Ideally a sequence of isothermal and adiabatic processes can result in a reversible cyclic process, about which you will learn in this unit.

THE FIRST LAW AND ITS APPLICATIONS

Structure

STUDY GUIDE

In Unit 6, the concept of temperature was introduced through the Zeroth law of thermodynamics. In this unit, you will learn about the nature of heat. You are aware of the thermodynamic concept of work from your school physics curriculum. We will build upon that knowledge to introduce the concept of internal energy and formulate the first law of thermodynamics. You will appreciate that this law is universal and explains various phenomena observed in nature as well as in a laboratory – from fall in temperature with height in outer atmosphere to pressure oscillations in sound waves. This will require a basic knowledge of ordinary as well as partial differentiation and it will be a good idea to revise your prior knowledge up-front.

To enable you to grasp various important concepts and develop problem solving skills, we have interspersed solved examples in the text. Try to solve these SAQs and TQs on your own.

"Suppose we take a quantity of heat and change it into work. In doing so, we haven't destroyed the heat, we have only transferred it to another place or perhaps changed it into another energy form."

Isaac Asimov

7.1 INTRODUCTION

From your +2 physics curriculum you know that a question that puzzled the best brains of the 19th century for a long time and confronted them with many conceptual problems was 'what is the nature of heat?' The answer to this and other related questions was ultimately provided by Joule through a series of classical experiments when he concluded that '*heat is some form of motion'.* It tells us that heat is equivalent to other forms of energy. Much of our world works because of this equivalence. The electrical energy that lights our houses, operates machines and runs trains originates in heat released in burning of coal, oil, gas, etc.

We begin this unit by discussing the nature of heat in Sec. 7.2. This is followed by a discussion of work done on or by a system in Sec. 7.3. In Sec. 7.4, you will obtain the expression for the work done by a gaseous system. The efforts made to develop analytical theory of heat based on dynamical view-point led to introduction of the concept of *internal energy*, which is defined as the sum of the energies of the individual constituents of the system. (You have learnt about molecular nature of matter in Block 1 of this course.) This is discussed in Sec. 7.5.

The recognition of heat as a form of energy led to the formulation of the first law of thermodynamics, which is essentially a statement about the conservation of energy for thermodynamic systems. This constitutes the subject matter of discussion in Sec. 7.6. The first law of thermodynamics is universal and has been successfully used to understand diverse physical phenomena observed in the nature as well as in a laboratory. Using this law, we can explain interesting phenomena like the pressure oscillations in a sound wave and fall in the temperature as we move upward in the outer atmosphere.

In Sec.7.7, we begin by considering applications of the first law of thermodynamics and obtain the expression for the difference in molar heat capacities of a gas at constant pressure and constant volume. For a typical substance, the difference between heat capacities can be related to measurable quantities like volume expansion coefficient and bulk modulus of elasticity.

In Sec. 7.8, we have used this law to derive the equation of state for adiabatic processes. You know that the sound waves are propagated in a medium due to pressure oscillations. This is an adiabatic process. You will learn here to correlate the thermodynamic parameters with the speed of sound.

Expected Learning Outcomes

After studying this unit, you should be able to:

❖ explain the nature of heat;

❖ discuss the thermodynamic concept of work and obtain expressions for work done by different thermodynamic systems;

❖ define internal energy and use it to formulate the first law of thermodynamics;

❖ apply the first law of thermodynamics to obtain an expression for the difference between heat capacities of a gas at constant pressure and at constant volume;

❖ derive the equation of state for an adiabatic process; and

❖ obtain the expressions for speed of sound in air.

7.2 NATURE OF HEAT

We know from experience that a glass of ice-cold water left on a table on a hot summer day eventually warms up, whereas a cup of hot tea on the same table cools down. It means that when temperature of a closed system – water or tea in this case – is different from that of the surroundings, energy is exchanged till such time that thermal equilibrium is established. That is, energy transfer continues till the body and the surroundings are at the same temperature. We also know that in the case of cold water, energy flows spontaneously from the surroundings to the glass, whereas in the case of hot tea, energy flows from the cup to the environment. In other words, the natural direction of energy transfer is always from the body at higher temperature to that at lower temperature.

You may now ask: In what form is energy being transferred? In the above cases, energy is said to be transferred in the form of *heat*. So, we can say that *heat is the form of energy transferred between two (or more) systems or a system and its surroundings by virtue of temperature difference.* (The system at higher temperature is called the *source* and the one at lower temperature is called the *sink.*)

In 1840, Joule performed a classical experiment on the equivalence of heat and mechanical work. In the apparatus used by him, heat was produced by churning water contained in a cylinder by means of brass paddles. It means that the mechanical energy of the paddles was converted into heat. Joule argued that the heat must have been produced through chaotic motion of water molecules. Thus, he established that *molecular motion was associated with heat.*

We often say that a cup of hot coffee has heat or there is tremendous heat in the Sun. But henceforth, we shall use the word 'heat' only when it enters or leaves a system. **Heat is a form of energy in transit**. It is wrong to say heat 'in' a body. You will learn soon that when we speak of heat in a body, we essentially mean its internal energy. You will learn about the difference between 'heat' and 'internal energy' a little later in this unit.

Since heat is a directional quantity, we adopt a sign convention to represent it. Heat transferred to a system is taken as positive whereas heat taken out of a system is taken as negative. If there is no heat transfer in a process, it is said to be **adiabatic**.

Now go through the following example to grasp the ideas discussed so far.

Source of heat at temperature T is a body or a system which supplies heat to its surroundings or a body in its contact and continues to remain at constant temperature T, without exchange of any work. A *sink* of heat at temperature T is a body which receives heat from its surroundings or a body in contact with it without any change of temperature or exchange of work.

$\mathcal{E}$ *XAMPLE 7.1* : **HEAT TRANSFER IN A THERMODYNAMIC SYSTEM**

A potato is initially at room temperature (30°C). It is baked in an oven maintained at 200°C. Take the potato to be the system of interest and explain whether any heat is transferred during the process.

SOLUTION ■ The skin of the potato can be considered as the system boundary. Now owing to the difference of temperature between the oven and the potato, a part of the energy of the oven will pass through the skin of the potato in the form of heat.

Recap

HEAT

- Heat is a form of energy in transit;

- The natural direction of energy transfer is always from the body at higher temperature to that at lower temperature;

- Energy is transferred in the form of heat by virtue of temperature difference; and

- Heat is closely connected to the molecular motion.

7.3 WORK

We now know that if the cause of transfer of energy is temperature difference between the system and the surroundings, then that form of energy is heat. But it is possible that energy interaction is not caused by temperature difference between the system and the surroundings. When energy crosses the boundary of a system and it is not in the form of heat, it is work.

If a system as a whole exerts force on its surroundings so that a displacement takes place, the work that is done by or on the system is called *external work.* If gas contained in a cylinder at uniform pressure expands, it imparts motion to the piston and does external work on its surroundings.

On the other hand, the work done by a part of the system on another part is called *internal work.* In thermodynamics, internal work is of no consequence. Let us take an example of a storage battery. When it is not in operation, the changes that take place in its cells, such as internal-diffusion of chemicals, are not accompanied by the performance of any work, and so are not significant for us.

We adopt the convention that work done *by* a system is positive and the work done *on* a system is negative. According to this convention, the work produced by car engines or gas turbines is positive, whereas the work consumed by compressors or mixers is negative.

You may now like to answer an SAQ.

$\mathcal{SAQ}\ 1$ – **Work done by a system**

a) Explain whether any work is done or not in the following processes.

   (i) A magnet is brought near an electrical circuit carrying conductor. A change in magnetisation takes place by way of realignment of domains within the magnet.

   (ii) A galvanometer coil is set into motion by sending a current in it.

b) What are the signs of work (i) we get from a steam engine (ii) done on an electric motor attached to a pump?

7.4 EXPRESSION FOR WORK

In thermodynamics, we express the work in terms of the state variables of the system. This permits simple mathematical analysis. To do so, we have to ensure that the system is always near an equilibrium state, i.e. the process is quasi-static. With this understanding, we now proceed to obtain the corresponding expressions for work done on/by gaseous system .for different processes.

7.4.1 A Gaseous System

Refer to Fig. 7.1, which shows a cylinder fitted with a frictionless piston and filled with a gas of mass M. Let the area of cross-section of the piston be A and the pressure exerted on it by the system at any instant be p. Obviously, the force acting on the piston will be equal to pA. This force pushes the piston
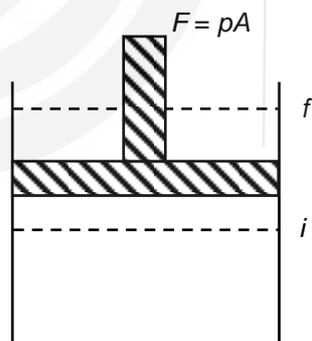

Fig. 7.1: Work done during expansion of a gaseous system. Here i and f stand for the initial and final states, respectively.

outwards. If the piston moves in the direction of the force through dx, we can write down the work done by the system as

$$\delta W = p\,A\,dx$$

Note that $A\,dx$ signifies the increase in volume of the system due to outward movement of the piston and we can write dV for $A\,dx$. Thus, the work done by the system when the piston moves outward through dx is given by

$$\delta W = p\,dV \tag{7.1}$$

You will learn that the internal energy (U) is a function of the state whereas work (W) and heat (Q) are not. An infinitesimal change in a quantity which is not a function of state is indicated by putting the symbol δ (pronounced as delta) on the left of the quantity of interest. The infinitesimal change in a quantity which is a state function is indicated by putting 'd' on the left of the quantity. Hence, an infinitesimal amount of work is denoted by δW, an infinitesimal amount of heat by δQ. And an infinitesimal amount of internal energy is denoted by dU.

