CHAPTER

5

The First Law of Thermodynamics

5.1 INTRODUCTION

Scope and limitations of thermodynamics: Thermodynamics, literally speaking, means flow of heat and deals with the quantitative relationship between heat and other forms of energy in physico-chemical transformations. It is sometimes called *energetics*. The subject matter of thermodynamics is based on three fundamental laws. They are applicable to all the phenomena in nature. These laws are not based on any theory but are based on experimental facts. The laws have been subjected to rigorous mathematical treatment and have yielded correlations between different observable properties of matter. These have been proved to be very convenient and useful in describing the states of systems in chemical and physical transformations. The results of thermodynamic deductions have been proved to be correct by experiments and found to be rigidly valid. Thermodynamics is, therefore, an exact science.

Thermodynamics has a great predicting power. It can predict whether a given process will occur spontaneously or not under a given set of conditions. The laws provide necessary criteria for predicting the feasibility of a process. However, it gives no information with regard to the rate at which a given change will proceed. Thermodynamics deals only with the states of the system and makes no mention of the mechanism of how the change is accomplished. Thermodynamics answers to why a change occurs but not to how it occurs.

Classical thermodynamics is based on the behaviour of bulk or macroscopic properties of the systems, *i.e.*, systems having many molecules and is independent of the atomic and molecular structure. Consequently, no information can be obtained regarding the molecular structure. This difficulty is, however, obviated in statistical thermodynamics where the laws of mechanics are applied to the behaviour of individual molecules and then a suitable statistical average is taken. The results obtained from classical and statistical thermodynamics are, however, complementary to each other.

The first law deals with the equivalence between various forms of energy, but does not say anything about the conditions under which such an equivalence is achieved. The second law places a restriction on the first law and is concerned with the directions of physico-chemical transformations and the relationships between the properties of the systems at equilibrium. The third law attempts to evaluate the thermodynamic functions. The zeroth law provides an operational definition of temperature.

In this text, we shall be applying the laws of thermodynamics to systems at equilibrium and hence time as a variable will not appear in all our discussions.

5.2 THERMODYNAMIC TERMS

In the study of thermodynamics, it is essential to understand the meaning of terms employed in thermodynamics. These terms have definite meanings. Some of the most commonly used terms are:

(*a*) **System and surroundings:** A thermodynamic system is defined as *the part of the universe which is selected for thermodynamic considerations*. A system usually has a definite amount(s) of specific substance(s). It is separated from the rest of the universe called *surroundings* by a definite boundary. The boundary may be real or imaginary. A system is *homogeneous if it is uniform throughout in all respects and is heterogeneous if it is not uniform throughout and consists of more than one phase separated from each other by sharp boundaries*. A system consisting of a pure mixture of gases or a liquid or a solid, etc. are examples of homogeneous systems while a liquid and its vapour or a mixture of two immiscible liquids or two different solids, etc. constitute heterogeneous systems.

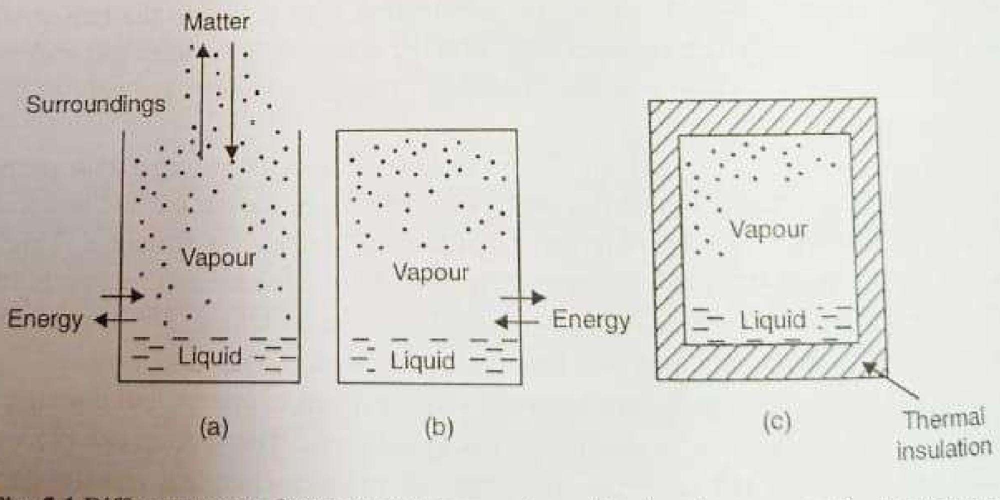
The *boundary* (wall) between the system and the surroundings differs in its ability to allow the passage of energy and matter through it. A *permeable wall* allows the passage of both matter and energy, a *diathermal wall* prevents the passage of matter but allows the flow of energy while an *adiabatic wall* neither allows the passage of energy nor matter.

(*b*) **Types of systems:** In thermodynamics, we deal mainly with three different types of systems depending on the interactions between the system and the surroundings. These are (*i*) *open systems*, (*ii*) *closed systems and* (*iii*) *isolated systems*.

(*i*) **Open systems:** *A system which can exchange both matter and energy with the surroundings is known as an open system* [Fig. 5.1 (*a*)]. Due to these exchanges, matter and energy do not remain constant in open systems.

(*ii*) **Closed systems:** *These are systems in which exchange of energy with the surroundings is possible while the transfer of matter to and from the surroundings does not take place* [Fig. 5.1 (*b*)]. Consequently, in a closed system mass remains constant and only the energy changes.

