

CLASSICAL THERMODYNAMICS

3.1 INTRODUCTION

Thermodynamics is the branch of science which deals with study of conversion of heat energy into useful work and vice versa. The inter-conversion of various forms of energy has been discussed in this chapter in the light of laws of thermodynamics. Before going to discuss mathematical formulation of these laws, we should describe some fundamental aspects of thermodynamics. The understanding of system, surrounding and boundary separating system from surrounding is very important for a person who wants to know about thermodynamics.

System is a part of universe on which we focus our attention for a particular purpose. For example, a gas present in a container is a system which has some particular properties. Everything outside system is called surrounding. System and surrounding as a whole is known as universe. System is a part of universe. The imaginary or real layer separating system from surrounding is called boundary. The system can be classified into three types. The open system can exchange energy and matter from surrounding. The closed system can exchange energy with surrounding but cannot exchange matter with surrounding. The isolated system cannot exchange energy and matter, both with surrounding. A system has both intensive and extensive properties. The properties which depend upon quantity of matter are called extensive properties. Volume and mass are examples of extensive properties. The properties of system which are independent of quantity of matter are called intensive properties. The ratio of two extensive properties is an intensive property. For example, the ratio of volume to mass of the system is called density which is an intensive property. Refractive index of the system is an intensive property.

3.2 STATE OF SYSTEM AND THERMODYNAMIC VARIABLES

A system has a particular state which is described in term of different variables. At a particular state, system has particular and defined values of these variables. For example, we have an ideal gas in a closed vessel. The state of this system is described by amount of gas, temperature and volume of a gas. The concept of state of a system and thermodynamic variables can be explained in a following diagram (Fig. 3.1).

We have n moles of an ideal gas in a container. The temperature of the gas is T_1 , pressure is P_1 and volume is V_1 . When we heat the system by some means, system moves from one state to another state, as shown in Fig. 3.1. The change in state of a system by some means is called a thermodynamic process. P , V and T in the above

system are called state variables or state functions. State functions are those thermodynamic variables which are independent of path and depend only on initial and final state of the system. Internal energy, enthalpy and entropy are some examples of state functions.

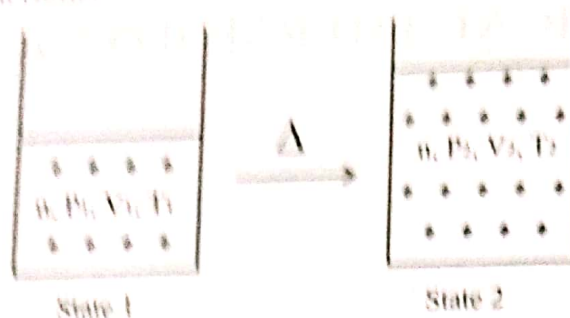


Fig. 3.1 Change in state of system and thermodynamic variables

3.3 CONCEPT OF EQUILIBRIUM AND ZEROth LAW OF THERMODYNAMICS

The variables which specify the state of a system may or may not change with passage of time. When value of state functions does not change with time, then system is at equilibrium. For example, when two bodies at two different temperatures are brought together then the temperature of hot body decreases with passage of time and that of cold body increases with passage of time until the temperature of both objects becomes equal. Both these bodies are said to be in thermal equilibrium.

When two objects X and Y are in thermal equilibrium, if a third body Z is in equilibrium with object X, then Y and Z are also in thermal equilibrium. This is called zeroth law of thermodynamics which is used to measure the temperature of a body.

3.4 FIRST LAW OF THERMODYNAMICS (CONCEPT OF HEAT, WORK AND INTERNAL ENERGY)

First law of thermodynamics is in fact law of conservation of energy. According to this law, energy cannot be created or destroyed although it can be converted from one form into another form. This is the qualitative aspect of first law of thermodynamic, but here we are also interested in mathematical formulation of this law. Because mathematical formulation this law can be used to measure change in internal energy of the system. For example, we have an ideal gas in a container which has internal energy E_1 at state 1. When heat Q is added into the system. The system gets a new state which is state 2. At state 2, system has internal energy E_2 . E_1 and E_2 are not measurable quantities but the change in internal energy $\Delta E = E_2 - E_1$ will be equal to heat supplied to the system at constant volume. Hence

$$\Delta E = Q \quad (3.1)$$

Equation (3.1) holds for the case when no work has done on the system or by the system. The internal energy of the system can be increased by doing work on the system. In such case increase in internal energy of the system will be equal to work done on the system i.e.

$$\Delta E = W \quad (3.2)$$

Equation (3.2) is applicable when no heat is added into the system.