If the system expands quasi-statically from initial volume V_i to final volume V_f, the total work done by the gaseous system on its surroundings is given by

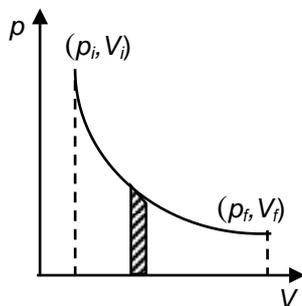$$W = \int_{V_i}^{V_f} p\,dV \qquad (7.2)$$

Fig. 7.2: p-V **diagram for a gaseous system undergoing expansion.**

For evaluating the integral in Eq. (7.2), we need to know how p varies with V, which depends on the nature of the process. The pressure p and the volume V at any instant can be shown on an indicator diagram (Fig. 7.2) as a point. The curve joining a series of such points gives the path of the process of expansion or compression. The nature of the curve depends on how p varies with V. Note that $p\,dV$ is represented by the area of the shaded strip in the figure. The total work done W between the initial and final states is the sum of the areas of strips obtained for all the infinitesimal changes from the initial to the final state. This is equal to the total area under the p-V curve of the system.

Work done in an isothermal process

Let us now calculate the work done in an isothermal expansion (or compression) of an ideal gas. You will recall that n mole of ideal gas obeys the perfect equation of state:

$$pV = nRT \qquad (7.3)$$

On substituting for p from Eq. (7.3) in Eq. (7.2), we obtain the expression for total work done:

$$W_{isotherm} = \int_{V_i}^{V_f} (nRT / V)\,dV$$

$$= nRT \ln(V_f / V_i) = 2.303\, nRT \log_{10}(V_f / V_i) \qquad (7.4)$$

From this equation we note that when an ideal gas expands isothermally, the work done by it depends on the temperature T and the expansion ratio of final to initial volumes rather than the difference $(V_f - V_i)$. We know that during expansion, $V_f > V_i$ and $\ln(V_f / V_i) > 0$. It means that the work done by the system when it expands isothermally is positive.

However, in the case of compression, $V_f < V_i$ so that $\ln(V_f / V_i) < 0$ and $W_{isotherm}$ is negative. This means that when a system is compressed isothermally, work is done on the system.

You may now like to answer an SAQ to check your progress.

SAQ 2 – **Work done by a gaseous system**

a) Express Eq. (7.4) in terms of pressure.

b) Obtain the expression for work done in expanding the gas from volume V_i to V_f in an isobaric process.

Work done in an isochoric process

Next let us consider a gas that undergoes an isochoric process. In this case, $dV = 0$, and hence, $\delta W = pdV = 0$. So, no work is done either on or by the system in an isochoric process.

We now give a solved example to help you grasp the concept.

$\mathcal{E}$*XAMPLE 7.2*: **WORK DONE BY AN IDEAL GAS**

Two mole perfect gas at STP is expanded isothermally to twice its original volume. The gas is then made to undergo an isochoric change to attain its initial pressure. Calculate the total work done. Given: $R = 8.3 \, \mathrm{JK^{-1}mol^{-1}}$.

SOLUTION ■ Here $V_f / V_i = 2$. Hence work done by the gas in the isothermal expansion is

$$nRT \ln(V_f/V_i) = (2 \text{ mol}) \times \left(8.3 \text{ JK}^{-1}\text{mol}^{-1}\right) \times (273 \text{ K}) \times (\ln 2) = 3.1 \times 10^3 \text{ J}$$

Since no work is done during an isochoric process, the total work done by the gas $= 3.1 \times 10^3$ J.

7.4.2   Path Dependence of Work and Heat

You know that the work done by a gaseous system can be represented by the area under the p-V diagram of the system from the initial to the final state. Refer to Fig. 7.3, which depicts three processes *ACB, ADB* and *AEB* between initial and final states defined by *A* and *B* on an indicator diagram. The path *ACB* indicates a general process. The path *ADB* is the combination of an isochoric and an isobaric process, whereas the path *AEB* is the combination of an isobaric and isochoric process. The work done for the process *ACB* is equal to the area *ACBFG*. Similarly, the work done during the processes *ADB* and *AEB* are given by areas *DBFG* and *AEFG,* respectively. Since these areas are not equal, we can say that that the work done between the same initial and final states during these processes is not the same. It means that *the work done by a system between any initial and final state depends on the path taken*. In other words, **work is not a function of the state**.

Fig.7.3: The points *A* and *B*, are connected by different paths.

Is the same true about heat content? To understand this let us take an example. Suppose you have a glass of milk at 30ºC and you wish to have its temperature raised by 5ºC. This can be done by adding heat to it or churning it vigorously or by a combination of heating and churning. However, in all the cases we ultimately arrive at a state which can be defined as 'milk at 35ºC'. In all the cases, the initial state was 'milk at 30ºC'. The processes connecting these states were different and the quantities of heat given to the system in the three processes were not the same. So we can say that *heat given to the system depends on the process*, i.e.*, the path followed between the initial and the final state*. Hence, **heat is not a function of the state**.

Before proceeding further, you should recapitulate what you have learnt so far in this unit.
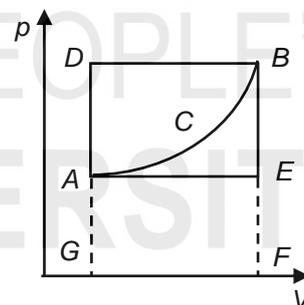
Recap

WORK DONE BY AN IDEAL GAS

- The work done by a gaseous system on its surroundings is given by

$$W = \int_{V_1}^{V_2} p \, dV$$

- For an isothermal process $W_{iso} = 2.303 \, nRT \, log_{10} [V_2 / V]_1$

- Heat and work are function of the path followed, i.e., these depend on the process rather than the state.

So, we now know that work and heat are not functions of the state. You may now ask: Is there any function which is independent of the path followed between the initial and final states? Yes, such a function does exist. It is known as *internal energy*. You will now learn about it in some detail.

7.5 INTERNAL ENERGY

We know that on heating, ice melts to form water at 0ºC. On the basis of the kinetic theory of gases we can say that if temperature remains constant, the kinetic energy remains constant. Since energy has to be conserved, what can you say about the added thermal energy? When ice is converted into water, its specific volume changes from 0.92 cc g^{-1} to 1 cc g^{-1}. To bring about this change, work is done at the expense of added energy.

However, the major share of the additional energy is used up in breaking the bonds of intermolecular attraction in ice and this energy is stored in water. (It is released when water freezes into ice.) The energy apparently shown by a system during a phase transition is termed as **internal energy**.

In thermodynamics, it is not necessary to know the source of internal energy. But it can be easily understood that the sum of kinetic energies of all the molecules in a system defines *internal kinetic energy*. Also, due to the inter-atomic/ intermolecular attractions, each atom / molecule making up the system possesses potential energy.

The total energy stored in the system due to the interactions defines *total internal potential energy*. *The sum of internal kinetic and potential energies of all the molecules constitutes the internal energy of the system*. We denote it by the symbol *U*.

The internal energy depends only on the state variables like pressure, temperature and volume. It is therefore a 'state function'. In SAQ 3, you will learn that for a cyclic process, there is no change in the internal energy. In fact, this result holds for all functions of state.

You can now answer an SAQ on the concept of internal energy.

$\mathcal{SAQ}$ 3 – **Internal energy of a cyclic process**

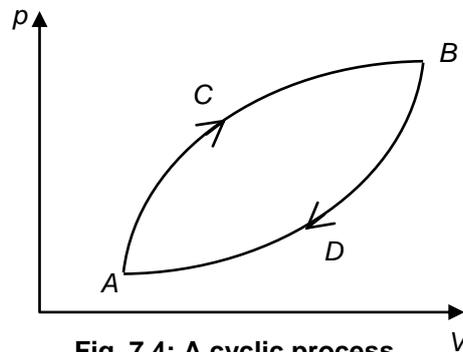Show that the change in the internal energy during a cyclic process depicted in (Fig, 7.4) is zero.

Fig. 7.4: A cyclic process.