(*iii*) **Isolated systems:** *It is a system that prevents any interaction between the system and the surroundings* [Fig. 5.1(*c*)]. Both mass and energy of the system remains constant as there is no interaction of the system with the surroundings.



(a) (b) (c)

Fig. 5.1 Different types of systems (*a*) open system; (*b*) closed system; (*c*) isolated system

(*c*) **Properties of a system:** Measurable properties of a system may be divided into two classes, viz., *extensive and intensive*. An extensive property of a system depends upon the total amount of material in the system. Mass, volume, internal energy, heat contents, free energy, entropy, heat capacity are some examples of extensive properties. An intensive property, on the other hand, is defined as a *property which is independent of the amount of material in the system*. Density, molar properties, (molar volume, molar energy, molar entropy, molar heat capacity etc.), surface tension, viscosity, specific heat, thermal conductivity, refractive index, pressure, temperature, boiling and freezing points, vapour pressure of a liquid, etc., are some examples of intensive properties.

(*d*) **State of a system:** A thermodynamic system is said to be in a definite state when the properties have definite values. Various measurable properties of a system which completely define the state of a system are pressure, volume, temperature and concentration. These are known as the *state variables* or *thermodynamic variables*. Any change in the property due to a change in the state of the system depends only on the initial and the final states of the system. These variables are directly measureable from experiments and do not require any assumption regarding the structure of matter and related to one another by an equation called the *equation of state*. For an ideal gas, the equation of state for n moles is $PV = nRT$ while for a van der Waals gas, the equation of state is $\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$. The thermodynamic state of a system in such cases can be defined completely by specifying any two of the three variables. Any change in the value of these variables will change the state of the system which will attain a new state. If it is desired to bring the system back to its initial state, the variables will have their original values.

(*e*) **Change in state:** Change in the state of the system is completely defined when the initial and final states are specified.

(*f*) **Path:** *It is the sequence of intermediate steps or stages arranged in order, followed by the system in going from its initial to the final state.*

(*g*) **Thermodynamic equilibrium**: *A system is said to be in a state of thermodynamic equilibrium if none of the observable properties of the system appears to change with time.* Actually, the term thermodynamic equilibrium assumes the existence of three types of equilibria in the system. They are (*i*) *thermal equilibrium*, (*ii*) *mechanical equilibrium* and (*iii*) *chemical equilibrium*.

(*i*) **Thermal equilibrium**: *A system is said to be in thermal equilibrium if the temperature remains the same in all parts of the system.* Systems in thermal equilibrium with each other will have the same temperature while systems not in thermal equilibrium with each other will have different temperatures. This state is known as the *zeroth law of thermodynamics*.

(*ii*) **Mechanical equilibrium:** *It implies the uniformity of pressure throughout the whole system.*

(*iii*) **Chemical equilibrium:** *If the composition of the system remains constant and uniform throughout, the system is said to be in chemical equilibrium.*

An equilibrium may be stable, metastable or unstable. If after displacement to a new state and release of the constraint causing displacement, it goes back to its original state, the system is said to be in a state of stable equilibrium. But if the system fails to return to its original state, it is said to be in a state of unstable equilibrium. In metastable equilibrium, the system is stable for smaller displacements and unstable for larger displacements.

(*h*) **Process:** A thermodynamic process is defined *as the method of operation with the help of which a change in the state of a system is effected.* The various processes are:

(*i*) **Cyclic process:** If a system after undergoing through a series of changes in its state comes back to its initial state, then the process is termed as a *cyclic process* and the path followed is known as the *cyclic path*.

(ii) **Isothermal process:** *A process that is carried out under conditions of constant temperature is called as isothermal process.* The constancy of temperature is achieved either by extracting heat from the system or supplying heat to it.

(iii) **Adiabatic process:** *A process in which there is no exchange of heat between the system and the surroundings is known as an adiabatic process.* The system is enclosed by adiabatic walls which do not permit heat exchanges with the surroundings. In an adiabatic process, there is a change in the temperature of the system.

(iv) **Isochoric process:** *A process in which volume of the system remains constant.*

(v) **Isobaric or isopiestic process:** *A process that is carried out under conditions of constant pressure.*

(vi) **Reversible process:** *A process is said to be reversible if at any instant during the transformation, the system does not deviate from equilibrium by more than an infinitesimal amount.* A reversible process must be carried out extremely slowly so that the properties of the system virtually remain unchanged at any stage of the change. In a reversible process, all the changes occurring in any part of the process are exactly reversed when the process is carried out in the reverse direction. On completing a reversible cyclic path, the system and the surroundings are both restored exactly to their original states. A reversible process is, therefore, always in a state of equilibrium at each of the small stages. As an example of a reversible process, consider a case in which a system absorbs heat from the surroundings. Reversibility in this case implies that the temperature of the surroundings should be infinitesimally higher than that of the system. If heat is to flow from the system to the surroundings, the temperature of the latter must be only infinitesimally lower than that of the system. Similarly, the expansion of a gas at constant temperature enclosed in a cylinder fitted with a weightless and frictionless piston will be reversible only if the pressure on the gas during expansion is reduced by an infinitesimal amount. During compression, the pressure on the gas at each stage is increased by a very small amount.

A truly reversible process has to be carried out in an infinite number of steps or stages and would thus require infinite time for its completion. In actual practice, the small changes in a process have definite magnitudes and are only approximately closer to a strictly reversible process. A reversible process has, therefore, only a conceptual importance. It is an ideal process and extremely useful in dealing with problems related to energy transfers.

