Thermodynamics is the branch of physics that deals with the concepts of heat and temperature and the inter-conversion of heat and other forms of energy. Thermodynamics is a macroscopic science. It deals with bulk systems and does not go into the molecular constitution of matter. In fact, its concepts and laws were formulated in the nineteenth century before the molecular picture of matter was firmly established. Thermodynamic description involves relatively few macroscopic variables of the system, which are suggested by common sense and can be usually measured directly. A microscopic description of a gas, for example, would involve specifying the co-ordinates and velocities of the huge number of molecules constituting the gas. The description in kinetic theory of gases is not so detailed but it does involve molecular distribution of velocities. Thermodynamic description of a gas, on the other hand, avoids the molecular description altogether. Instead, the state of a gas in thermodynamics is specified by macroscopic variables such as pressure, volume, temperature, mass and composition that are felt by our sense perceptions and are measurable*.

The distinction between mechanics and thermodynamics is worth bearing in mind. In mechanics, our interest is in the motion of particles or bodies under the action of forces and torques. Thermodynamics is not concerned with the motion of the system as a whole. It is concerned with the internal macroscopic state of the body. When a bullet is fired from a gun, what changes is the mechanical state of the bullet (its kinetic energy, in particular), not its temperature. When the bullet pierces a wood and stops, the kinetic energy of the bullet gets converted into heat, changing the temperature of the bullet and the surrounding layers of wood. Temperature is related to the energy of the internal (disordered) motion of the bullet, not to the motion of the bullet as a whole.

12.2 THERMAL EQUILIBRIUM

Equilibrium in mechanics means that the net external force and torque on a system are zero. The term 'equilibrium' in thermodynamics appears in a different context : we say the state of a system is an equilibrium state if the macroscopic variables that characterise the system do not change in time. For example, a gas inside a closed rigid container, completely insulated from its surroundings, with fixed values of pressure, volume, temperature, mass and composition that do not change with time, is in a state of thermodynamic equilibrium.

In general, whether or not a system is in a state of equilibrium depends on the surroundings and the nature of the wall that separates the system from the surroundings. Consider two gases *A* and *B* occupying two different containers. We know experimentally that pressure and volume of a given mass of gas can be chosen to be its two independent variables. Let the pressure and volume of the gases be (P_A, V_A) and (P_B, V_B) respectively. Suppose first that the two systems are put in proximity but are separated by an **adiabatic wall** – an insulating wall (can be movable) that does not allow flow of energy (heat) from one to another. The systems are insulated from the rest of the surroundings also by similar adiabatic walls. The situation is shown schematically in Fig. 12.1 (a). In this case, it is found that any possible pair of values (P_A, V_A) will be in equilibrium with any possible pair of values (P_B, V_B). Next, suppose that the adiabatic wall is replaced by a **diathermic wall** – a conducting wall that allows energy flow (heat) from one to another. It is then found that the macroscopic variables of the systems *A* and *B* change spontaneously until both the systems attain equilibrium states. After that there is no change in their states. The situation is shown in Fig. 12.1(b). The pressure and volume variables of the two gases change to (P_B', V_B') and (P_A', V_A') such that the new states of *A* and *B* are in equilibrium with each other**. There is no more energy flow from one to another. We then say that the system *A* is in thermal equilibrium with the system *B*.

What characterises the situation of thermal equilibrium between two systems ? You can guess the answer from your experience. In thermal equilibrium, the temperatures of the two systems

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* *Thermodynamics may also involve other variables that are not so obvious to our senses e.g. entropy, enthalpy, etc., and they are all macroscopic variables.*

** *Both the variables need not change. It depends on the constraints. For instance, if the gases are in containers of fixed volume, only the pressures of the gases would change to achieve thermal equilibrium.*

are equal. We shall see how does one arrive at the concept of temperature in thermodynamics? The Zeroth law of thermodynamics provides the clue.

12.3 ZEROTH LAW OF THERMODYNAMICS

Imagine two systems *A* and *B*, separated by an adiabatic wall, while each is in contact with a third system *C*, via a conducting wall [Fig. 12.2(a)]. The states of the systems (i.e., their macroscopic variables) will change until both *A* and *B* come to thermal equilibrium with *C*. After this is achieved, suppose that the adiabatic wall between *A* and *B* is replaced by a conducting wall and *C* is insulated from *A* and *B* by an adiabatic wall [Fig.12.2(b)]. It is found that the states of *A* and *B* change no further i.e. they are found **to be in thermal equilibrium with each other**. This observation forms the basis of the **Zeroth Law of Thermodynamics**, which states that **'two systems in thermal equilibrium with a third system separately are in thermal equilibrium with each other'**. R.H. Fowler formulated this law in 1931 long after the first and second Laws of thermodynamics were stated and so numbered.

