq_{rev}/T \dots\dots\dots(36)$$

Thus, the quantity $\int_A^B dq_{rev}/T$ is not dependent on the path chosen and is only dependent on the initial and final states of the system. This means that it represents a change in some thermodynamic property. This property is called entropy (S), and we write,

$$dq_{rev}/T = dS \dots\dots\dots(37)$$

$$\text{Thus, } \int dS = 0 \dots\dots\dots(38)$$

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

$$\Delta S = S_B - S_A = \int_A^B dq_{rev}/T \dots\dots\dots(39)$$

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

If we now put $dq = TdS$ (from Eq. 37), $dU = nC_vdT$ (from Eq. 26) and

$dw = -pdV$ (from Eq. 12, Unit 1) in Eq. 7 (Unit 1), we get Eq. 40.

$$dU = dq + dw$$

Hence,

$$dU = nC_vdT = TdS - pdV \dots\dots\dots(40)$$

As per Eq. 29 of Unit 1,

$$H = U + pV$$

Differentiation of this gives,

$$dH = dU + pdV + Vdp$$

$$\text{using Eq. 40, } dH = TdS - pdV + pdV + Vdp = TdS + Vdp \dots\dots\dots(41)$$

Eqs. 40 and 41 are the combined mathematical statements of the first and second laws of thermodynamics. The first law of thermodynamics is concerned with the conservation of energy and the second law of thermodynamics introduces the concept of entropy. It is worth mentioning that the entropy change in a system is given by,

$$dS = \frac{dq_{rev}}{T} \dots\dots\dots(42)$$

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

On the basis of the above ideas, answer the following **SAE**.

Self-Assessment Exercise 2

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

3.5 Entropy Changes in Isolated Systems

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

3.5.1 Isothermal Reversible Expansion and Reversible Compression

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

$$\Delta S_1 = q_{rev}/T \dots\dots\dots(43)$$

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

$$\Delta S_2 = - q_{rev}/T \dots\dots\dots (44)$$

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

$$\Delta S_a = \Delta S_1 + \Delta S_2 = q_{rev}/T - q_{rev}/T = 0 \dots\dots\dots (45)$$

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

$$\Delta S_b = 0 \dots\dots\dots(46)$$

$$\text{Hence, } \Delta S \text{ in this cyclic process} = \Delta S_a + \Delta S_b = 0 \dots\dots\dots(47)$$

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

3.5.2 Isothermal Irreversible Expansion and Reversible Compression

Let the gas undergo isothermal irreversible expansion from a volume V_1 to V_2 at a temperature T . In this process, let us assume that the gas absorbs heat q irreversibly whereas the reservoir loses the same heat reversibly. However, the entropy change of the system (ΔS_1) is still given by Eq. 43 as per definition.

$$\Delta S_1 = q_{rev}/T \dots\dots\dots (48)$$

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

$$\Delta S_2 = - q/T \dots\dots\dots (49)$$

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

$$\Delta S_a = \Delta S_1 + \Delta S_2 = q_{rev}/T - q/T > 0 \dots\dots\dots(50)$$

Since $q_{rev} > q$ as per Eq. 6.

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

$$\Delta S_b = 0 \dots\dots\dots (51)$$

[A substance of high heat capacity does not suffer much of temperature change by gain or loss of even significant amount of heat. A reservoir losing or gaining heat

reversibly implies that it contains a substance of high heat capacity. The entropy change in a process is calculated by dividing the heat change under reversible condition by temperature whether or not the process is reversible].

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

$$= \Delta S_a + \Delta S_b > 0 \dots\dots\dots(52)$$

Hence for any reversible process or cycle $\Delta S_{total} = 0 \dots\dots\dots(53)$

For any irreversible process or cycle $\Delta S_{total} > 0 \dots\dots\dots(54)$

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

The first law: Energy of the universe is constant.

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

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

Example 3

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

Solution

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

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

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

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

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

Using Eq. 43, the entropy change of the gas (ΔS_{gas})

$$\begin{aligned}
&= \frac{\text{Heat change under reversible conditions}}{\text{Temperature}} \\
&= \frac{7.47 \times 10^5 \text{ J}}{3.00 \times 10^2 \text{ K}} \\
&= 2490 \text{ J K}^{-1}
\end{aligned}$$

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

Using Eq. 37, the entropy change of the heat reservoir ($\Delta S_{\text{reservoir}}$)

$$\begin{aligned}
&= - \frac{2.37 \times 10^5 \text{ J}}{3.00 \times 10^2 \text{ K}} \\
&= - 790 \text{ J K}^{-1}
\end{aligned}$$

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

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

Hence the entropy of the isolated system increases by 1700 J K^{-1} in this irreversible expansion. To calculate the entropy change in the universe for a particular process, we should know the entropy change of the system and of the surroundings. We shall study in Secs. 3.7 to 3.10 the ways of calculating the entropy changes in the system. Let us now see how to calculate the entropy change of the surroundings in any particular process. The surroundings of a system constitute a huge heat reservoir..Hence, the heat loss or gain from the surroundings (q_{surr}) is always' considered reversible; this is true whether the system behaves reversibly or irreversibly.

Let the temperature of the surroundings be T_{surr} .

$$\text{Hence, the entropy change of the surroundings} = \frac{q_{\text{surr}}}{T_{\text{surr}}}$$

This is true for all types of processes.

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

$$\text{Hence, the entropy change of the surroundings} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{-\Delta H}{T_{\text{surr}}}$$

Self-Assessment Exercise 3

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

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

3.6 Statements of the Second Law of Thermodynamics

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

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

3.7 Entropy Changes in Chemical Reactions

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



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

$$\Delta S = (cS_C + dS_D + \dots) - (aS_A + bS_B + \dots) \quad \dots \dots \dots (56)$$

where c, d, a, b, \dots etc., are the stoichiometric coefficients in Eq. 55,

The variation of entropy change for a reaction with temperature can be readily deduced from Eq. 56.