(vii) **Irreversible process:** *A process that occurs rapidly or spontaneously such that it does not remain in equilibrium during the transformation is called an irreversible process.* Such processes do not involve a succession of equilibrium states of the system. After undergoing a change, such processes do not return themselves to their initial states but can be reversed only with the help of external agencies. Expansion of a gas against zero applied pressure, dissolution of a solute in a solvent, mixing of gases, flow of liquid from higher to lower levels, etc. are examples of irreversible processes. All irreversible processes take finite time for their completion and are real processes in actual practice.

5.3 COMPLETE DIFFERENTIALS AND HOMOGENEOUS FUNCTIONS

Thermodynamic functions like pressure, volume, temperature, energy, entropy, etc. are state functions. The change in the values of these quantities does not depend on how the change is carried out but depends only on the initial and final states of the system. If Z is any thermodynamic property of a homogeneous system of constant composition then its value is completely determined by the three thermodynamics variables, pressure, volume and temperature. They are related to one another by an equation of state. Any two of these three variables are sufficient to define any thermodynamic property. We can write

$$Z = f(P, T)$$

where Z may be energy, volume, enthalpy content or any other property to be considered in details at a later stage. Any change in Z resulting from changes in the values of P and T is given by

$$\Delta Z = Z_{\text{final state}} - Z_{\text{initial state}} \qquad ...(5.1)$$

Utilising the principle of calculus, we may write for an infinitesimal change dZ in the property Z as

$$dZ = \left(\frac{\partial Z}{\partial P}\right)_T dP + \left(\frac{\partial Z}{\partial T}\right)_P dT \qquad ...(5.2)$$

where the partial derivatives $(\partial Z/\partial P)_T$ represents the rate of change of Z with pressure at constant temperature and $(\partial Z/\partial T)_P$ denotes the rate of change of Z with temperature at constant pressure. In Eq. (5.2), the first term on the right hand side denotes the contribution of changes in pressure and the second term indicates the contribution for changes in temperature to Z. The differential dZ of a function Z as defined by Eq. (5.2) is called a *complete* or *exact differential*. If we put $(\partial Z/\partial P)_T = L\ (P, T)$ and $(\partial Z/\partial T)_P = M\ (P, T)$ in Eq. (5.2), we get

$$dZ = L(P, T)\ dP + M(P, T)\,dT$$

on differentiating $L\ (P, T)\ [= (\partial Z/\partial P)_T]$ with respect to T keeping P constant and $M\ (P, T)\ [= (\partial Z/\partial T)_P]$ with respect to P maintaining T constant, we get

$$\left(\frac{\partial L}{\partial T}\right)_P = \frac{\partial^2 Z}{\partial T \partial P}$$

and

$$\left(\frac{\partial M}{\partial P}\right)_T = \frac{\partial^2 Z}{\partial P \partial T}$$

Since

$$\frac{\partial^2 Z}{\partial T\, \partial P} = \frac{\partial^2 Z}{\partial P\, \partial T}$$

we have

$$\left(\frac{\partial L}{\partial T}\right)_P = \left(\frac{\partial M}{\partial P}\right)_T \qquad ...(5.3)$$

Hence, if Z is any thermodynamic function, dZ is an exact differential then the cross derivatives, $\left(\frac{\partial L}{\partial T}\right)_P$ and $\left(\frac{\partial M}{\partial P}\right)_T$ must be equal. This is known as *Euler's theorem of exactness*. Another characteristic of an exact differential is that its value for a cyclic transformation is zero, *i.e.*,

$$\oint dZ = 0$$

where $\oint$ denotes the cyclic integral.

Considering V as a function of P and T, *i.e.*,

$$V = f(P, T)$$

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

Hence

$$-dW = P\left(\frac{\partial V}{\partial P}\right)_T dP + P\left(\frac{\partial V}{\partial T}\right)_P dT$$

If $dP = 0$, then

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

or

$$-\frac{\partial^2 W}{\partial P\,\partial T} = P\frac{\partial^2 V}{\partial P\,\partial T} + \left(\frac{\partial V}{\partial T}\right)_P$$

and at constant temperature $dT = 0$ and

$$-\left(\frac{\partial W}{\partial P}\right)_T = P\left(\frac{\partial V}{\partial P}\right)_T$$

or

$$-\frac{\partial^2 W}{\partial T\,\partial P} = P\frac{\partial^2 V}{\partial P\,\partial T}$$

If dW is an exact differential

$$\frac{\partial^2 W}{\partial T\,\partial P} = \frac{\partial^2 W}{\partial P\,\partial T}$$

or

$$P\frac{\partial^2 V}{\partial P\,\partial T} + \left(\frac{\partial V}{\partial T}\right)_P = P\frac{\partial^2 V}{\partial T\,\partial P}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = 0$$

The conclusion is obviously incorrect which mean dW is not an exact differential.

For a cyclic transformation carried out reversibly and irreversibly, the value of W for two different processes would be different. This can be shown as follows:

(*i*) **Isothermal reversible transformation:** Suppose the gas is expanded from V_1 to V_2 with P_{ext} = P, the pressure of the gas and then compressed from V_2 to V_1 with $P_{ext} = P$. The network for the comple reversible cycle is

$$W_{cyc} = W_{exp} + W_{comp}$$

$$= -\int_{V_1}^{V_2} PdV - \int_{V_2}^{V_1} PdV$$

then
$$\left(\frac{\partial Z}{\partial V}\right)_T dV = -\left(\frac{\partial Z}{\partial T}\right)_V dT$$

$$\left(\frac{\partial Z}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_Z = -\left(\frac{\partial Z}{\partial T}\right)_V$$