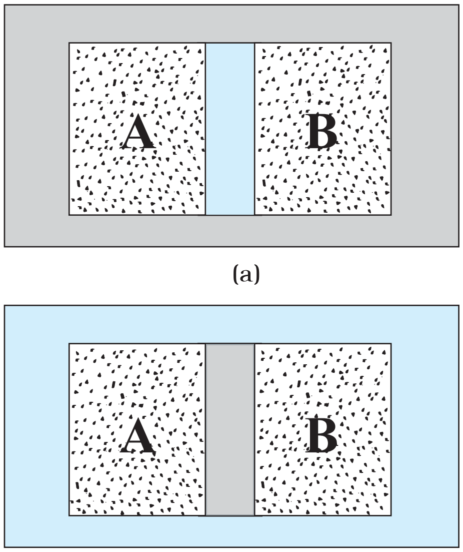


Fig. 12.1 *(a) Systems A and B (two gases) separated by an adiabatic wall – an insulating wall that does not allow flow of heat. (b) The same systems A and B separated by a diathermic wall – a conducting wall that allows heat to flow from one to another. In this case, thermal equilibrium is attained in due course.*

The Zeroth Law clearly suggests that when two systems *A* and *B*, are in thermal equilibrium, there must be a physical quantity that has the same value for both. This thermodynamic variable whose value is equal for two systems in thermal equilibrium is called temperature (T). Thus, if *A* and *B* are separately in equilibrium with *C*, $T_A = T_C$ and $T_B = T_C$. This implies that $T_A = T_B$ i.e. the systems *A* and *B* are also in thermal equilibrium.

We have arrived at the concept of temperature formally via the Zeroth Law. The next question is : how to assign numerical values to temperatures of different bodies ? In other words, how do we construct a scale of temperature ? Thermometry deals with this basic question to which we turn in the next section.

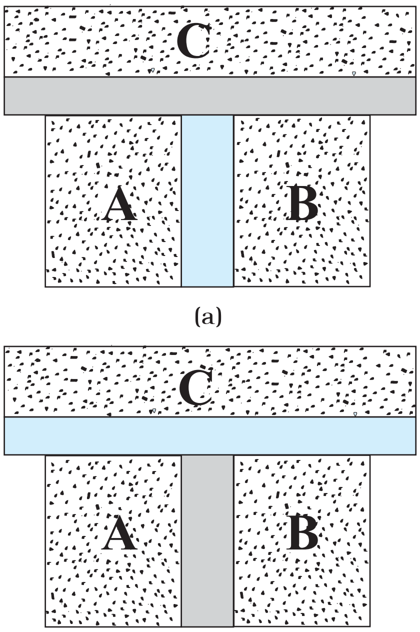


Fig. 12.2 *(a) Systems A and B are separated by an adiabatic wall, while each is in contact with a third system C via a conducting wall. (b) The adiabatic wall between A and B is replaced by a conducting wall, while C is insulated from A and B by an adiabatic wall.*

12.4 HEAT, INTERNAL ENERGY AND WORK

The Zeroth Law of Thermodynamics led us to the concept of temperature that agrees with our commonsense notion. Temperature is a marker of the 'hotness' of a body. It determines the direction of flow of heat when two bodies are placed in thermal contact. Heat flows from the body at a higher temperature to the one at lower temperature. The flow stops when the temperatures equalise; the two bodies are then in thermal equilibrium. We saw in some detail how to construct temperature scales to assign temperatures to different bodies. We now describe the concepts of heat and other relevant quantities like internal energy and work.

The concept of internal energy of a system is not difficult to understand. We know that every bulk system consists of a large number of molecules. Internal energy is simply the sum of the kinetic energies and potential energies of these molecules. We remarked earlier that in thermodynamics, the kinetic energy of the system, as a whole, is not relevant. Internal energy is thus, the sum of molecular kinetic and potential energies in the frame of reference relative to which the centre of mass of the system is at rest. Thus, it includes only the (disordered) energy associated with the random motion of molecules of the system. We denote the internal energy of a system by U.

Though we have invoked the molecular picture to understand the meaning of internal energy, as far as thermodynamics is concerned, U is simply a macroscopic variable of the system. The important thing about internal energy is that it depends only on the state of the system, not on how that state was achieved. Internal energy U of a system is an example of a thermodynamic 'state variable' – its value depends only on the given state of the system, not on history i.e. not on the 'path' taken to arrive at that state. Thus, the internal energy of a given mass of gas depends on its state described by specific values of pressure, volume and temperature. It does not depend on how this state of the gas came about. Pressure, volume, temperature, and internal energy are thermodynamic state variables of the system (gas) (see section 12.7). If we neglect the small intermolecular forces in a gas, the internal energy of a gas is just the sum of kinetic energies associated with various random motions of its molecules. We will see in the next chapter that in a gas this motion is not only translational (i.e. motion from one point to another in the volume of the container); it also includes rotational and vibrational motion of the molecules (Fig. 12.3).