We now know that heat and work inputs into a system cause its internal energy to rise. Likewise, if heat is taken out of the system or some work is done by the system, its internal energy is lowered. In Figs. 7.5a and b, we have shown schematically two methods, viz. adding heat energy and doing work on it, respectively, by which the internal energy of a system can change. We shall now invoke the well-known principle of conservation of energy to analyse the aspect of change of internal energy and in the process, we shall arrive at the first law of thermodynamics.
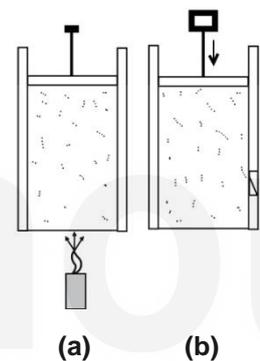
7.6   THE FIRST LAW OF THERMODYNAMICS

The principle of conservation of energy states that 'Energy can neither be created nor destroyed; it can be transformed from one form to another, the total amount of energy (in the universe) remaining constant. According to this principle, we cannot get energy out of nowhere. *If energy of a system increases, there must have been an equivalent loss of energy of the surroundings.*

Let us again consider the example of raising the temperature of a cup of milk. We can say that the internal energy of the milk can be increased in three ways: (i) by way of heat input only, (ii) by way of work input only and (iii) by way of heat and work input. For (i), let the heat absorbed by the system be $\Delta Q'$. The work done on the system is zero and the work done by the system is also zero. For (ii), the heat absorbed is zero. Let the work done by the system be $\Delta W'$ so that the work done on the system is $-\Delta W'$. For (iii), let the heat absorbed be ΔQ and let the work done by the system be ΔW, so that the work done on the system is $-\Delta W$. However, the change in internal energy is the same in each case. Let us denote it by ΔU. Here all the quantities are expressed in heat units. From the principle of conservation of energy, we have

Increase in internal energy = (Heat absorbed) + (work done on the system)

Mathematically, we can write

$$\Delta U = \Delta Q + (-\Delta W) = \Delta Q - \Delta W \qquad (7.5)$$

Fig. 7.5: Internal energy of a system can be changed by a) Adding thermal energy; b) by doing work on it.

When heat is converted into other forms of energy (as in a steam engine) or vice versa (as in an electric heater), in each form it is equivalent. If a quantity of heat, Q, is converted entirely into work, W, then W is equivalent to Q and W/Q = constant known as the mechanical equivalent of heat. It is denoted by J and its value is approximately equal to 4.2 J cal^{-1}. Thus, one calorie of heat is equivalent to 4.2J of work. Likewise, work can be expressed in heat units. We shall express both work and heat by the same units.

This is the mathematical form of the first law of thermodynamics. The formal statement of the first law is: '*Internal energy of a system is a function of the state of the system and any change in it during a thermodynamic process is equal to the sum of the heat given to the system and the work done on the system.*' According to this law, we can say that for a thermodynamic process taking place between two particular states, the difference between the heat absorbed and the work done by the system is always constant; equal to the change in internal energy of the system.

You may recall that the heat required to convert 1 g of water at 100°C to 1 g of steam at 100°C is 540 cal at normal atmospheric pressure. This is termed as latent heat as it does not induce temperature rise. You may naturally wonder, as to what happens with this heat? A part of it is utilised in performing external work by the system. The rest is utilised in breaking up intermolecular bonds so that water is converted from liquid to vapour state, i.e. to raise the internal energy of the system. Let us now look at this from a quantitative point of view. Go through the following numerical example carefully.

$\mathcal{E}$*XAMPLE* 7.3 : **PHASE CHANGE AND INTERNAL ENERGY**

1g of water and steam at normal atmospheric pressure (1.013×10^5 Nm^{-2}) occupy 1 cm^3 and 1671 cm^3 volumes, respectively. Calculate the change in internal energy for vaporisation of 1g of water at 100°C. (Latent heat of steam is 540 cal and mechanical equivalent of heat $= 4.2\,$Jcal^{-1}).

SOLUTION ■ For 1g of water vaporising to steam, $\Delta U = \Delta Q - \Delta W$, where ΔQ = 540 cal, $\Delta W = p\,(V_2 - V_1)$, and V_1 and V_2 are volumes of water and steam, respectively.

Here, $p = 1.013 \times 10^5$ Nm^{-2}, $V_1 = 1$ cm^3, $V_2 = 1671$ cm^3.

$\therefore \Delta W = (1.013 \times 10^5$ Nm$^{-2}) \times (1671 - 1) \times 10^{-6}$ m$^3 = 169.2$ J $= 40.3$ cal.

and, $\Delta U = (540 - 40.3)$ cal $= 499.7$ cal.

Thus we see that out of 540 cal, only 40.3 cal is spent in doing external work, while the rest goes to raise the internal energy of the system. ΔU (= 499.7 cal) for this process is often referred to as the internal latent heat.
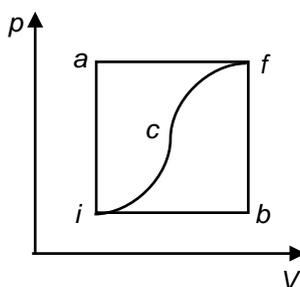

Now before proceeding further, attempt the following SAQ.

Fig. 7.6: Change of state of a system along different paths.

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$\mathcal{SAQ}$ *4* - **First law of thermodynamics**

Refer to Fig. 7.6. When a system is taken from state i to state f following the path *iaf*, it is found that $\Delta Q = 45$J and $\Delta W = 20$J. But along the path *ibf*, $\Delta Q = 30$J.

a) What is ΔW along the path *ibf* ?

b) If $\Delta W = -13$J for the curved return path *fci*, what is ΔQ for this path?

c) Taking $U_i = 10$ J, what is U_f?

d) If $U_b = 21$ J, what are ΔQ's for the processes *ib* and *bf* ?

To study further applications of the first law of thermodynamics, we need to know the differential form of the law. You will now learn about it.

7.6.1 Differential Form of the First Law

You now know that functions like work and heat are path dependent and so will be the changes in these. But the change in internal energy is independent of path.

We may now extend Eq. (7.5) to write the differential form of the first law of thermodynamics as

$$dU = \delta Q - \delta W$$

or,

$$\delta Q = dU + \delta W \qquad (7.6)$$

Eq. (7.6) is the *differential form of the first law of thermodynamics.*

You may now like to work out an SAQ on the first law of thermodynamics.

> If a physical quality is a function of state rather than the path, it is said to be exact differential. On the other hand, if a physical quality depends on the path, it is said to be an inexact differential. In order to indicate this difference mathematically, we put 'd' before the exact differential *U*, while we put 'δ' before the inexact differentials (*Q* and *W*).

SAQ 5 – **Mathematical form of the first law**

a) Write down the mathematical form of the first law of thermodynamics applied to a thermally insulated system and comment on the nature of change in its internal energy.

b) Using the symbols used in the text write down the differential form of the first law for a gas in a cylinder fitted with a piston.

c) Suppose you place a tray filled with water in a freezer. What will be the signs of δW, δQ and dU for the contents of the tray? Justify your answer.

Significance of the First Law

So far, we have learnt that the first law of thermodynamics is very significant since it defines 'internal energy' as a function of the state of the system and heat as energy in transit. Being an extension of the principle of conservation of energy, it rules out the possibility of constructing a machine which can work on its own, without any input. There are several physical situations, where this law can be successfully applied. In the next sections we will discuss some important applications of the first law.

7.7 HEAT CAPACITIES OF A GAS

You may recall that according to kinetic theory, molar heat capacity of an ideal gas is independent of its nature, i.e., for all gases of given atomicity, molar heat capacity at constant volume or at constant pressure is same. But, physical conditions under which heat is given introduce change in the value of heat capacity of a gas. Let us, therefore, obtain an expression for the difference in the heat capacities of an ideal gas at constant pressure and constant volume. Assume that one kilomole of a gas is contained in a cylinder fitted with a frictionless piston. In Unit 5, you have learnt that the state of a gas

You may recall that heat capacity of a substance varies with temperature as well as amount of the substance. The amount of substance is expressed in **kg** or by **number of moles. The corresponding measures of heat capacity are specific heat capacity and molar heat capacity.** At constant volume, the specific heat capacity is denoted by small letter c_V and molar heat capacity is denoted by C_V. These are connected through the relation

$$c_v = \frac{C_V}{m}$$

where m is the mass of one kilomole of the substance. The specific heat capacity is measured in $J\,kg^{-1}\,K^{-1}$ and molar heat capacity is measured in the units of $J\,kmol^{-1}\,K^{-1}$.

can be described in terms of any two thermodynamic variables out of p, V and T. Let us choose T and V as independent variables. Since internal energy is a function of state, we can write

$$U = U(T, V)$$

Then the differential of U can be written as sum of its partial differential with respect to T at constant V multiplied by dT and that with respect to V at constant T multiplied by dV:

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{7.7}$$

The symbol ∂ (pronounced as del) denotes a partial derivative. On combining Eqs. (7.6) and (7.7), and expressing the work done by the gas as $\delta W = pdV$, that you have worked out in SAQ 5b, we can write

$$\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]dV \tag{7.8}$$

Now suppose that the piston was tightly clamped. As we heat the gas, it cannot expand, i.e., it cannot do any work and all the heat goes to raise its internal energy and hence, its temperature. **The heat required to raise the temperature of one kilo mole of a gas through one degree when its volume is kept constant is termed as molar heat capacity at constant volume.** It is denoted by the symbol C_V and generally expressed in $J\,kmol^{-1}\,K^{-1}$. For such a system, Eq. (7.8) reduces to

$$C_V = \left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \tag{7.9}$$

Note that different symbols have been used to depict changes in heat, internal energy and temperature because heat is not a function of state. Now suppose that the piston was allowed to move in or out so that the gas is kept at constant pressure. The gas does work on the piston and some of the heat ends up as mechanical energy given to the surroundings. So, to achieve the same rise in temperature, more heat has to be supplied to the gas in a constant pressure (isobaric) process. **The molar heat capacity of a gas at constant pressure is defined as the amount of heat required to raise the temperature of one kilo mole of a gas by one degree.** It is denoted by the symbol C_p. Mathematically, we can write

$$C_p = \left(\frac{\delta Q}{\partial T}\right)_p \tag{7.10}$$

On combining Eqs. (7.8 and 7.10), we can write

$$C_p = \left(\frac{\partial U}{\partial T}\right)_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p$$

The first term on the right-hand side of this result is molar heat capacity at constant volume [Eq. (7.9)]. Then on rearranging terms, we can write

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right]\left(\frac{\partial V}{\partial T}\right)_p \tag{7.11}$$

Let us pause for a while and interpret this result. The first term in the square brackets on the right-hand side tells us that the internal energy of a gas may vary with volume even when temperature is kept fixed. This implies that for change in volume, work has to be done against intermolecular forces in the gas. It means that knowledge of the difference of heat capacities at constant pressure and at constant volume gives us information about variation of internal energy of a substance with volume.

We recall that according to kinetic theory, there are no intermolecular forces in an ideal gas. This implies that internal energy of a perfect gas is wholly kinetic and $(\partial U / \partial V)_T = 0$. Using this result in Eq. (7.11), we get

$$C_p - C_V = p\left(\frac{\partial V}{\partial T}\right)_p \qquad (7.12)$$

This shows that the difference in the molar heat capacities of a gas depends on how the volume of a system changes with temperature at constant pressure. We expect this difference to be substantial since a small change in temperature brings about significant change in the volume of a gas. Using the gas law ($pV = RT$), we can write

$$p\left(\frac{\partial V}{\partial T}\right)_p = R$$

Using this result in Eq. (7.12), we get

$$C_p - C_V = R \qquad (7.13)$$

This result is known as **Mayer's formula**. It shows that the difference between constant pressure and constant volume molar heat capacities is equal to the molar gas constant; independent of temperature; and same for all gases.

You may now ask: How do these predictions compare with the observed results? To know the answer to this question, refer to Table 7.1, where we have given molar heat capacities of some gases (in units of R) at constant pressure as well as at constant volume.

Table 7.1: Molar heat capacities of a few gases at constant pressure and constant volume

Type of Gas	Gas	C_p / R	C_V / R	$(C_p - C_V)/R$
Monoatomic	He	2.5	1.5	1.0
	Ar	2.5	1.5	1.0
Diatomic	H_2	3.45	2.45	1.0
	O_2	3.53	2.53	1.0
	Cl_2	4.17	3.09	1.08
Polyatomic	CO_2	4.43	3.42	1.01
	NH_3	4.42	3.34	1.08
	C_2H_6	6.21	5.18	1.03

You must have noted that but for Cl_2 and polyatomic gases, Mayer's formula holds rather well. Before proceeding further, you should answer an SAQ.

$\mathcal{SAQ}$ 6 – **Heat capacities of gases and the first law**

a) For hydrogen, the molar heat capacities at constant pressure and constant volume are 28.8 J mol^{-1} K^{-1} and 20.5 J mol^{-1} K^{-1}, respectively. Calculate the gas constant.

b) The constant pressure molar heat capacity of a gas is 160 J mol^{-1}K^{-1}. Calculate the ratio of specific heat capacities at constant pressure to that at constant volume.

c) Show that for an ideal gas, the first law of thermodynamics can also be written as

$$\delta Q = C_V \, dT + p dV \quad \text{and} \quad \delta Q = C_p \, dT - V dp$$

Proceeding further, we recall that a real gas is made up of molecules having small but finite size and non-zero inter-molecular forces. This suggests that we should use the van der Waals' equation of state. The mathematical steps are somewhat cumbersome and we will just quote the result (TQ 4):

$$C_p - C_V = R\left(1 + \frac{2a}{VRT}\right) \tag{7.14}$$

On comparing Eqs. (7.13) and (7.14) we note that the difference between heat capacities at constant pressure and at constant volume is more for a real gas than for a perfect gas. Did you not expect this result? We know that for a real gas, the internal energy changes with volume because work has to be done against the intermolecular forces. Also, at high pressures, molecules experience a repulsive force. Thus, we may expect some change, howsoever small, in temperature when a real gas is made to undergo expansion/compression.

You may now ask: Do we distinguish heat capacities at constant volume and constant pressure for solids and liquids as well? For these substances, such a distinction is of little significance because they are incompressible. In fact, for solids and liquids, measured values are quoted at constant pressure. Before proceeding further, let us summarise what you have learnt about the heat capacities of different substances.

Recap

HEAT CAPACITIES OF A GAS

- The molar heat capacity of a gas at constant pressure (volume) is defined as the amount of heat required to raise the temperature of one kilo mole of a gas by one degree.

- For one mole of an ideal gas, the difference in molar heat capacities at constant pressure and constant volume is given by Mayer's formula:

$$C_p - C_V = R$$

- For a van der Waals' gas, we have: $C_p - C_V = R\left(1 + \frac{2a}{VRT}\right)$

- For solids and liquids, the difference in molar heat capacities at constant pressure and constant volume is almost negligible.

So far, we have obtained the expression for the difference between molar heat capacities at constant pressure and constant volume for an ideal and a van der Waal's gas. Let us now consider a process in which no heat is exchanged between the system and surroundings. You may have experienced that if you let air out of a tyre, you feel that the air is cool. You can do a simple activity yourself. Blow on the back of your hand with your mouth wide open. You will feel that your breath is warm. Now close your lips into a small opening and blow again. Your breath now feels cool. Does this mean that your body temperature is different in the two cases or do the conditions induce this apparent change? It happens because in the latter case, air undergoes adiabatic expansion.

You may be aware of some adiabatic processes occurring around you. Sound propagation in air, drop in temperature with altitude, existence of Deep Ocean currents are a few important examples of adiabatic processes. Here, we will consider propagation of sound in air. To be able to do so, we must know the equation of state for an adiabatic process. We now derive it using the first law of thermodynamics.

7.8 EQUATION OF STATE FOR AN ADIABATIC PROCESS

In an adiabatic process, *no heat exchange takes place*. That is, the system and the surroundings are not in thermal contact and $\delta Q = 0$. Then the first law of thermodynamics can be written as

$$dU + \delta W = 0 \tag{7.15}$$

From this expression we note that internal energy will decrease in an adiabatic expansion. Since internal energy is a function of temperature, a fall in internal energy implies drop in temperature, i.e., the system cools. You may now ask: What happens in an adiabatic compression? We expect that the temperature will increase as work is done *on* the system. From this you may conclude that adiabatic expansion produces cooling and adiabatic compression produces heating. This finds an important application in the production of low temperatures. We will not discuss this here but those of you who are interested in details should read the books given in the references at the end of this volume.

Proceeding further, let us suppose that one mole of an ideal gas is made to undergo quasi-static adiabatic expansion. Then, using the result obtained in SAQ 6c, we can write

$$C_V dT + pdV = 0 \tag{7.16}$$

During the expansion, the gas passes through an infinite number of equilibrium states. This means that the equation of state ($pV = RT$) will hold for each state. On substituting $p = RT/V$ in Eq. (7.16), dividing throughout by $C_V T$ and rearranging the resulting expression, we get

$$\frac{dT}{T} = -\frac{R}{C_V}\frac{dV}{V} \tag{7.17}$$

In general, the heat capacity at constant volume changes with temperature. But this is significant only when the change in temperature is very large (~ 1000K). Therefore, it is pertinent to assume that C_V remains independent of temperature.

For a quasi-static process, V and T are well defined for each state. So, if we assume that C_V is independent of temperature, we can readily integrate Eq. (7.17) to obtain

$$\ln T = -\frac{R}{C_V}\ln V + \ln K \qquad (7.18)$$

where $\ln K$ is constant of integration.

Taking antilog and rearranging terms, we get

$$TV^{R/C_V} = K$$

Using Eq. (7.13) we can rewrite it as

$$TV^{(C_p - C_V)/C_V} = K$$

From Block 1, you may recall that the ratio of heat capacity at constant pressure to that at constant volume is denoted by the Greek symbol gamma; $\gamma = C_p / C_V$. It is referred to as *adiabatic index*. So, we can rewrite the equation for an adiabatic transformation as

$$TV^{\gamma-1} = K \qquad (7.19)$$

This relation tells us that when a perfect gas undergoes a quasi-static adiabatic change and temperature increases, volume will decrease and vice versa. Note that the change is not linear. This is an important result.