Rearranging we get

$$\left(\frac{\partial Z}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_Z \left(\frac{\partial T}{\partial Z}\right)_V = -1 \qquad \text{...(5.6)}$$

Equation (5.6) expresses the cyclic rule. Similar types of expressions can be deduced for any other thermodynamic quantity. For example, Z is the pressure of a gas, Eq. (5.6) would be

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V = -1 \qquad \text{...(5.7)}$$

Homogeneous Functions

A function $f(x, y, z, \ldots)$ is homogeneous of degree n, if upon replacement of each independent variable by an arbitrary parameter λ times the variable, the function is multiplied by λ^n, that is

$$f(\lambda_x, \lambda_y, \lambda_z, \ldots) = \lambda^n f(x, y, z, \ldots)$$

As a simple example, consider the function

$$f(x, y) = ax^2 + bxy + cy^2$$

If we replace the variable x by λx and y by λy, we can write

$$f(\lambda x, \lambda y) = a\lambda^2 x^2 + b\lambda^2 xy + c\lambda^2 y^2$$

$$= \lambda^2 \left(ax^2 + bxy + cy^2\right)$$

$$= \lambda^2 f(x, y)$$

The net result is a change in the function by a factor of λ^2. The function is called a *homogeneous function*. In the above equation, the exponent of λ gives the degree of homogeneity. All extensive variables are homogeneous functions of first degree in moles and intensive variables are functions of zero degree with respect to moles. Volume is a homogeneous function of first degree in mole because at constant pressure and temperature doubling the number of moles doubles the volume, *i.e.*,

$$V = f(P, T, n)$$

$$V_1 = f(P, T, 2n) = 2f(P, T, n) = 2V$$

Euler's theorem: According to the theorem, if $f(x, y, z)$ is a homogeneous function of degree n, then

$$x\frac{\partial f}{\partial x} + y\frac{\partial f}{\partial y} + z\frac{\partial f}{\partial z} = nf(x, y, z)$$

It is useful in the discussions of partial molar quantities.

Problem 5.1: *If the equation of state for 1 mole of a gas is*

$$P(V-b)=RT$$

prove that P is a state function, dP is an exact differential and

$$\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P=-1$$

Solution: dP would be exact differential if

$$\frac{\partial^2 P}{\partial V\,\partial T}=\frac{\partial^2 P}{\partial T\,\partial V}$$

From the equation of state we have

$$P=\frac{RT}{V-b}$$

Hence,
$$\left(\frac{\partial P}{\partial T}\right)_V=\frac{R}{V-b};\ \frac{\partial^2 P}{\partial V\,\partial T}=-\frac{R}{(V-b)^2}$$

and
$$\left(\frac{\partial P}{\partial V}\right)_T=\frac{RT}{(V-b)^2};\ \frac{\partial^2 P}{\partial T\partial V}=-\frac{R}{(V-b)^2}$$

From (i) and (ii) we see that

$$\frac{\partial^2 P}{\partial V\,\partial T}=\frac{\partial^2 P}{\partial T\,\partial V}$$

therefore, dP is an exact differential.

The differential $\left(\frac{\partial V}{\partial T}\right)_P$ from the above equation of state is

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{R}{P}$$

and
$$\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial T}{\partial V}\right)_P=-\frac{(V-b)^2}{RT}\frac{R}{(V-b)}\frac{P}{R}$$

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

$$=-\frac{1}{P}P\left(\because\frac{V-b}{RT}=\frac{1}{P}\right)$$

$$=-1$$

The change in P will depend only on the initial and the final states of the system. Hence P is a state function.

Problem 5.2: The coefficient of thermal expansion, α is defined as

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P$$

while the compressibility coefficient k is defined as

$$k = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T$$

Evaluate them for an ideal gas and prove that

$$\left(\frac{dP}{dT}\right)_V = \frac{\alpha}{k}$$

Solution: For a mole of an ideal gas $PV = RT$

Differentiating V with respect to T at constant P yields

$$P\left(\frac{dV}{dT}\right)_P = R$$

$$\left(\frac{dV}{dT}\right)_P = \frac{R}{P}$$

$$\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P = \frac{1}{V}\frac{R}{P} = \frac{R}{RT} = \frac{1}{T}$$

Differentiation of V with respect to P at constant T gives

$$\left(\frac{dV}{dP}\right)_T = -\frac{RT}{P^2}$$

and

$$k = -\frac{1}{V}\left(\frac{dV}{dP}\right)_T = \frac{RT}{VP^2} = \frac{RT}{RT \cdot P} = \frac{1}{P}$$

From the cyclic rule, we have

$$\left(\frac{dV}{dT}\right)_P\left(\frac{dT}{dP}\right)_V\left(\frac{dP}{dV}\right)_T = -1$$

$$\alpha V\left(\frac{dT}{dP}\right)_V \frac{1}{-kV} = -1$$

$$\frac{\alpha}{k}\left(\frac{dT}{dP}\right)_V = 1$$

$$\left(\frac{dP}{dT}\right)_V = \frac{\alpha}{k}$$

Problem 5.3: Show that $\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial k}{\partial T}\right)_P = 0$

Solution: Since $\alpha = \frac{1}{V}\left(\frac{dV}{dT}\right)_P$

$$\left(\frac{\partial \alpha}{\partial P}\right)_T = \frac{\partial}{\partial P}\left(\frac{1}{V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \frac{1}{V}\frac{\partial^2 V}{\partial P\,\partial T}$$

$$= -\frac{1}{V^2}\left(\frac{\partial V}{\partial P}\right)_T\left(\frac{\partial V}{\partial T}\right)_P + \frac{1}{V}\frac{\partial^2 V}{\partial P\,\partial T}$$

and $k = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$

$$\left(\frac{\partial k}{\partial T}\right)_P = \frac{\partial}{\partial T}\left(-\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V}\frac{\partial^2 V}{\partial T\,\partial P}$$

$$= \frac{1}{V^2}\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial V}{\partial P}\right)_T - \frac{1}{V}\frac{\partial^2 V}{\partial T\,\partial P}$$