What are the ways of changing internal energy of a system ? Consider again, for simplicity, the system to be a certain mass of gas contained in a cylinder with a movable piston as shown in Fig. 12.4. Experience shows there are two ways of changing the state of the gas (and hence its internal energy). One way is to put the cylinder in contact with a body at a higher temperature than that of the gas. The temperature difference will cause a flow of energy (heat) from the hotter body to the gas, thus increasing the internal energy of the gas. The other way is to push the piston down i.e. to do work on the system, which again results in increasing the internal energy of the gas. Of course, both these things could happen in the reverse direction. With surroundings at a lower temperature, heat would flow from the gas to the surroundings. Likewise, the gas could push the piston up and do work on the surroundings. In short, heat and work are two different modes of altering the state of a thermodynamic system and changing its internal energy.

The notion of heat should be carefully distinguished from the notion of internal energy. Heat is certainly energy, but it is the energy in transit. This is not just a play of words. The distinction is of basic significance. The state of a thermodynamic system is characterised by its internal energy, not heat. A statement like **'a gas in a given state has a certain amount of heat'** is as meaningless as the statement that **'a gas in a given state has a certain amount of work'**. In contrast, **'a gas in a given state has a certain amount of internal energy'** is a perfectly meaningful statement. Similarly, the statements **'a certain amount of heat is supplied to the system' or 'a certain amount of work was done by the system'** are perfectly meaningful.

To summarise, heat and work in thermodynamics are not state variables. They are modes of energy transfer to a system resulting in change in its internal energy, which, as already mentioned, is a state variable.

In ordinary language, we often confuse heat with internal energy. The distinction between them is sometimes ignored in elementary physics books. For proper understanding of thermodynamics, however, the distinction is crucial.

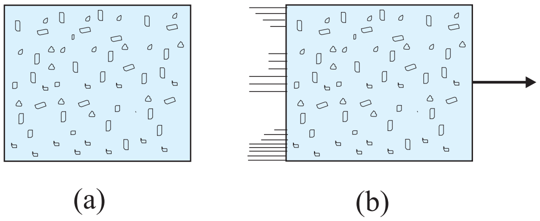


Fig. 12.3 *(a) Internal energy U of a gas is the sum of the kinetic and potential energies of its molecules when the box is at rest. Kinetic energy due to various types of motion (translational, rotational, vibrational) is to be included in U. (b) If the same box is moving as a whole with some velocity, the kinetic energy of the box is not to be included in U.*

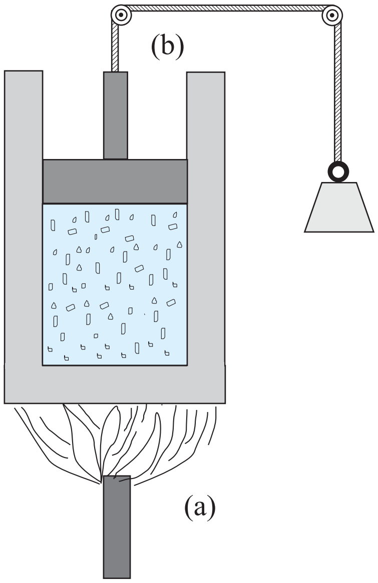


Fig. 12.4 *Heat and work are two distinct modes of energy transfer to a system that results in change in its internal energy. (a) Heat is energy transfer due to temperature difference between the system and the surroundings. (b) Work is energy transfer brought about by means (e.g. moving the piston by raising or lowering some weight connected to it) that do not involve such a temperature difference.*

12.5 FIRST LAW OF THERMODYNAMICS

We have seen that the internal energy U of a system can change through two modes of energy transfer : heat and work. Let

ΔQ = Heat supplied *to* the system *by* the surroundings

ΔW = Work done *by* the system *on* the surroundings

ΔU = Change in internal energy of the system

The general principle of conservation of energy then implies that

$$\Delta Q = \Delta U + \Delta W \qquad (12.1)$$

i.e. the energy (ΔQ) supplied to the system goes in partly to increase the internal energy of the system (ΔU) and the rest in work on the environment (ΔW). Equation (12.1) is known as the **First Law of Thermodynamics**. It is simply the general law of conservation of energy applied to any system in which the energy transfer from or to the surroundings is taken into account.