The internal energy of a system can be increased by doing work on the system and adding heat into the system together. In this case increase in internal energy of the system will be equal to sum of work done on the system and heat added to the system as given below

$$\Delta E = Q + W \quad (3.3)$$

Equation (3.3) is mathematical form of first law of thermodynamics. According to International Union of Pure and Applied Chemistry (IUPAC), work done on the system and heat added into the system are taken as positive because both increase the internal energy of the system. Equation (3.3) in differential form can be written as

$$dE = dQ + dW \quad (3.4)$$

In the above equation dE is exact differential while dQ and dW are inexact differential. The quantity which is a state function has exact differential and can be written as

$$\int_1^2 dx = x_2 - x_1 = \Delta x$$

Therefore dE can be written as

$$\int_1^2 dE = E_2 - E_1 = \Delta E$$

While the quantity y which is not a state function has inexact differential and can be written as

$$\int_1^2 dy \neq y_2 - y_1$$

The quantity E in equation (3.3) is independent of path and depends upon initial and final state of the system but Q and W are path dependent quantities.

3.5 PRESSURE-VOLUME WORK

Suppose our system is an ideal gas enclosed in a container having moveable frictionless piston of cross-sectional area equal to A . The piston moves upward under pressure exerted by the gas due to its expansion. An equal but opposite opposing force acts on the piston which is equal to PA as shown in Fig. 3.2. The force F is opposite to displacement dx , therefore work done can be written as

$$W = \int \vec{F} \cdot d\vec{x}$$

$$W = \int F dx \cos 180^\circ$$

$$W = - \int F dx$$

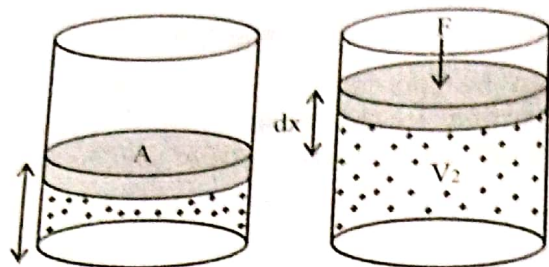


Fig. 3.2 Pressure-volume work

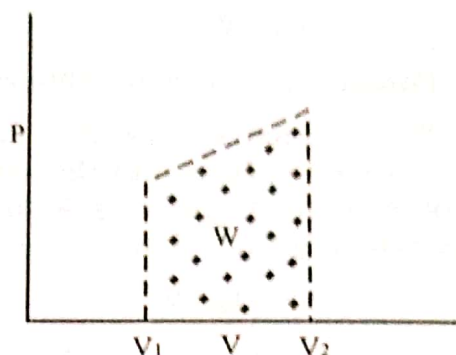


Fig. 3.3 PV diagram of work done

Force per unit area is pressure. So, $P = F/A$ and $PA = F$. By putting the value of F in the above equation, we get

$$W = - \int P A dx$$

Where, $A dx$ is equal to change in volume of gas. So

$$W = - \int P dV$$

When system moves from initial volume V_1 to final volume V_2 , then work in the form of definite integral can be written as

$$W = - \int_{V_1}^{V_2} P dV \quad (3.5)$$

So work is equal to area under a curve of PV diagram as shown in Fig. 3.3.

Mathematical expression (3.5) is very important in thermodynamics. When system does work on surroundings then volume of system increases and dV becomes positive. Therefore work will be negative. But when work is done on the system then dV will be negative and work will be a positive quantity as given in expression.

Equation (3.5) can be used to prove that work is not a state function as given in example 3.1.