Adding (*i*) and (*ii*) yields

$$\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial k}{\partial T}\right)_P = \frac{1}{V}\left(\frac{\partial^2 V}{\partial P\,\partial T} - \frac{\partial^2 V}{\partial T\,\partial P}\right) = 0$$

5.4 WORK, HEAT AND ENERGY

The concepts of work and heat are of fundamental importance in thermodynamics. Work and algebraic quantities and can be positive or negative. They appear only during a change in the the system and appear only at the boundary of the system. They are manifestations of energy

Work

If an object is displaced through a distance dx against a force $F(x)$ then the amount of work to be done is defined as

$$W = -F(x)\,dx$$

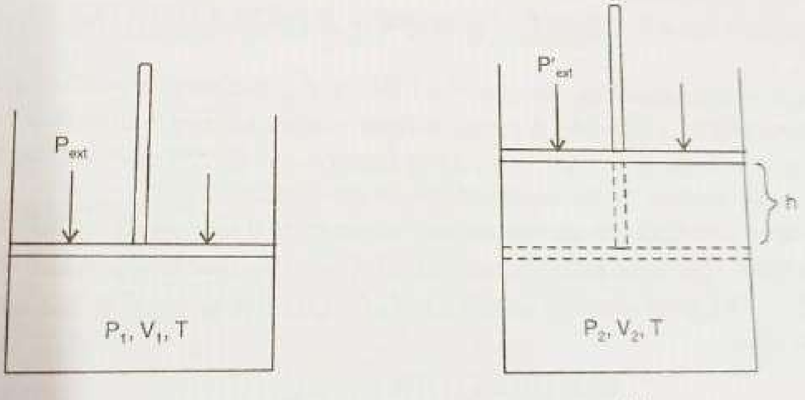
In SI system of units, work is expressed in Joule or kilojoule; 1 J = 1 Nm. When work is done on the system W is positive and when work is done by the system W is negative. There are many types of work and all of them could be expressed as the product of two factors; (*i*) an intensity factor, and (*ii*) a capacity factor. Some of these types are:

Gravitational work: Gravitational work is said to be done when a body is raised through a certain height against the gravitational field. If a body of mass *m* is raised through a height *h* against the gravitational field, the magnitude of the gravitational work is *mg*. In this expression mg, the force required to overcome the gravity is the intensity factor and height *h* is the capacity factor.

Electrical work: Electric work is said to be done when a charged body is moved from one potential region into another. If the charge is expressed in coulombs and the potential difference in volts, then the electrical work is given by QV. Here potential difference (V) is the intensity factor and the quantity of electricity (Q) is the capacity factor.

Mechanical work: Work associated with the change in volume of a system against an external pressure is referred to as the mechanical or pressure-volume work. The magnitude of this work in an isothermal expansion of a gas can be obtained as follows. Consider a certain quantity of a gas enclosed in a cylinder fitted with a weightless and frictionless piston. The gas is held in position by a constant external pressure, P_{ext}. The force acting on the piston is given by the product of the external pressure and the cross-sectional area of the piston ($P_{ext} \cdot A$), where A is its area of cross section. The cylinder is immersed in a thermostat to ensure constant temperature during the expansion of the gas. The initial state of the system is described by P_1, V_1 and T [Fig. 5.2(*a*)]. By lowering the external pressure, the gas tends to expand. During expansion, the piston moves to a new position where the variables of the system are P_2, V_2 and T. This is shown in Fig. 5.2 (*b*). Let the height upto which the piston has moved be h. The work done by the gas during expansion is given by

$$W = -(\text{Force} \times \text{distance})$$



(a) (b)

Fig. 5.2 Isothermal expansion of a gas (*a*) Initial state; (*b*) Final state

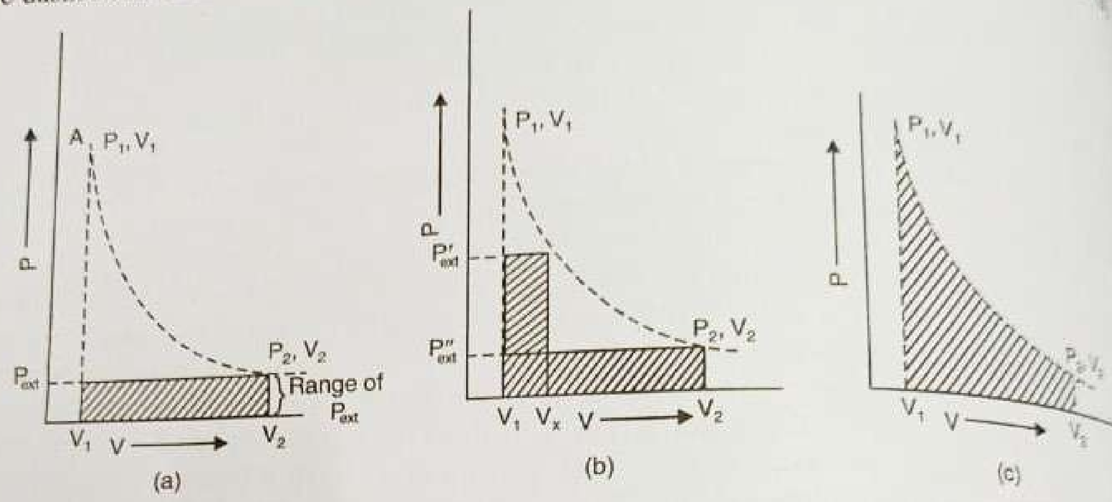
Since the work is being done by the system on the surroundings, it decreases the internal energy of the system and consequently, the work is given a negative sign. Similarly, if work is being done on the system, it increases the internal energy of the system, and, therefore, work is given a positive sign. The work of expansion is given as

$$W = -P_{ext}\,Ah \qquad \left(\because \text{Force} = \frac{P_{ext}}{A}\right.$$