Let us put Eq. (12.1) in the alternative form

$$\Delta Q - \Delta W = \Delta U \qquad (12.2)$$

Now, the system may go from an initial state to the final state in a number of ways. For example, to change the state of a gas from (P_1, V_1) to (P_2, V_2), we can first change the volume of the gas from V_1 to V_2, keeping its pressure constant i.e. we can first go the state (P_1, V_2) and then change the pressure of the gas from P_1 to P_2, keeping volume constant, to take the gas to (P_2, V_2). Alternatively, we can first keep the volume constant and then keep the pressure constant. Since U is a state variable, ΔU depends only on the initial and final states and not on the path taken by the gas to go from one to the other. However, ΔQ and ΔW will, in general, depend on the path taken to go from the initial to final states. From the First Law of Thermodynamics, Eq. (12.2), it is clear that the combination $\Delta Q - \Delta W$, is however, path independent. This shows that if a system is taken through a process in which $\Delta U = 0$ (for example, isothermal expansion of an ideal gas, see section 12.8),

$$\Delta Q = \Delta W$$

i.e., heat supplied to the system is used up entirely by the system in doing work on the environment.

If the system is a gas in a cylinder with a movable piston, the gas in moving the piston does work. Since force is pressure times area, and area times displacement is volume, work done by the system against a constant pressure P is

$$\Delta W = P \Delta V$$

where ΔV is the change in volume of the gas. Thus, for this case, Eq. (12.1) gives

$$\Delta Q = \Delta U + P \Delta V \qquad (12.3)$$

As an application of Eq. (12.3), consider the change in internal energy for 1 g of water when we go from its liquid to vapour phase. The measured latent heat of water is 2256 J/g. i.e., for 1 g of water ΔQ = 2256 J. At atmospheric pressure, 1 g of water has a volume 1 cm^3 in liquid phase and 1671 cm^3 in vapour phase.

Therefore,

$$\Delta W = P(V_g - V_l) = 1.013 \times 10^5 \times (1670) \times 10^{-6} = 169.2 \text{ J}$$

Equation (12.3) then gives

$$\Delta U = 2256 - 169.2 = 2086.8 \text{ J}$$

We see that most of the heat goes to increase the internal energy of water in transition from the liquid to the vapour phase.

12.6 SPECIFIC HEAT CAPACITY

Suppose an amount of heat ΔQ supplied to a substance changes its temperature from T to $T + \Delta T$. We define heat capacity of a substance (see Chapter 11) to be

$$S = \frac{\Delta Q}{\Delta T} \qquad (12.4)$$

We expect ΔQ and, therefore, heat capacity S to be proportional to the mass of the substance. Further, it could also depend on the temperature, i.e., a different amount of heat may be needed for a unit rise in temperature at different temperatures. To define a constant characteristic of the substance and independent of its amount, we divide S by the mass of the substance m in kg :

$$s = \frac{S}{m} = \left(\frac{1}{m}\right)\frac{\Delta Q}{\Delta T} \qquad (12.5)$$

s is known as the specific heat capacity of the substance. It depends on the nature of the substance and its temperature. The unit of specific heat capacity is J kg^{-1} K^{-1}.

If the amount of substance is specified in terms of moles μ (instead of mass m in kg), we can define heat capacity per mole of the substance by

$$C = \frac{S}{\mu} = \frac{1}{\mu}\frac{\Delta Q}{\Delta T} \qquad (12.6)$$

C is known as molar specific heat capacity of the substance. Like s, C is independent of the amount of substance. C depends on the nature of the substance, its temperature and the conditions under which heat is supplied. The unit of C is J mol^{-1} K^{-1}. As we shall see later (in connection with specific heat capacity of gases), additional conditions may be needed to define C or s. The idea in defining C is that simple predictions can be made in regard to molar specific heat capacities.

Table 12.1 lists measured specific and molar heat capacities of solids at atmospheric pressure and ordinary room temperature.

We will see in Chapter 13 that predictions of specific heats of gases generally agree with experiment. We can use the same law of equipartition of energy that we use there to predict molar specific heat capacities of solids. Consider a solid of N atoms, each vibrating about its mean position. An oscillator in one dimension has average energy of $2 \times ½\, k_BT = k_BT$. In three dimensions, the average energy is $3\, k_BT$. For a mole of a solid, the total energy is

$$U = 3\, k_BT \times N_A = 3\, RT$$

Now, at constant pressure, $\Delta Q = \Delta U + P\,\Delta V \cong \Delta U$, since for a solid ΔV is negligible. Therefore,

$$C = \frac{\Delta Q}{\Delta T} = \frac{\Delta U}{\Delta T} = 3R \qquad (12.7)$$

Table 12.1 **Specific and molar heat capacities of some solids at room temperature and atmospheric pressure**

Substance	Specific$^{-\mathrm{v}}$ heat (J kg^{-1}K^{-1})	Molar specific Heat(J mol^{-1} K^{-1})
Aluminium	900.0	24.4
Carbon	506.5	6.1
Copper	386.4	24.5
Lead	127.7	26.5
Silver	236.1	25.5
Tungsten	134.4	24.9

As Table 12.1 shows, the experimentally measured values which generally agrees with predicted value 3R at ordinary temperatures. (Carbon is an exception.) The agreement is known to break down at low temperatures.