You may now ask: Can we similarly relate pressure and temperature or pressure and volume for an adiabatic process? To get the answer to this question, we would like you to solve an SAQ.

SAQ 7 – **Other equations of state for an adiabatic process**

Starting from Eq. (7.19), show that

$$\frac{T^{\gamma}}{p^{\gamma-1}} = K_1 \qquad (7.20)$$

and $\qquad\qquad pV^{\gamma} = K_2 \qquad (7.21)$

where K_1 and K_2 are constants.

[**Hint:** Use Equation of state $pV = RT$]

Eq. (7.20) predicts that during an adiabatic process, change in pressure is accompanied by a corresponding change in temperature. What can you say about Eq. (7.21)?

Note that Eqs. (7.19), (7.20) and (7.21) are equivalent forms of the so-called *adiabatic equation*. These equations will hold provided

i)   the initial and final states are equilibrium states,

ii)   the perfect gas equation $pV = RT$ holds, and

iii)   the internal energy of the gas is proportional to temperature only.

Before proceeding further, you should assess your understanding by answering the following SAQ.

$\mathcal{SAQ}$ 8 – Application of adiabatic process

Differentiate Eq. (7.21) w.r.t. V and calculate $(dp/dV)_{ad}$. Also calculate the corresponding expression for an isothermal change. Compare the results. What do you conclude?

While answering SAQ 8 you must have noted that an adiabat is steeper than an isotherm by a factor of γ. You will obtain the same result if you plot Eq. (7.21) on a p-V diagram (Refer to Fig. 7.7).
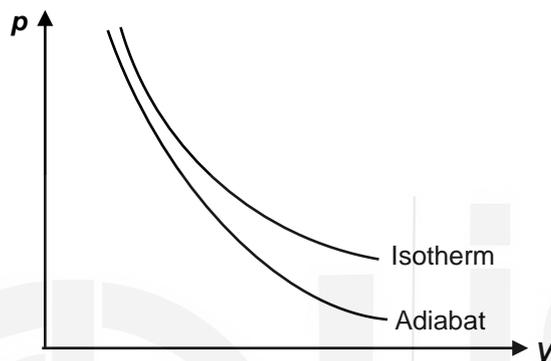

Fig. 7.7: Plot of Eq. (7.21)

From the solution of SAQ 8 you will recall that $(\partial p / \partial V)_S$, which defines the slope of an adiabat, is equal to $-\gamma(p/V)$. It is γ times the slope $(\partial p / \partial V)_T$ of an isotherm. It implies that relative change in volume in an adiabatic process is less than that in an isothermal process.

Before proceeding further, you should carefully go through the example given below based on adiabatic change.

Since the physical properties of a gas depend on the physical conditions under which a process is carried out, we put a suffix to denote the type of change. It is for this reason that p and V were used to denote heat capacities at constant pressure and constant volume. Similarly, for adiabatic and isothermal processes we put the suffixes S and T, respectively with the physical quantity of interest.

$\mathcal{E}$XAMPLE 7.5 : ADIABATIC CHANGE

The nozzle of a bicycle pump is blocked. With no force on the handle, the pump contains a volume V of air at 300K and atmospheric pressure. The handle is pushed down with a constant force of magnitude F reducing the volume to one-third. No air escapes from the pump. Assume the change to be adiabatic. Taking γ for air to be 1.4, calculate the final temperature of air in the pump.

SOLUTION ■ For an adiabatic change, we use Eq. (7.21) and write

$$p_i V^\gamma = p_f \left(\frac{V}{3}\right)^\gamma$$

where p_f is pressure of the gas when the handle is in final equilibrium state. On simplifying this equation, we get

$$p_f = p_i 3^\gamma = 4.66 p_i.$$

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Using the perfect gas equation of state, you can write: $\dfrac{p_i V}{T_i} = \dfrac{p_f (V/3)}{T_f}$

or $\qquad\qquad T_f = \dfrac{p_f}{3p_i} T_i = \dfrac{4.66}{3} T_i = 1.55 \times (300K) = 465K$

Note that this temperature is higher than the boiling point of water! So, you are advised not to touch the nozzle of a blocked pump after you have used it. This is a vivid demostration of theoretical prediction that adiabatic compression produces heating.

You may now like to answer an SAQ.

$\mathcal{SAQ}$ 9 – Adiabatic expansion

The pressure inside a scooter tyre is 2 atm at 300K. It bursts sudenly. Assuming the change to be adiabatic, calculate the final temperature. Use $\gamma = 1.4$.

Earlier in this unit, you have learnt how to obtain an expression for work done in an isothermal and isochoric processes. Let us now obtain the expression for work done in an adiabatic change.

7.8.1 Work done in an Adiabatic Change

Suppose that one mole of a perfect gas undergoes adiabatic change and its volume changes from V_1 to V_2 and pressure changes from p_1 to p_2. We know that during an adiabatic process, a system is thermally insulated from its surroundings.

So, when a gas expands from volume V_1 to V_2, the work done by it is given by

$$W_{ad} = \int_{V_1}^{V_2} p\, dV$$

On substituting the value for pressure from Eq. (7.21) in this expression, we obtain

$$W_{ad} = \int_{V_1}^{V_2} \frac{K}{V^\gamma}\, dV = \frac{K}{1-\gamma}\left(\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}} \right) = \frac{1}{1-\gamma}\left[p_2 V_2 - p_1 V_1 \right]$$

$$= \frac{R(T_1 - T_2)}{\gamma - 1} \tag{7.22}$$

An important manifestation of adiabatic process is found in the troposphere in that as we move up, the temperature gradually drops. This is referred to as *adiabatic lapse rate*. You can read about it in Appendix 7A.

Another important manifestation of adiabatic processes is the transmission of sound in air. You will now find out the relationship between the speed of sound and thermodynamic parameters.

7.8.2   The Speed of Sound

In your school physics classes, you have studied propagation of sound in air. This essentially consists of pressure oscillations in the medium and are accompanied by local changes in temperature. However, the total energy of the system is conserved. That is, we can say that adiabatic changes occur in air when sound propagates. You may now like to know as to how the speed of sound is related to the properties of the medium. It is given by

$$v_s = \sqrt{\frac{E_s}{\rho}} \qquad\qquad (7.23)$$

where E_s and ρ, respectively, denote the adiabatic bulk modulus of elasticity and density of the medium. By definition, the bulk modulus of elasticity is given by

$$E = \frac{\text{Stress}}{\text{Volume strain}} = \frac{\Delta p}{(\Delta V / V)} = V\left(\frac{\Delta p}{\Delta V}\right)$$

In the language of calculus, we can write: $E = -V\dfrac{dp}{dV}$

The negative sign appears because for all known systems, *V decreases* as *p* increases. Therefore, we can write the expression for the adiabatic bulk modulus of elasticity as:

$$E_s = -V\left(\frac{\partial p}{\partial V}\right)_s \qquad\qquad (7.24)$$

From Eq. (7.21), we know that $pV^\gamma = K$. On differentiation, we get

$$\gamma p V^{\gamma-1} dV + V^\gamma dp = 0$$

which gives $\left(\dfrac{\partial p}{\partial V}\right)_s = -\dfrac{\gamma p}{V}$

Using this result in Eq. (7.24), we get

$$E_s = \gamma p \qquad\qquad (7.25)$$

This shows that adiabatic elasticity is γ times pressure. Upon using this result in Eq. (7.23), you will get the expression for speed of sound in terms of pressure:

$$v_s = \sqrt{\frac{\gamma p}{\rho}} \qquad\qquad (7.26)$$

This expression for speed of sound is known as *Laplace formula*. For air, $\gamma = 1.4$, $\rho = 1.29$ kg m^{-3} and $p = 1.01 \times 10^5$ N m^{-2} so that Eq. (7.26) gives speed of sound in air to be $v_s = 331$ ms^{-1}. This value is in excellent agreement with the measured value of 332 ms^{-1}. From this we can conclude that thermodynamic arguments work really well in this case.

You may now like to answer an SAQ.

SAQ 10 – **Speed of sound**

Newton proposed that when sound wave propagates in air, isothermal changes take place. Then speed of sound can be defined as

$$v = \sqrt{\frac{E_T}{\rho}}$$

Using this definition, derive the relation equivalent to Eq. (7.26) and estimate the percentage difference from the value obtained using Laplace formula.

Using the equation of state in Eq. (7.26) for one mole of air, the expression for speed of sound can also be written as

$$v = \sqrt{\frac{\gamma RT}{V\rho}} = \sqrt{\frac{\gamma RT}{M}} \tag{7.27}$$

This result shows that speed of sound in air is directly proportional to square root of temperature and inversely proportional to square root of the molecular weight of air. Do these predictions agree with the observations? Indeed, there is remarkable agreement.