But (Ah) is the change in volume, ΔV during the expansion and is equal to $(V_2 - V_1)$. Hence the work of expansion is

$$W = -P_{ext}\,\Delta V \qquad ...(5.8)$$

It may be mentioned that P_{ext} is not the pressure of the gas, it is the pressure that resists the expansion of the gas. The work done as given by Eq. (5.8) is indicated by the shaded area in Fig. 5.3 (a). The dashed curve A is the usual isotherm of the gas.



(a) (b) (c)

Fig. 5.3 Work done in (*a*) one-step expansion; (*b*) two-step expansion and (*c*) multi step expansion of an ideal gas

The magnitude of work depends on the value of external pressure that opposes expansion and can have any values in the range $0 \le P_{ext} \le P_2$. Consequently, W can have values ranging from zero to some upper limit.

The sign of W is determined by the sign of ΔV. Since P_{ext} is always a positive quantity. In expansion, ΔV is positive and W is negative. A negative value of work implies that work is being done by the system on the surroundings. In compression, ΔV is negative and therefore W will be positive meaning thereby that the work is done by the surroundings on the system.

The above expansion has been carried out in a single step. If the same expansion were carried out in two steps, first from V_1 to some intermediate volume V_x with an opposing pressure P'_{ext} and then from V_x to V_2 with P''_{ext}. The total work W in two steps of expansion is equal to the sum of the amount produced in each step.

$$\delta W = \delta W_1 + \delta W_2$$

or

$$-W = P'_{ext}(V_x - V_1) + P''_{ext}(V_2 - V_x) \qquad ...(5.9)$$

Fig. 5.3 (*b*) shows the graphical representation of this two-step expansion work and its magnitude is obviously more than the single-step expansion for the same change in the state of the system. If the expansion is carried out in infinite number of steps with a constant external pressure such that the volume increases by a very small amount dV, then the quantity of work for each step is given by

$$-\delta W = P_{ext}\,dV \qquad ...(5.10)$$

and the total work of expansion is

$$-W = \int_{V_1}^{V_2} P_{\text{ext}}\, dV \qquad \text{...(5.11)}$$

Work done in free expansion of the gas: If the external pressure is zero, *i.e.*, the gas expands in vacuum, no work is done by the system

$$-\delta W = P_{\text{ext}} dV = 0$$

Work Involved in Reversible Expansion of a Gas

As seen above, in a two-step expansion the magnitude of the work produced is more than that involved in a single-step expansion. If the expansion were carried out in an infinite number of steps such that the external pressure at each stage of the expansion is only infinitesimally less than the pressure of the gas, the magnitude of the work goes on increasing and attains a maximum value. This is given by integrating Eq. (5.10).

$$W_{\text{rev}} = -\int_{V_1}^{V_2} P_{\text{ext}}\, dV$$

For expansion of the gas, P_{ext} should be less than the pressure (P) of the gas *i.e.*, $P_{\text{ext}} = P - dP$, where dP is infinitesimally small. Therefore the magnitude of work involved is

$$W_{\text{rev}} = -\int_{V_1}^{V_2} (P - dP)\, dV$$

Since dP is exceedingly small and in the limit $P - dP \approx P$, hence

$$W_{\text{rev}} = -\int_{V_1}^{V_2} P\, dV$$

If the gas behaves ideally, then

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

and

$$-W_{\text{rev}} = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

Since the temperature is constant therefore integration of the above equation yields

$$-W_{\text{rev}} = nRT \ln \frac{V_2}{V_1} \qquad \text{...(5.12)}$$

$$= nRT \ln \frac{P_1}{P_2} \qquad \text{...(5.13)}$$

Figure 5.3 (*c*) gives the graphical representation of work in a reversible isothermal expansion. The work as given by Eq. (5.12) or (5.13) is obtained only under reversible conditions such that the system does not deviate from its equilibrium state. This is the maximum amount of work that can be obtained from the system. If the expansion is carried out rapidly the equilibrium of the system will be disturbed and the process will be irreversible. Consequently, the magnitude of work would be less. This can be seen from the following comparison in which an ideal gas expands reversibly and irreversibly from state P_1, V_1 to state P_2, V_2 under isothermal conditions

$$-W_{rev} = nRT \ln \frac{V_2}{V_1} = nRT \ln \frac{P_1}{P_2}$$

$$= nRT \ln \left[1 - \left(1 - \frac{P_1}{P_2}\right)\right]$$

Expanding $\ln \left[1 - \left(1 - \frac{P_1}{P_2}\right)\right]$ and neglecting higher terms we get

$$-W_{rev} = nRT\left(\frac{P_1}{P_2} - 1\right)$$

When the gas expands irreversibly at constant pressure P_2, we have

$$-W_{irr} = P_2 (V_2 - V_1)$$

$$= P_2\left(\frac{nRT}{P_2} - \frac{nRT}{P_1}\right)$$

$$= nRT\left(1 - \frac{P_2}{P_1}\right)$$

Therefore, the difference in the magnitude of W_{rev} and W_{irr} is

$$|W_{rev}| - |W_{irr}| = nRT\left[\frac{P_1}{P_2} - 1 - 1 + \frac{P_2}{P_1}\right]$$

$$= nRT\left[\frac{P_1^2 - 2P_1P_2 + P_2^2}{P_1P_2}\right]$$

$$= \frac{nRT}{P_1P_2}(P_1 - P_2)^2$$

Since $(P_1 - P_2)^2$ is always positive irrespective of whether P_1 is less than, equal to or greater than P_2, hence

$$|W_{rev}| - |W_{irr}| > 0$$

nal expansion. The
ch that the system
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irreversibly from