Specific heat capacity of water

The old unit of heat was calorie. One calorie was earlier defined to be the amount of heat required to raise the temperature of 1g of water by 1°C. With more precise measurements, it was found that the specific heat of water varies slightly with temperature. Figure 12.5 shows this variation in the temperature range 0 to 100 °C.

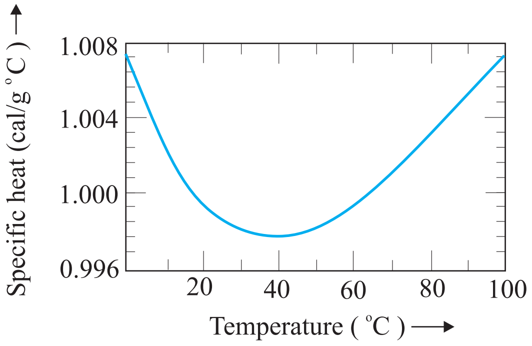


Fig. 12.5 *Variation of specific heat capacity of water with temperature.*

For a precise definition of calorie, it was, therefore, necessary to specify the unit temperature interval. One calorie is defined to be the amount of heat required to raise the temperature of 1g of water from 14.5 °C to 15.5 °C. Since heat is just a form of energy, it is preferable to use the unit joule, J. In SI units, the specific heat capacity of water is 4186 J kg^{-1} K^{-1} i.e. 4.186 J g^{-1} K^{-1}. The so called mechanical equivalent of heat defined as the amount of work needed to produce 1 cal of heat is in fact just a conversion factor between two different units of energy : calorie to joule. Since in SI units, we use the unit joule for heat, work or any other form of energy, the term mechanical equivalent is now superfluous and need not be used.

As already remarked, the specific heat capacity depends on the process or the conditions under which heat capacity transfer takes place. For gases, for example, we can define two specific heats : **specific heat capacity at constant volume and specific heat capacity at constant pressure**. For an ideal gas, we have a simple relation.

$$C_p - C_v = R \qquad (12.8)$$

where C_p and C_v are molar specific heat capacities of an ideal gas at constant pressure and volume respectively and R is the universal gas constant. To prove the relation, we begin with Eq. (12.3) for 1 mole of the gas :

$$\Delta Q = \Delta U + P\,\Delta V$$

If ΔQ is absorbed at constant volume, $\Delta V = 0$

$$C_{\mathrm{v}} = \left(\frac{\Delta Q}{\Delta T}\right)_{\mathrm{v}} = \left(\frac{\Delta U}{\Delta T}\right)_{\mathrm{v}} = \left(\frac{\Delta U}{\Delta T}\right) \qquad (12.9)$$

where the subscript v is dropped in the last step, since U of an ideal gas depends only on temperature. (The subscript denotes the quantity kept fixed.) If, on the other hand, ΔQ is absorbed at constant pressure,

$$C_{\mathrm{p}} = \left(\frac{\Delta Q}{\Delta T}\right)_{\mathrm{p}} = \left(\frac{\Delta U}{\Delta T}\right)_{\mathrm{p}} + P\left(\frac{\Delta V}{\Delta T}\right)_{\mathrm{p}} \qquad (12.10)$$

The subscript p can be dropped from the first term since U of an ideal gas depends only on T. Now, for a mole of an ideal gas

$$PV = RT$$

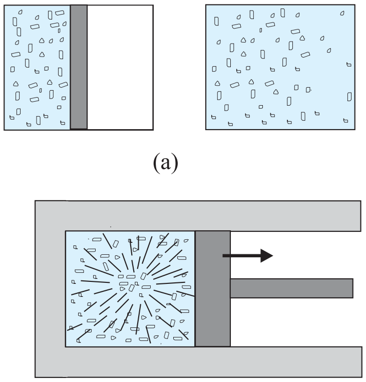
which gives

$$P\left(\frac{\Delta V}{\Delta T}\right)_{\mathrm{p}} = R \qquad (12.11)$$

Equations (12.9) to (12.11) give the desired relation, Eq. (12.8).

12.7 THERMODYNAMIC STATE VARIABLES AND EQUATION OF STATE

Every **equilibrium state** of a thermodynamic system is completely described by specific values of some macroscopic variables, also called state variables. For example, an equilibrium state of a gas is completely specified by the values of pressure, volume, temperature, and mass (and composition if there is a mixture of gases). A thermodynamic system is not always in equilibrium. For example, a gas allowed to expand freely against vacuum is not an equilibrium state [Fig. 12.6(a)]. During the rapid expansion, pressure of the gas may not be uniform throughout. Similarly, a mixture of gases undergoing an explosive chemical reaction (e.g. a mixture of petrol vapour and air when ignited by a spark) is not an equilibrium state; again its temperature and pressure are not uniform [Fig. 12.6(b)]. Eventually, the gas attains a uniform temperature and pressure and comes to thermal and mechanical equilibrium with its surroundings.