Example 3.1

Using Fig. 3.4 prove that work done depends upon the path and it is not a state function.

Solution

There are two paths for a system to move it from state a to state d. One is abd path and other is acd path as shown in Fig. 3.4.

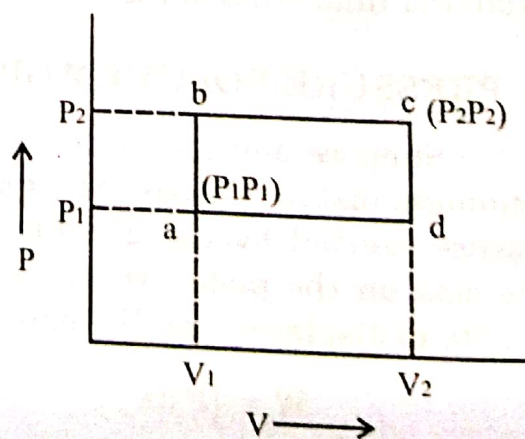


Fig. 3.4 PV diagram of work done

Work done along abd path

$$W_{abd} = W_{ab} + W_{bd}$$

$$W_{abd} = 0 - \int P dV$$

$$W_{abd} = 0 - \int_{V_1}^{V_2} P_2 dV$$

$$W_{abd} = -P_2 \int_{V_1}^{V_2} dV$$

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

Work done along acd path

$$W_{acd} = W_{ac} + W_{cd}$$

$$W_{acd} = - \int P dV + 0$$

$$W_{acd} = - \int_{V_1}^{V_2} P_1 dV$$

$$W_{acd} = -P_1 \int_{V_1}^{V_2} dV$$

$$W_{acd} = -P_1 (V_2 - V_1)$$

Since, $W_{abd} \neq W_{acd}$, so work done depends upon path. So it is not a state function.

3.6 WORK DONE FOR AN IDEAL GAS IN DIFFERENT PROCESSES

Various mathematical relations can be derived for work done by the gas or work done on the gas using ideal gas as a system under going various processes. A thermodynamic process may be isochoric, isobaric, isothermal and adiabatic. Equation (3.5) can be used to derive a mathematical expression for each thermodynamic process as discussed below.

3.6.1 Work Done in an Isochoric Process

The thermodynamic process in which volume of the system remains constant during the process is called isochoric process. So change in volume will be zero and work done will be zero also, i.e.

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

Since dV is zero or $V_2 = V_1$, therefore

$$W = 0$$

3.6.2 Work Done in an Isobaric Process

The thermodynamic process in which pressure of the system remains constant during the process is called isobaric process. Work done during this process can be given as

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

Since P is constant, So

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

$$W = -P(V_2 - V_1)$$

3.6.3 Work Done in an Isothermal Process

That thermodynamic process in which temperature remains constant, when system moves from one state to another state is called isothermal process.

During isothermal process, product of pressure and volume for given mass of a gas always remains constant according to Boyle's law. The plot as a function of V is called isotherm and is shown in Fig. 3.5.

The work done during isothermal process can be calculated by using equation of state for an ideal gas system as

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

We know that

$$PV = nRT$$

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

By putting the value of P in above equation we get

$$W = - \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

Since nRT is a constant term. So

$$W = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

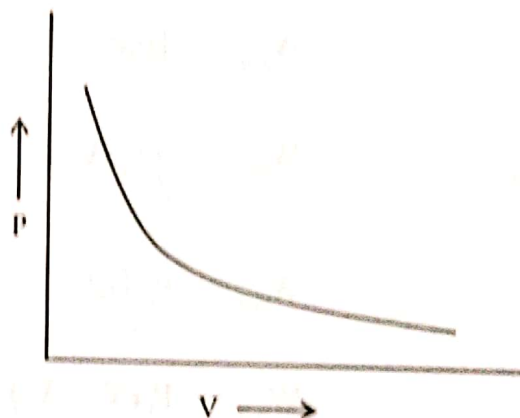


Fig. 3.5 Plot of P versus V

By integrating we get

$$W = -nRT \ln V \Big|_{V_1}^{V_2}$$

$$W = -nRT(\ln V_2 - \ln V_1)$$

$$W = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

When work is done on the gas then V_2 is smaller than V_1 and the ratio V_2/V_1 will be less than 1. The logarithm of a number which is less than 1 is negative number, so work will be positive and vice versa. The above equation can also be written as