...(5.14)

...(5.16)

ter than

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or

$$|W_{rev}| > |W_{irr}|$$

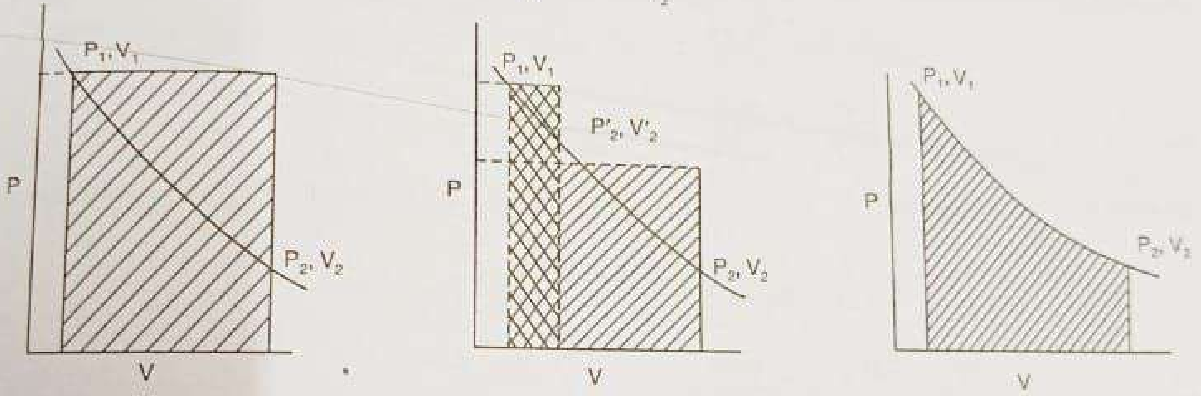
This shows that the magnitude of work in a reversible process is more than that in an irreversible process.

In compression, the external pressure should be larger than the pressure of the gas. If the compression of the gas is done from P_2, V_2 to P_1, V_1 in one step, then the minimum value of external pressure should be P_1 and the work done on the system would be given by

$$-W = P_{ext}(V_1 - V_2) = P_1(V_1 - V_2)$$

It is equal to the area of the shaded rectangle in Fig. 5.4 (*a*). If larger external pressure is used, the surroundings will have to do more work in bringing about the desired change. If the compression is done in two stages — from P_2, V_2 to some intermediate value P_2', V_2' and then to P_1, V_1, lesser amount of work will be done by the surroundings (Fig. 5.4 (*b*)). By carrying out compression in a large number of steps taking P_{ext} at each stage only, slightly greater than the pressure (P) of the gas, *i.e.*, $P_{ext} = P + dP$, then the work involved is given by

$$-W_{min} = \int_{V_2}^{V_1} P_{ext}\, dV = \int_{V_2}^{V_1} (P + dP)\, dV$$



(a) (b) (c)

Fig. 5.4 Work done in (*a*) one-step compression; (*b*) two-step compression and (*c*) multi-step compression of an ideal gas

Since dP is very small and can be neglected, therefore the work done on the ideal gas is given by

$$-W_{min} = nRT \ln \frac{V_1}{V_2} \qquad ...(5.17)$$

This is the limiting minimum value of the work which the surroundings will perform on the system during compression and is obviously the area under the curve (Fig. 5.4 (*c*)). The magnitudes of the reversible work of expansion and compression as may be seen from Eqs. (5.13) and (5.17) are equal.

Nature of work: W is not a thermodynamic quantity. Its value as seen from Eqs. (5.8), (5.9) and (5.12) for the same change in state depends on the path followed for the isothermal transformation of the system. Mathematically, one can prove that W is not an exact differential. If W is an exact differential for mechanical work, one may write

$$-dW = PdV$$

Figure 5.3 (*c*) gives the graphical representation of work in a reversible isothermal expansi work as given by Eq. (5.12) or (5.13) is obtained only under reversible conditions such that the sy does not deviate from its equilibrium state. This is the maximum amount of work that can be de from the system. If the expansion is carried out rapidly the equilibrium of the system will be dis and the process will be irreversible. Consequently, the magnitude of work would be less. This ca seen from the following comparison in which an ideal gas expands reversibly and irreversibly f state P_1, V_1 to state P_2, V_2 under isothermal conditions

$$-W_{\text{rev}} = nRT\ln\frac{V_2}{V_1} = nRT\ln\frac{P_1}{P_2}$$

$$= nRT\ln\left[1-\left(1-\frac{P_1}{P_2}\right)\right]$$

Expanding $\ln\left[1-\left(1-\frac{P_1}{P_2}\right)\right]$ and neglecting higher terms we get