(a)

(b)

Fig. 12.6 *(a) The partition in the box is suddenly removed leading to free expansion of the gas. (b) A mixture of gases undergoing an explosive chemical reaction. In both situations, the gas is not in equilibrium and cannot be described by state variables.*

In short, thermodynamic state variables describe equilibrium states of systems. The various state variables are not necessarily independent. The connection between the state variables is called the equation of state. For example, for an ideal gas, the equation of state is the ideal gas relation

$$P V = \mu R T$$

For a fixed amount of the gas i.e. given μ, there are thus, only two independent variables, say P and V or T and V. The pressure-volume curve for a fixed temperature is called an **isotherm**. Real gases may have more complicated equations of state.

The thermodynamic state variables are of two kinds: **extensive** and **intensive**. Extensive variables indicate the 'size' of the system. Intensive variables such as pressure and temperature do not. To decide which variable is extensive and which intensive, think of a relevant system in equilibrium, and imagine that it is divided into two equal parts. The variables that remain unchanged for each part are intensive. The variables whose values get halved in each part are extensive. It is easily seen, for example, that internal energy U, volume V, total mass M are extensive variables. Pressure P, temperature T, and density ρ are intensive variables. It is a good practice to check the consistency of thermodynamic equations using this classification of variables. For example, in the equation

$$\Delta Q = \Delta U + P\,\Delta V$$

quantities on both sides are extensive*. (The product of an intensive variable like P and an extensive quantity ΔV is extensive.)

12.8 THERMODYNAMIC PROCESSES

12.8.1 Quasi-static process

Consider a gas in thermal and mechanical equilibrium with its surroundings. The pressure of the gas in that case equals the external pressure and its temperature is the same as that of its surroundings. Suppose that the external pressure is suddenly reduced (say by lifting the weight on the movable piston in the container). The piston will accelerate outward. During the process, the gas passes through states that are not equilibrium states. The non-equilibrium states do not have well-defined pressure and temperature. In the same way, if a finite temperature difference exists between the gas and its surroundings, there will be a rapid exchange of heat during which the gas will pass through non-equilibrium states. In due course, the gas will settle to an equilibrium state with well-defined temperature and pressure equal to those of the surroundings. The free expansion of a gas in vacuum and a mixture of gases undergoing an explosive chemical reaction, mentioned in section 12.7 are also examples where the system goes through non-equilibrium states.

Non-equilibrium states of a system are difficult to deal with. It is, therefore, convenient to imagine an idealised process in which at every stage the system is an equilibrium state. Such a

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* *As emphasised earlier, Q is not a state variable. However, ΔQ is clearly proportional to the total mass of system and hence is extensive.*

process is, in principle, infinitely slow-hence the name quasi-static (meaning nearly static). The system changes its variables (P, T, V) so slowly that it remains in thermal and mechanical equilibrium with its surroundings throughout. In a quasi-static process, at every stage, the difference in the pressure of the system and the external pressure is infinitesimally small. The same is true of the temperature difference between the system and its surroundings. To take a gas from the state (P, T) to another state (P', T') via a quasi-static process, we change the external pressure by a very small amount, allow the system to equalise its pressure with that of the surroundings and continue the process infinitely slowly until the system achieves the pressure P'. Similarly, to change the temperature, we introduce an infinitesimal temperature difference between the system and the surrounding reservoirs and by choosing reservoirs of progressively different temperatures T to T', the system achieves the temperature T'.

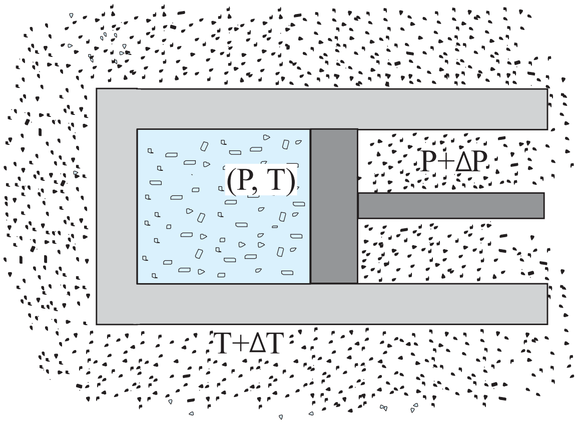

Fig. 12.7 *In a quasi-static process, the temperature of the surrounding reservoir and the external pressure differ only infinitesimally from the temperature and pressure of the system.*

A quasi-static process is obviously a hypothetical construct. In practice, processes that are sufficiently slow and do not involve accelerated motion of the piston, large temperature gradient, etc. are reasonably approximation to an ideal quasi-static process. We shall from now on deal with quasi-static processes only, except when stated otherwise.