$$W = -(2.303)nRT \ln \left(\frac{V_2}{V_1} \right)$$

P and V , both are variable in an isothermal process but the product PV is a constant quantity. Work can be measured from initial and final values of volume using above equation. The work done can also be calculated from initial and final values of pressure at constant temperature as

$$\frac{P_1}{P_2} = \frac{V_2}{V_1}$$

By putting the value of V_2/V_1 in equation (3.5), we get

$$W = -(2.303)nRT \ln \left(\frac{P_1}{P_2} \right)$$

3.6.4 Work Done in Adiabatic Process

Adiabatic process is that thermodynamic process in which no heat is added into the system and no heat is removed from the system. The system is totally thermodynamically isolated. We have an ideal gas in a cylinder having insulating

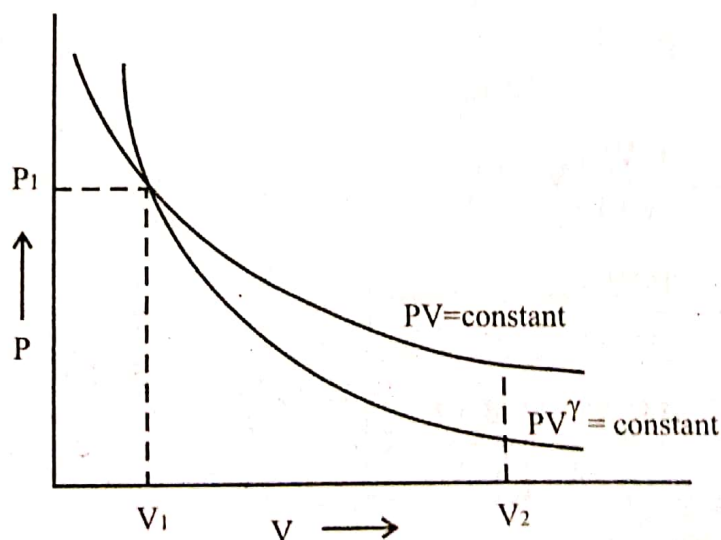


Fig. 3.6 PV diagram for isothermal and adiabatic processes

wall, base and piston. Work is done on the system or by the system during which temperature changes. Another important property of adiabatic process is that P and V are variables but PV^γ is constant. γ is the ratio of specific heat at constant pressure to the specific heat at constant volume for an ideal gas. The value of γ varies from 1.1 to 1.8. Since γ is greater than 1, so PV diagram for $PV^\gamma = \text{constant}$ in an adiabatic process is steeper than $PV = \text{constant}$ curve in an isothermal process as shown in Fig. 3.6.

The work done during adiabatic process can be written as

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

Since PV^γ is constant. So

$$P_1 V_1^\gamma = \text{constant}$$

$$P_1 V_1^\gamma = P V^\gamma$$

$$P = \frac{P_1 V_1^\gamma}{V^\gamma}$$

By putting mathematical value of P in pressure-volume work equation, we get

$$W = - \int_{V_1}^{V_2} \frac{P_1 V_1^\gamma}{V^\gamma} dV$$

Since PV^γ is a constant, so

$$W = - \int_{V_1}^{V_2} \frac{P_1 V_1^\gamma}{V^\gamma} dV$$

$$W = -P_1 V_1^\gamma \int_{V_1}^{V_2} \frac{1}{V^\gamma} dV$$

$$W = -P_1 V_1^\gamma \int_{V_1}^{V_2} V^{-\gamma} dV$$

$$W = -P_1 V_1^\gamma \left[\frac{V^{-\gamma+1}}{-\gamma+1} \right]_{V_1}^{V_2}$$

$$W = -\frac{P_1 V_1^\gamma}{-\gamma+1} \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right]$$