$$-W_{\text{rev}} = nRT\left(\frac{P_1}{P_2}-1\right)$$ ...(5.1

When the gas expands irreversibly at constant pressure P_2, we have

$$-W_{\text{irr}} = P_2\left(V_2 - V_1\right)$$

$$= P_2\left(\frac{nRT}{P_2}-\frac{nRT}{P_1}\right)$$

$$= nRT\left(1-\frac{P_2}{P_1}\right)$$

Therefore, the difference in the magnitude of W_{rev} and W_{irr} is

$$|W_{\text{rev}}| - |W_{\text{irr}}| = nRT\left[\frac{P_1}{P_2}-1-1+\frac{P_2}{P_1}\right]$$

$$= nRT\left[\frac{P_1^2 - 2P_1P_2 + P_2^2}{P_1P_2}\right]$$

$$= \frac{nRT}{P_1P_2}\left(P_1 - P_2\right)^2 \qquad \text{...(5.16)}$$

Since $(P_1 - P_2)^2$ is always positive irrespective of whether P_1 is less than, equal to or greater than P_2, hence

$$|W_{\text{rev}}| - |W_{\text{irr}}| > 0$$

$$\oint \delta W = W_{\text{cyc}} = -\int_{V_1}^{V_2} PdV + \int_{V_2}^{V_1} PdV = 0$$

Hence, in an isothermal reversible process

$$\oint \delta W = 0$$

(ii) **Isothermal irreversible transformation:** The expansion of the gas is carried out from V_1 to V_2 with $P_{\text{ext}} = P_2$. The gas is then compressed from V_2 to V_1 with $P_{\text{ext}} = P_1$. Both the steps are irreversible and the network (W'_{cyc}) is given as

$$\oint \delta W = W'_{\text{cyc}} = -P_2(V_2 - V_1) - P_1(V_1 - V_2)$$

$$= (P_1 - P_2)(V_2 - V_1)$$

Since $V_2 > V_1$ and $P_2 < P_1$, therefore, W'_{cyc} is positive indicating that work has been done on the system. In other words, the surroundings have to do more work in bringing the system back to its original state than the work done by the system during expansion. From this one can state that W is not a state function or δW is an inexact differential.

If the system contains n moles of a real gas obeying van der Waals equation

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

then the work ($-W_{\text{vd}}$) in isothermal reversible expansion is given by

$$-W_{\text{vd}} = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \left(\frac{nRT}{V - nb} - \frac{an^2}{V^2}\right) dV$$

$$= \left[nRT \ln(V - nb) + \frac{an^2}{V}\right]_{V_1}^{V_2}$$

$$= 2.303\, nRT \log \frac{V_2 - nb}{V_1 - nb} + an^2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \qquad \text{...(5.18)}$$

The difference in the magnitude of work of expansion for an ideal and a van der Waals gas is given by

$$|W_{\text{id}}| - |W_{\text{vd}}| = nRT \ln \frac{V_2}{V_1} - nRT \ln \frac{V_2 - nb}{V_1 - nb} + an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

If $nb << V$, so that $V - nb \simeq V$, then

$$|W_{\text{id}}| - |W_{\text{vd}}| = an^2\left(\frac{1}{V_1} - \frac{1}{V_2}\right) = an^2\left(\frac{V_2 - V_1}{V_1 V_2}\right)$$

$$= \frac{an^2 \Delta V}{V_1 V_2} = \text{a positive quantity}$$

The magnitude of reversible work of expansion for an ideal gas is always greater than that for a van der Waals gas as work has to be done in overcoming the attractive forces between the molecules of a van der Waals gas.

Energy

Energy is defined as *the capacity to do work*. Every system containing some quantity of matter possesses a store of energy. It may occur in various forms such as kinetic energy due to the motion of the body; potential energy by virtue of its position in a force field; thermal energy due to the temperature of the body; chemical energy due to constitution of the compounds; nuclear energy; mechanical energy; electrical energy, etc.

The energy possessed by a system due to translational, vibrational and rotational motions of the molecules along with the energy of the electrons, nuclei and molecular interactions is known as its *internal* or *intrinsic energy* or *energy content* of the system. The energy acquired by a system in a force field like electrical, magnetic, gravitational surface, etc., are termed as *external energies* and are usually not considered as part of the internal energy of the system. The energy content of a system is denoted by E and depends on the internal structure and the constitution of the material composing the system. It is independent of the previous history of the system. The magnitude of energy is determined by the state of the system and in turn by the variables of the system like pressure, volume and temperature. As these variables are related to one another by an equation of state, the energy of a system of fixed composition may be described in terms of any two of these state variables, *i.e.*,

$$E = f_1(P, T) = f_2(V, T) = f_3(P, V)$$

Energy is an extensive property, *i.e.*, its magnitude depends upon the quantity of material in the system. In SI system, it is expressed in J or kJ.

If in a transformation the system changes from state A to some other state B, the energy change ΔE $= (E_B - E_A)$ is determined by the values of variables in the two states. The change in the state of the system can be brought about by a number of paths but the change in E is always the same, viz., $E_B - E_A$) is determined by the values of variables in the two states. The change in the state of the system can be brought about by a number of paths but the change in E is always the same, viz., $E_B - E_A$ and is independent of the paths by which the transformation is carried out. Energy is, therefore, a state function. In a cyclic process, the initial state of the system is restored and the energy change would be zero. These facts can be stated mathematically as

(*i*) energy is a state function;

(*ii*) dE is an exact differential;

(*iii*) $\oint dE = 0$; and

(*iv*) Euler's theorem of exactness applied to dE yields

$$\frac{\partial^2 E}{\partial V \, \partial T} = \frac{\partial^2 E}{\partial T \, \partial V}$$