A process in which the temperature of the system is kept fixed throughout is called an **isothermal process**. The expansion of a gas in a metallic cylinder placed in a large reservoir of fixed temperature is an example of an isothermal process. (Heat transferred from the reservoir to the system does not materially affect the temperature of the reservoir, because of its very large heat capacity.) In **isobaric processes** the pressure is constant while in **isochoric processes** the volume is constant. Finally, if the system is insulated from the surroundings and no heat flows between the system and the surroundings, the process is **adiabatic**. The definitions of these special processes are summarised in Table. 12.2

Table 12.2 **Some special thermodynamic processes**

Type of processes	Feature
Isothermal	Temperature constant
Isobaric	Pressure constant
Isochoric	Volume constant
Adiabatic	No heat flow between the system and the surroundings ($\Delta Q = 0$)

We now consider these processes in some detail :

Isothermal process

For an isothermal process (T fixed), the ideal gas equation gives

$$PV = \text{constant}$$

i.e., pressure of a given mass of gas varies inversely as its volume. This is nothing but Boyle's Law.

Suppose an ideal gas goes isothermally (at temperature T) from its initial state (P_1, V_1) to the final state (P_2, V_2). At any intermediate stage with pressure P and volume change from V to $V + \Delta V$ (ΔV small)

$$\Delta W = P \Delta V$$

Taking ($\Delta V \to 0$) and summing the quantity ΔW over the entire process,

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

$$= \mu RT \int_{V_1}^{V_2} \frac{dV}{V} = \mu RT \ \ln \frac{V_2}{V_1} \qquad (12.12)$$

where in the second step we have made use of the ideal gas equation $PV = \mu RT$ and taken the constants out of the integral. For an ideal gas, internal energy depends only on temperature. Thus, there is no change in the internal energy of an ideal gas in an isothermal process. The First Law of Thermodynamics then implies that heat supplied to the gas equals the work done by the gas : $Q = W$. Note from Eq. (12.12) that for $V_2 > V_1$, $W > 0$; and for $V_2 < V_1$, $W < 0$. That is, in an isothermal expansion, the gas absorbs heat and does work while in an isothermal compression, work is done on the gas by the environment and heat is released.

Adiabatic process

In an adiabatic process, the system is insulated from the surroundings and heat absorbed or released is zero. From Eq. (12.1), we see that work done by the gas results in decrease in its internal energy (and hence its temperature for an ideal gas). We quote without proof (the result that you will learn in higher courses) that for an adiabatic process of an ideal gas.

$$P V^{\gamma} = \text{const} \tag{12.13}$$

where γ is the ratio of specific heats (ordinary or molar) at constant pressure and at constant volume.

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

Thus if an ideal gas undergoes a change in its state adiabatically from (P_1, V_1) to (P_2, V_2) :

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \tag{12.14}$$

Figure 12.8 shows the *P-V* curves of an ideal gas for two adiabatic processes connecting two isotherms.

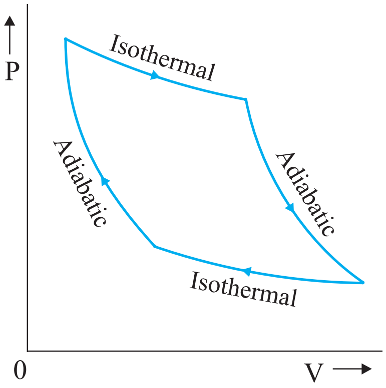

Fig. 12.8 *P-V curves for isothermal and adiabatic processes of an ideal gas.*

We can calculate, as before, the work done in an adiabatic change of an ideal gas from the state (P_1, V_1, T_1) to the state (P_2, V_2, T_2).

$$W = \int_{V_1}^{V_2} P\,\mathrm{d}V$$

$$= constant \times \int_{V_1}^{V_2} \frac{\mathrm{d}V}{V^{\gamma}} = constant \times \left.\frac{V^{-\gamma+1}}{1-\gamma}\right|_{V_1}^{V_2}$$

$$= \frac{constant}{(1-\gamma)} \times \left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right] \tag{12.15}$$

From Eq. (12.34), the constant is $P_1V_1^{\gamma}$ or $P_2V_2^{\gamma}$

$$W = \frac{1}{1-\gamma}\left[\frac{P_2V_2^{\gamma}}{V_2^{\gamma-1}} - \frac{P_1V_1^{\gamma}}{V_1^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right] = \frac{\mu R(T_1 - T_2)}{\gamma - 1} \tag{12.16}$$

As expected, if work is done by the gas in an adiabatic process ($W > 0$), from Eq. (12.16), $T_2 < T_1$. On the other hand, if work is done on the gas ($W < 0$), we get $T_2 > T_1$ i.e., the temperature of the gas rises.