We now recapitulate important results obtained in this section.

Recap

ADIABATIC PROCESS

- The equation of state for an adiabatic process is given by pV^γ = constant. Other equivalent forms are $TV^{\gamma-1}$ = constant and $T^\gamma p^{1-\gamma}$ = constant.

- The work done in an adiabatic process is given by

$$W_{ad} = \frac{1}{\gamma - 1}(p_2 V_2 - p_1 V_1) = \frac{1}{\gamma - 1} R(T_2 - T_1)$$

Let us now sum up what you have learnt in this unit.

7.9 SUMMARY

Concept	Description
Heat	■ Heat is a form of energy that is transferred between systems or a system and its surroundings by virtue of temperature difference.
	■ Heat added to a system is considered positive and heat taken away from the system is considered as negative.

Work

■ If an energy interaction takes place between a system and its surroundings, not by way of difference of temperature, then it is called work.

■ Work done *by* a thermodynamic system is taken as positive and that done *on* the system is taken as negative.

■ The expressions of work done in different systems undergoing finite changes are:

- Expansion of a gaseous system from volume V_i to V_f:

$$W = \int_{V_i}^{V_f} p \, dV$$

- Isothermal expansion of a perfect gas from volume V_i to V_f:

$$W = nRT \ln(V_f / V_i)$$

■ Work done by or on the system during a process as well as heat absorbed or evolved by a system during a process are path dependent. Therefore, work and heat are not functions of the state of the system.

Internal energy

■ The internal energy of a system is the sum of the energies of individual constituents of the system. It is a function of the state of the system.

The first law of thermodynamics

■ The first law of thermodynamics states that when a system undergoes a process, its internal energy changes by an amount equal to the difference in the quantity of heat transferred to and the work done by it and the change in internal energy is the same for all processes connecting the same initial and final states. The differential form of the first law is:

$$\delta Q = dU + \delta W$$

Heat capacities

■ For one mole of a perfect gas, the difference of heat capacities at constant pressure and constant volume is equal to the molar gas constant:

$$C_p - C_V = R$$

Equation of state of an adiabatic process

■ The equation of state for an adiabatic process in terms of temperature and volume is:

$$TV^{\gamma-1} = \text{constant}$$

In terms of temperature and pressure, it is:

$$\frac{T^\gamma}{p^{\gamma-1}} = \text{constant}$$

In terms of pressure and volume, it is:

$$pV^\gamma = \text{constant}$$

where γ is ratio of heat capacities at constant pressure and constant volume and is known as adiabatic index.

■ The propagation of sound in air is an adiabatic process. The
    expression for the speed of sound is

$$v = \sqrt{\frac{E_s}{\rho}} = \sqrt{\frac{\gamma RT}{M}}$$

where E_s is adiabatic elasticity and ρ is average density of air.

7.10 TERMINAL QUESTIONS

1. Two moles of a perfect gas occupy a volume of 0.050 m^3 and exert a
    pressure of 2.6×10^5 Nm^{-2}. It is compressed isobarically to a volume of
    0.035 m^3. Determine the work done on/by the gas and the change in its
    temperature. (Given R = 8.3 JK^{-1} mol^{-1}).

2. A perfect gas at 300K occupies a volume of 0.2 m^3 at a pressure of
    5×10^6 Nm^{-2}. It is allowed to expand isothermally until its volume is 0.5 m^3.
    Next the gas is compressed isobarically up to its original volume. And
    finally, the pressure is increased isochorically until the gas returns to its
    initial state. Calculate the work done during the cycle.

3. A person consumes a diet of 10^{4}J per day and spends total energy of
    1.2×10^4J per day. Determine the daily change in the internal energy. If
    the net energy spent comes from sucrose at the rate of 1.6×10^4J kg^{-1}, in
    how many days will the person reduce his mass by 1 kg?

4. Obtain the expression for the difference in the heat capacities for a real
    gas given by Eq. (7. 14).

5. Starting from the first law of thermodynamics, show that

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\alpha} - p$$

$$\left(\frac{\partial U}{\partial T}\right)_p = C_p - pV\alpha$$

$$\left(\frac{\partial U}{\partial p}\right)_T = \frac{pV}{E_T} - \frac{C_p - C_V}{E_T \alpha}$$

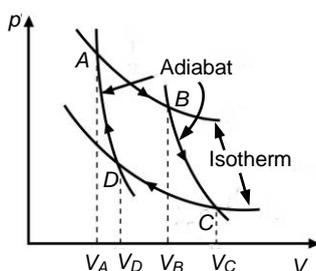where E_T is isothermal elasticity and α is volume expansion coefficient.

6. Isothermal compressibility (β_T) is inverse of isothermal elasticity.
    Calculate β_T for (i) an ideal gas, and (ii) a van der Waals' gas.

7. A reversible cyclic process consists of four steps: isothermal expansion
    (*AB*) at temperature T_1, adiabatic expansion (*BC*), isothermal
    compression (*CD*) at temperature T_2 and adiabatic compression (*DA*) as
    shown in Fig. 7.8. Using the first law of thermodynamics, obtain an
    expression for the total work done.

**Fig. 7.8: A reversible
cyclic process.**

8. Two identical gaseous systems, each containing 0.06 mol of ideal gas, are
    at 300K and 2.0 atm. The ratio of heat capacities of the gas is 1.4. One of
    the gases is made to expand adiabatically and the other isothermally till
    they reach atmospheric pressure. Calculate the final volume in each case.

7.11   SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. a) (i) When the magnetic domains are realigned against frictional forces inside a magnet, some work is done. This work results in the rise in the temperature of the magnet.

    (ii) In this case, current flows in the coil and it gains kinetic energy. So work is done.

   b) (i) +ve (ii) –ve.

2. a) For an ideal gas undergoing isothermal process from state (p_i, V_i) to state (p_f, V_f), we have $p_iV_i = p_fV_f$. Therefore $V_f / V_i = p_i / p_f$. Substituting this in Eq. (7.4), we get

$$W_{iso} = nRT \ln (p_i / p_f)$$

   b) Since the system expands from volume V_i to V_f at constant pressure, we can write

$$W_p = \int_{V_i}^{V_f} \delta W = \int_{V_i}^{V_f} pdV = p(V_f - V_i) = p\Delta V$$

3. Refer to Fig. 7.4. During the process *ACB*, the change in internal energy is $U_B - U_A$ and that during the process *BDA* is $U_A - U_B$. So, the overall change of *U* during the cyclic process is $(U_B - U_A) + (U_A - U_B) = 0$.

4   a)   We know that $U_f - U_i$ = constant independent of path joining *i* and *f*. For *iaf*, ΔQ = 45 J and ΔW = 20J. So from Eq. (7.5), we get

     ΔU = (45 – 20) J = 25J and hence, $U_f - U_i$ = 25 J.

     Therefore, for *ibf*, we have 25 J = 30 J – ΔW or ΔW = 5 J

   b) $U_f - U_i$ = 25 J. So, for the return path *fci*, we have

        – 25 J = $\Delta Q - \Delta W = \Delta Q$ + 13 J

        or ΔQ = (– 25 – 13) J = – 38J

   c) $U_f - U_i$ = 25 J. Hence, $U_f = U_i$ + 25 J = 10 J + 25 J = 35 J

   d)   We have already obtained in (a) that ΔW for *ibf* = 5 J. But *bf* being an isochoric process, no work is done in it. Hence, for *ib*, ΔW = 5 J.

        Now, ΔQ – 5 J = $U_b - U_i$ = 21 J – 10 J = 11 J

        $\therefore$ For *ib,* ΔQ = 16 J. Again for *bf*, ΔW = 0J,

        $\therefore \Delta Q = \Delta W + U_f - U_b$ = 0 + 35 J – 21 J = 14 J

5. a)   For a thermally insulated system, δQ = 0. Then Eq. (7.6) implies that $dU = - \delta W$. Therefore, increase in internal energy is equal to the work done on the system. Alternatively, the work done by the system equals the decrease in internal energy i.e. the system does work at the cost of its internal energy.

   b) $\delta Q = dU + pdV$

c) $\delta W \approx 0$, since change in volume is negligible; δQ is negative since the system loses heat and dU is negative since temperature decreases.