According to Eq. 41, $dH = TdS + Vdp$

or $C_p dT = TdS + Vdp$

At constant pressure ($dp=0$),

$C_p dT = TdS_p$ or

$dS_p = \frac{C_p}{T} dT$

$dS_p = \frac{C_p}{T} dT$

or $(\partial S / \partial T)_p = \frac{C_p}{T}$

Cp is the molar heat capacity of a substance at constant pressure.

$$d(\Delta S) = \Delta C_p dT/T \dots\dots\dots(57)$$

Assume that ΔS_1 and ΔS_2 are the entropy changes at temperatures T_1 and T_2 and, C_p is independent of temperature. Then Eq, 57 on integration gives,

$$\int_{\Delta S_1}^{\Delta S_2} d(\Delta S) = \Delta C_p \int_{T_1}^{T_2} dT/T \dots\dots\dots(58)$$

$$\text{or } \Delta S_2 - \Delta S_1 = \Delta C_p \ln T_2/T_1 \dots\dots\dots(59)$$

Eq, 59 is useful in determining ΔS value of a reaction at any particular temperature, if it is known at any other temperature along with C_p values.

Entropy values of substances can be determined using the third law of thermodynamics; we shall study this in the next unit. The entropy values of some of the substances in their standard states at 298.15 K are given in Table 1. These are known as standard entropy (S°) values. Similar to the calculation of ΔS as per Eq. 56, we can calculate ΔS° from the standard entropy values of the reactants and the products.

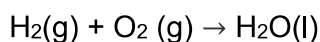
Table 1: Standard Entropy (S°) values at 298.15 K

Substance	$S^\circ/\text{JK}^{-1}\text{mol}^{-1}$	Substance	$S^\circ/\text{JK}^{-1}\text{mol}^{-1}$
C(Graphite)	5.7	$\text{C}_6\text{H}_6(l)$	173.3
C(Diamond)	2.4	$\text{He}(g)$	126.2
$\text{AgCl}(s)$	96.2	$\text{H}_2(g)$	130.7
$\text{AgBr}(s)$	107.1	$\text{Cl}_2(g)$	223.1
$\text{Ag}(s)$	42.6	$\text{CO}_2(g)$	213.7
$\text{Hg}(l)$	76.0	$\text{O}_2(g)$	205.1
$\text{Br}_2(l)$	152.2	$\text{CH}_4(g)$	186.3
$\text{H}_2\text{O}(l)$	69.9		

Example

Calculate the standard entropy of formation of $\text{H}_2\text{O}(l)$ at 298.15 K using Table 1.

Solution



The standard entropy of formation of water ($\Delta S^\circ(\text{H}_2\text{O})$) can be calculated using Eq. 56. Note that the substances are in their standard states at 298.15 K; hence S° values are used instead of S .

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

Since one mole of water is formed,

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

Self-Assessment Exercises 4

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

4.0 Conclusion

Entropy changes can be used to distinguish between reversible and irreversible processes. Entropy changes under different conditions can be calculated with the aid of some useful expressions.

5.0 Summary

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

The method of calculation of entropy changes in chemical reactions was indicated towards the end of the unit. Also, the physical meaning of entropy was discussed. For a spontaneous change, the total entropy of the system and the surroundings must increase. If entropy is used as a criterion for spontaneity, it is necessary to determine the entropy change for both the system and the surroundings. This is inconvenient as one has to consider the changes taking place both in the system and the surroundings. Therefore, a criterion for spontaneity is developed in such a manner that only changes in the properties of the system are considered.

6.0 Tutor-Marked Assignments

1. If the efficiency of a Carnot engine is 20% and the temperature of the sink is $3.00 \times 10^2 \text{ K}$, calculate the temperature of the source.
2. A Carnot engine works between $5.00 \times 10^2 \text{ K}$ and $3.00 \times 10^2 \text{ K}$. Calculate the minimum amount of heat that must be absorbed by the engine from the source at $5.00 \times 10^2 \text{ K}$ in order to obtain 1.50 kJ of work.
- 3 (a) $2.80 \times 10^{-2} \text{ kg}$ of nitrogen at 415 K has an initial pressure of $1.50 \times 10^6 \text{ Pa}$. It is isothermally and reversibly expanded such that its final pressure is $1.00 \times 10^5 \text{ Pa}$. Calculate the entropy change in the process.
(b) Also, assuming that the process is irreversible calculate the entropy change.

(Hint: Assume that the gas expands against an external pressure of 1×10^5 Pa.)

4. Assuming that air is made up of 80% nitrogen and 20% oxygen only, calculate the entropy of mixing of nitrogen and oxygen to form two moles of air at 298 K.

5. Calculate the standard entropy of formation of CO(g) at 298.15 K. Use Table 1.

7.0 References/ Further Reading

Principles of Physical Chemistry, Samuel H. Maron and Carl F. Prutton, Oxford and IBH Publishing Co., New Delhi, 4th ed., 1985.

Physical Chemistry, Gilbert W. Castellan, Narosa Publishing House, Addison-Wesley/Narosa (Indian Student Edition), Delhi, 3rd ed., 1983.

Physical Chemistry, P.c. Rakshit, Sarat Book House, Calcutta, 5th ed., 1988.

Physical-Chemistry through Problems, S.K. Dogra and S. Dogra, Wiley Eastern Ltd., New Delhi, 1984.

Physical Chemistry-Principles and Problems, D.V.S. Jain and P. Jauhar, Tata McGraw-Hill Pub. Company Ltd., New Delhi. 1990.