Isochoric process

In an isochoric process, V is constant. No work is done on or by the gas. From Eq. (12.1), the heat absorbed by the gas goes entirely to change its internal energy and its temperature. The change in temperature for a given amount of heat is determined by the specific heat of the gas at constant volume.

Isobaric process

In an isobaric process, P is fixed. Work done by the gas is

$$W = P(V_2 - V_1) = \mu R(T_2 - T_1) \tag{12.17}$$

Since temperature changes, so does internal energy. The heat absorbed goes partly to increase internal energy and partly to do work. The change in temperature for a given amount of heat is determined by the specific heat of the gas at constant pressure.

Cyclic process

In a cyclic process, the system returns to its initial state. Since internal energy is a state variable, $\Delta U = 0$ for a cyclic process. From

Eq. (12.1), the total heat absorbed equals the work done by the system.

12.9 HEAT ENGINES

Heat engine is a device by which a system is made to undergo a cyclic process that results in conversion of heat to work.

(1) It consists of a **working substance**–the system. For example, a mixture of fuel vapour and air in a gasoline or diesel engine or steam in a steam engine are the working substances.

(2) The working substance goes through a cycle consisting of several processes. In some of these processes, it absorbs a total amount of heat Q_1 from an external reservoir at some high temperature T_1.

(3) In some other processes of the cycle, the working substance releases a total amount of heat Q_2 to an external reservoir at some lower temperature T_2.

(4) The work done (W) by the system in a cycle is transferred to the environment via some arrangement (e.g. the working substance may be in a cylinder with a moving piston that transfers mechanical energy to the wheels of a vehicle via a shaft).

The basic features of a heat engine are schematically represented in Fig. 12.9.

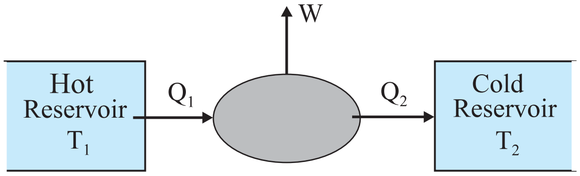

Fig. 12.9 *Schematic representation of a heat engine. The engine takes heat Q_1 from a hot reservoir at temperature T_1, releases heat Q_2 to a cold reservoir at temperature T_2 and delivers work W to the surroundings.*

The cycle is repeated again and again to get useful work for some purpose. The discipline of thermodynamics has its roots in the study of heat engines. A basic question relates to the efficiency of a heat engine. The efficiency (η) of a heat engine is defined by

$$\eta = \frac{W}{Q_1} \tag{12.18}$$

where Q_1 is the heat input i.e., the heat absorbed by the system in one complete cycle and W is the work done on the environment in a cycle. In a cycle, a certain amount of heat (Q_2) may also be rejected to the environment. Then, according to the First Law of Thermodynamics, over one complete cycle,

$$W = Q_1 - Q_2 \tag{12.19}$$

i.e.,

$$\eta = 1 - \frac{Q_2}{Q_1} \tag{12.20}$$

For $Q_2 = 0$, $\eta = 1$, i.e., the engine will have 100% efficiency in converting heat into work. Note that the First Law of Thermodynamics i.e., the energy conservation law does not rule out such an engine. But experience shows that such an ideal engine with $\eta = 1$ is never possible, even if we can eliminate various kinds of losses associated with actual heat engines. It turns out that there is a fundamental limit on the efficiency of a heat engine set by an independent principle of nature, called the Second Law of Thermodynamics (section 12.11).

The mechanism of conversion of heat into work varies for different heat engines. Basically, there are two ways : the system (say a gas or a mixture of gases) is heated by an external furnace, as in a steam engine; or it is heated internally by an exothermic chemical reaction as in an internal combustion engine. The various steps involved in a cycle also differ from one engine to another.

12.10 REFRIGERATORS AND HEAT PUMPS

A refrigerator is the reverse of a heat engine. Here the working substance extracts heat Q_2 from the cold reservoir at temperature T_2, some external work W is done on it and heat Q_1 is released to the hot reservoir at temperature T_1 (Fig. 12.10).

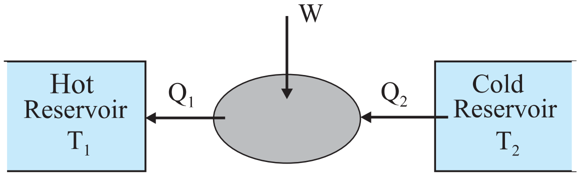

Fig. 12.10 *Schematic representation of a refrigerator or a heat pump, the reverse of a heat engine.*