6. a) We know that $C_p - C_V = R$. On substituting the given values, we get $R = 8.3\,\mathrm{J\,mol^{-1}K^{-1}}$.

   b) It is given that molar heat capacity at constant pressure is $160\,\mathrm{J\,mol^{-1}K^{-1}}$. Using Eq. (7.13) we can calculate C_V:

   $$C_V = C_p - R$$

   Since $R = 8.3\,\mathrm{J\,mol^{-1}K^{-1}}$, we find that

   $$C_V = (160\,\mathrm{J\,mol^{-1}K^{-1}}) - (8.3\,\mathrm{J\,mol^{-1}K^{-1}}) = 151.7\,\mathrm{J\,mol^{-1}K^{-1}}$$

   Hence, $\gamma = \dfrac{C_p}{C_V} = \dfrac{160\,\mathrm{J\,mol^{-1}K^{-1}}}{151.7\,\mathrm{J\,mol^{-1}K^{-1}}} = 1.05$

   c) The first law of thermodynamics is

   $$\delta Q = dU + pdV \tag{i}$$

   Using Eq. (7.9) you can write: $dU = C_V dT$

   Hence, $\delta Q = C_V dT + pdV \tag{ii}$

   From the equation of state for an ideal gas, $pV = RT$ we get

   $$pdV + Vdp = RdT \quad \Rightarrow \quad pdV = RdT - Vdp$$

   Using this result in (ii) we get

   $$\delta Q = (C_V + R)\,dT - Vdp = C_p\,dT - Vdp \tag{iii}$$

7. From Eq. (7.19), we recall that

   $$TV^{\gamma-1} = K \tag{i}$$

   For a perfect gas, the equation of state is $pV = RT$. On substituting for V we get

   $$T\left(\frac{RT}{p}\right)^{\gamma-1} = K \quad \text{or} \quad \frac{T^\gamma}{p^{\gamma-1}} = \frac{K}{R^{\gamma-1}} = K_1 \tag{ii}$$

   Similarly, on substituting for T in (i) you will get

   $$pV^\gamma = KR = K_2 \tag{iii}$$

8. From Eq. (7.21), for an adiabatic process, we have $pV^\gamma = K$. On differentiation

   $$\gamma pV^{\gamma-1}dV + V^\gamma\,dp = 0$$

   $\therefore \qquad \left(\dfrac{dp}{dV}\right)_s = -\gamma\left(\dfrac{p}{V}\right) \tag{i}$

   For an isothermal process, $pV = $ constant

   $\therefore \qquad pdV + Vdp = 0 \qquad \text{or} \qquad \left(\dfrac{dp}{dV}\right)_T = -\left(\dfrac{p}{V}\right) \tag{ii}$

   These results show that the curve depicting an adiabatic process is steeper than the one corresponding to an isothermal process since $\gamma > 1$. In fact, the slope of an adiabat is γ times the slope of an isotherm.

9. Since the change is adiabatic and we have to compute the variation in temperature, we use Eq. (7.20): $\dfrac{T^\gamma}{p^{\gamma-1}} = K_1$

So, for initial and final states defined by (T_i, p_i) and (T_f, p_f) we can write

$$\frac{T_i^\gamma}{p_i^{\gamma-1}} = \frac{T_f^\gamma}{p_f^{\gamma-1}} \quad \text{or} \quad T_f = \left(\frac{p_f}{p_i}\right)^{(\gamma-1)/\gamma} T_i$$

It is given that the initial pressure in the tube is 2 atm. When it bursts, it attains atmospheric pressure. On substituting the given data, we get

$$T_f = \left[\frac{1}{2}\right]^{(1.4-1)/1.4} \times (300\,\text{K}) = 0.82 \times 300\,\text{K} = 246.1\,\text{K}$$

This result shows that temperature drops in an adiabatic expansion.

10. We are told that according to Newton, the expression for speed of sound should be $v = \sqrt{\dfrac{E_T}{\rho}}$

For a perfect gas, $pV = RT$ and so, $\left(\dfrac{\partial p}{\partial V}\right)_T = -\dfrac{RT}{V^2}$

Hence, $E_T = -V\left(\dfrac{\partial p}{\partial V}\right)_T = \dfrac{RT}{V} = p$

and $v = \sqrt{\dfrac{E_T}{\rho}} = \sqrt{\dfrac{RT}{V\rho}} = \sqrt{\dfrac{p}{\rho}}$

Substituting for air, $\rho = 1.29\,\text{kg m}^{-3}$ and $p = 1.01 \times 10^5\,\text{N m}^{-2}$ we find that

$$v = \sqrt{\frac{1.01 \times 10^5\,\text{Nm}^{-2}}{1.29\,\text{kg m}^{-3}}} = 280\,\text{ms}^{-1}$$

The difference between the values obtained by Laplace and Newton formulations is

$$v = (331 - 280)\,\text{ms}^{-1} = 51\,\text{ms}^{-1}$$

% difference with respect to the standard (Laplace's) value = 15.4%

Terminal Questions

1. Work done by the gas under isobaric condition is given by $\Delta W_p = p\,(V_f - V_i)$. Inserting the given values, we get

$$\Delta W_p = 2.6 \times 10^5\,(0.035 - 0.050)\,\text{J} = -3.9 \times 10^3\,\text{J}.$$

The negative sign implies that work is done on the gas. Now for a perfect gas $pV = nRT$, so that

$$\Delta W_p = nR\,\Delta T$$

The change in the temperature is given by

$$T = \Delta W_p / nR = -3.9 \times 10^3\,\text{J} / (2\,\text{mol} \times 8.3\,\text{J mol}^{-1}\text{K}^{-1}) = -235\,\text{K}$$

2. The equation of state of a perfect gas is $pV = nRT$.

∴ $n = pV / RT = (5 \times 10^6 \times 0.2) / (8.3 \times 300) = 400$ moles.

(i) For the isothermal path, $V_i = 0.2$ m^3, $V_f = 0.5$ m^3, p = 5×10^6 Nm$^{-2.}$

∴ $p_f = p_i V_i / V_f = 5 \times 10^6$ Nm$^{-2} \times 0.2$ m^3 / 0.5 m^3 = 2×10^6 Nm^{-2}

∴ Work done by the gas, $\Delta W_T = nRT \ln (V_f / V_i)$

$\Delta W_T = 400$ mol $\times 8.3$ J mol^{-1} K$^{-1} \times 300$K $\times \ln (0.5 / 0.2)$

$= 9.1 \times 10^5$ J

(ii) Work done on the gas in compressing it from 0.5m^3 to 0.2m^3 at constant pressure of 2×10^6 Nm^{-2} is

$\Delta W_p = -p \, \Delta V = -2 \times 10^6$ Nm$^{-2} \times (0.5 - 0.2)$ m^3 = -6×10^5 J

(iii) No work is done along the isochoric path.

Hence, total work done by the gas

$= (9.1 - 6.0) \times 10^5$ J $= 3.1 \times 10^5$J.

3. The calorie content of the diet consumed is the heat supplied and energy spent is the work done by the system. Thus,

$\delta Q = 10^4$ J per day and $\delta W = 1.2 \times 10^4$ J per day.

∴ $dU = \delta Q - \delta W$

$= 1.0 \times 10^4 - 1.2 \times 10^4 = -2000$ J.

The decrease corresponds to loss of sucrose. The amount of sucrose lost per day is 2000J / (1.6 $\times 10^4$ J kg^{-1}) = 0.125 kg.

Required number of days = 1 kg / 0.125 kg = 8.

4. For one mole of a van der Waals' gas, the equation of state is

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \qquad\qquad (i)$$

where *a* and *b* are van der Waals' constants for a gas.

If we assume that internal energy of a real gas is given by

$U = -\dfrac{a}{V} +$ constant, we can write

$$\left(\frac{\partial U}{\partial V}\right)_T = +\frac{a}{V^2}$$

Using this result in Eq. (7.11), we get

$$C_p - C_V = \left(p + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p \qquad\qquad (ii)$$

To proceed further, we differentiate Eq. (i) with respect to *T* and obtain

$$\left[\left(p + \frac{a}{V^2}\right) - \frac{2a}{V^3}(V - b)\right]\left(\frac{\partial V}{\partial T}\right)_p = R$$

We can rewrite it as

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{\left(p+\dfrac{a}{V^2}\right)-\dfrac{2a}{V^3}(V-b)}$$

On multiplying both sides of this expression by $\left(p+\dfrac{a}{V^2}\right)$, we can write

$$\left(p+\frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p = \frac{R\left(p+\dfrac{a}{V^2}\right)}{\left(p+\dfrac{a}{V^2}\right)-\dfrac{2a}{V^3}(V-b)} = \frac{R}{1-\dfrac{2a(V-b)}{V^3\left(p+\dfrac{a}{V^2}\right)}}$$

On using this result in Eq. (ii), and replacing $\left(p+\dfrac{a}{V^2}\right)$ in the

denominator of above equation by $\dfrac{RT}{(V-b)}$, we get

$$C_p - C_V = \frac{R}{1-\dfrac{2a}{V^3 RT}(V-b)^2} \approx \frac{R}{1-\dfrac{2a}{VRT}}$$

since a and b are very small.

Using binomial expansion with $n=1$, we obtain the required result:

$$C_p - C_V = R\left(1+\frac{2a}{VRT}\right) \tag{iii}$$

Binomial expansion is

$$\frac{1}{(1-x)^n} = 1+nx$$

$$+\left(\frac{n(n-1)}{2!}\right)x^2 + ...$$

5.   From Eq. (7.11) we recall that $C_p - C_V = \left[\left(\dfrac{\partial U}{\partial V}\right)_T + p\right]\left(\dfrac{\partial V}{\partial T}\right)_p$

By definition, the volume expansion coefficient α is given by Eq. (6.7) as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$$

Hence, $C_p - C_V = \left[\left(\dfrac{\partial U}{\partial V}\right)_T + p\right]V\alpha$

On rearranging terms, we get the required result:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{C_p - C_V}{V\alpha} - p \tag{i}$$

To prove the second result, we take U as a function of p and T, i.e.

$U = U(p, T)$

Then, $dU = \left(\dfrac{\partial U}{\partial P}\right)_T dp + \left(\dfrac{\partial U}{\partial T}\right)_p dT$

so that $\delta Q = \left(\dfrac{\partial U}{\partial T}\right)_p dT + \left(\dfrac{\partial U}{\partial P}\right)_T dp + pdV$

On dividing throughout by dT and keeping pressure constant, we find that

$$\left(\frac{\delta Q}{\partial T}\right)_p = C_p = \left(\frac{\partial U}{\partial T}\right)_P + p\left(\frac{\partial V}{\partial T}\right)_p$$

Hence, $\left(\frac{\partial U}{\partial T}\right)_P = C_p - pV\alpha$ (ii)

To know pressure variation of internal energy you have to rewrite (i) as

$$\left(\frac{\partial U}{\partial p}\right)_T \left(\frac{\partial p}{\partial V}\right)_T = \frac{C_p - C_V}{\alpha V} - p$$ (iii)

By definition, isothermal elasticity is given by Eq. (6.8) as

$$E_T = -V\left(\frac{\partial p}{\partial V}\right)_T \qquad \text{or} \qquad \left(\frac{\partial p}{\partial V}\right)_T = -\frac{E_T}{V}$$

Using this result in (iii), we get pressure variation of internal energy:

$$\left(\frac{\partial U}{\partial p}\right)_T = \frac{pV}{E_T} - \frac{C_p - C_V}{\alpha E_T}$$ (iv)

6. For an ideal gas, the equation of state is

$$pV = RT$$ (i)

Hence, $(\beta_T)_{ideal} = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{p}{RT} \times \left(-\frac{RT}{p^2}\right) = \frac{1}{p}$ (ii)

That is, $(\beta_T)_{ideal}$ is the inverse of pressure for an ideal gas. You may have expected this result from Eq. (7.25). Similarly, for a van der Waals' gas

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT$$ (iii)

or $\qquad p = \frac{RT}{V - b} - \frac{a}{V^2}$

So, $\left(\frac{\partial p}{\partial V}\right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$ and $-V\left(\frac{\partial P}{\partial V}\right)_T = \frac{1}{\beta_T} = -\frac{2a}{V^2} + \frac{RT}{(V-b)^2}V$

On using (iii), we find that $\qquad \dfrac{1}{\beta_T} = -\dfrac{2a}{V^2} + \dfrac{\left(p + \dfrac{a}{V^2}\right)V}{V - b}$

If we ignore b in comparison with V, we get

$$\frac{1}{\beta_T} = -\frac{2a}{V^2} + \left(p + \frac{a}{V^2}\right) = \left(p - \frac{a}{V^2}\right) \qquad \text{or} \qquad (\beta_T)_{Van} = \frac{1}{p - \dfrac{a}{V^2}}$$

This shows that $(\beta_T)_{Van} > (\beta_T)_{Ideal}$. This is physically expected because of the presence of inter-atomic forces in a real gas.

7. For an isothermal process, $dU = 0$ so that all heat absorbed during this process is converted into work: $\delta Q = pdV$

Hence, $W_{A \to B} = \int\limits_{V_A}^{V_B} pdV = RT_1 \int\limits_{V_A}^{V_B} \frac{dV}{V} = RT_1 \ln\left(\frac{V_B}{V_A}\right)$ (i)

where T_1 is the temperature at which heat is absorbed by the system.

For an adiabatic expansion, $\delta Q = 0$ and increase in volume tends to decrease internal energy and hence temperature so that $T_2 < T_1$. Hence

$$W_{B \to C} = \int_{V_B}^{V_C} p dV = \int_{V_B}^{V_C} \frac{K \, dV}{V^{\gamma}} = -\frac{K}{\gamma - 1}\left[\frac{1}{V_C^{\gamma-1}} - \frac{1}{V_B^{\gamma-1}}\right]$$

Using the equation of state for an adiabatic process, we can rewrite it as

$$W_{B \to C} = \frac{R(T_1 - T_2)}{\gamma - 1} \tag{ii}$$

Similarly, for isothermal compression you can readily show that

$$W_{C \to D} = RT_2 \ln\left(\frac{V_D}{V_C}\right) = -RT_2 \ln\left(\frac{V_C}{V_D}\right) \tag{iii}$$

whereas for adiabatic compression

$$W_{D \to A} = -\left(\frac{R(T_1 - T_2)}{\gamma - 1}\right) \tag{iv}$$

On combining results contained in (i) to (iv), you will get

$$W = W_{A \to B} + W_{B \to C} + W_{C \to D} + W_{D \to A} = RT_1 \ln\left(\frac{V_B}{V_A}\right) - RT_2 \ln\left(\frac{V_C}{V_D}\right)$$

8. The initial volume of both gases may be obtained using the ideal gas law, $pV = nRT$. On solving for V, we get

$$V = \frac{nRT}{p} = \frac{(0.06 \, \text{mol}) \times \left(8.3 \, \text{JK}^{-1} \, \text{mol}^{-1}\right) \times (300 \, \text{K})}{(2.0 \, \text{atm}) \times \left(1.0 \times 10^5 \, \text{Pa atm}^{-1}\right)}$$

$$= 7.5 \times 10^{-4} \, \text{m}^3$$

For the isothermal process, temperature remains constant at 300K. So when pressure drops to half the initial value, the equation $pV = \text{const}$ implies that the volume will double. So the final volume will be $1.5 \times 10^{-3} \, \text{m}^3$. That is,

$$V_f = 1.5 \times 10^{-3} \, \text{m}^3 \tag{i}$$

For the adiabatic process, we have $p_i V_i^{\gamma} = p_f V_f^{\gamma}$

On solving for V_f, we get

$$V_f = \left(\frac{p_i}{p_f}\right)^{1/\gamma} V_i = \left(\frac{2.0 \, \text{atm}}{1.0 \, \text{atm}}\right)^{1/1.4} \times \left(7.5 \times 10^{-4} \text{m}^3\right)$$

$$= 1.2 \times 10^{-3} \, \text{m}^3 \tag{ii}$$

On comparing (i) and (ii), you will note that the volume of the gas undergoing an adiabatic expansion is less than that when it undergoes isothermal expansion.

APPENDIX-7A: ADIABATIC LAPSE RATE

The heat from the Sun, on being absorbed by the ground, heats up the air in immediate contact. The heated air rises upward and a vertical density gradient is established. This gives rise to convection currents which transport cooler air downwards and hot air upwards. As hot air rises, it expands. Will it exchange heat with its environment? It may not do so because air is a poor conductor of heat. This means that in intermixing of air, we have an adiabatic expansion.

To calculate the drop in temperature with height, we assume that air behaves as a perfect gas. That is, we ignore the presence of water vapour in atmosphere. This means that we can use Eq. (7.20). For one mole of the gas, Eq. (7.20) in logarithmic form becomes:

$$\gamma \ln T - (\gamma - 1) \ln p = \ln K_1$$

On differentiation, we can write the resultant expression as:

$$\frac{dT}{T} - \frac{\gamma - 1}{\gamma} \frac{dp}{p} = 0$$

which can be rearranged as:

$$\frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{dT}{T} \tag{7A.1}$$

Let us now pause for a moment and ask: What are we looking for? We wish to calculate variation of temperature with height, i.e. dT/dh. To do so, we must relate pressure with height. For this, we recall that as we go up, pressure decreases. Mathematically, this is expressed as:

$$dp = -\rho g dh$$

where ρ is average density of air and g is acceleration due to gravity. The negative sign signifies that pressure decreases as we move up.

Since we have assumed that air behaves as perfect gas, for one mole of air, we can use the equation of state $p = RT/V$ in the above expression. This gives:

$$\frac{dp}{p} = -\frac{Mg}{RT} dh \tag{7A.2}$$

where $M = \rho V$ is the mass of one mole of air . ($M = mN_A$, where m is the average mass of one air molecule.) On combining Eqs. (7.A.1) and (7.A.2), we get:

$$\frac{dT}{dh} = -\left(\frac{\gamma - 1}{\gamma}\right) \frac{Mg}{R} \tag{7A.3}$$

This is the expression for adiabatic lapse rate. The negative sign on the RHS indicates that temperature decreases as we move upwards.

Typically, $\dfrac{dT}{dh} = 9.8 \times 10^{-3}$ K m^{-1}. This means that over one kilometre, the temperature falls by about 10K.

FURTHER READINGS

1. **Thermal Physics: Kinetic Theory, Thermodynamics and Statistical Mechanics** by Garg, S.C., Bansal, R.M. and Ghosh, C.K., McGraw Hill Education (India) Pvt. Ltd., 2nd Edition, Seventh Reprint (2018).

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