$$W = -\frac{P_1 V_1^\gamma}{-\gamma+1} \left[V_2^{-\gamma+1} - V_1^{-\gamma+1} \right]$$

$$W = -\frac{P_1 V_1^\gamma V_1^{-\gamma+1}}{-\gamma+1} \left[\frac{V_2^{-\gamma+1}}{V_1^{-\gamma+1}} - 1 \right]$$

$$W = -\frac{P_1 V_1^{\gamma-1}}{-\gamma+1} \left[\left(\frac{V_2}{V_1} \right)^{-\gamma+1} - 1 \right]$$

$$W = -\frac{P_1 V_1}{-\gamma+1} \left[\left(\frac{V_2}{V_1} \right)^{-\gamma+1} - 1 \right]$$

$$W = \frac{P_1 V_1}{\gamma-1} \left[\left(\frac{V_2}{V_1} \right)^{\gamma-1} - 1 \right]$$

On expansion of gas, $V_2 > V_1$ and $(V_1/V_2)^{\gamma-1} < 1$. So work will be negative.

$$\frac{P_1}{P_2} = \frac{V_2^\gamma}{V_1^\gamma}$$

$$\frac{P_2}{P_1} = \frac{V_1^\gamma}{V_2^\gamma}$$

$$W = \frac{1}{\gamma-1} \left[\left(\frac{P_1 V_1 V_1^{\gamma-1}}{V_2^{\gamma-1}} \right) - P_1 V_1 \right]$$

$$W = \frac{1}{\gamma-1} \left[\left(\frac{P_1 V_1^\gamma}{V_2^{\gamma-1}} \right) - P_1 V_1 \right]$$

$$W = \frac{1}{\gamma-1} \left[\left(\frac{P_1 V_1^\gamma}{V_2^\gamma V_2^{-1}} \right) - P_1 V_1 \right]$$

$$W = \frac{1}{\gamma-1} [P_2 V_2 - P_1 V_1] \quad (3.6)$$

Example 3.2

PV diagram for expansion of a gas present in a container is shown in a Fig. 3.7. This system moves from state 1 to a state 2 by two different paths ac and abc. Path ac represents an isothermal reversible process. Show that work done along ac is greater than work done along path abc.

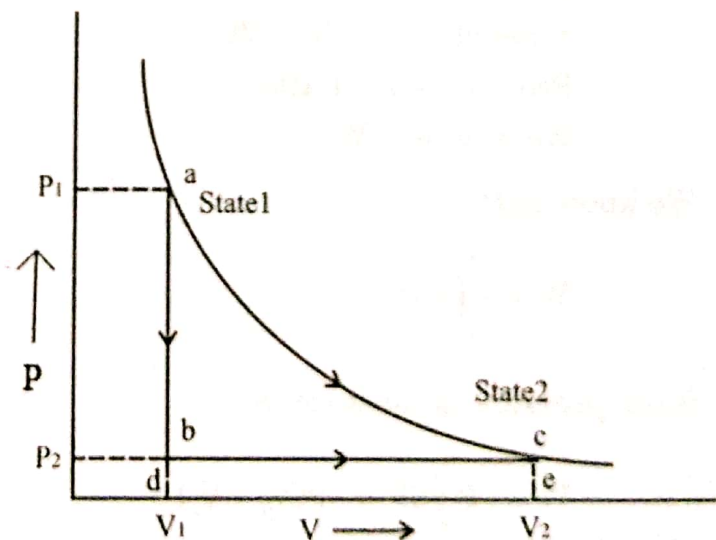


Fig. 3.7 PV diagram for expansion of gas from state 1 to 2 by different paths

Solution

Work done along ac

$$W_{ac} = - \int_{V_1}^{V_2} P dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

Work done along abc

$$W_{abc} = W_{ab} + W_{bc}$$

Since volume change is zero along ab. So $dV=0$

$$W_{abc} = 0 - \int_{V_1}^{V_2} P_2 dV$$

Since P_2 is constant along b to c. So

$$W_{abc} = - \int_{V_1}^{V_2} P_2 dV$$

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

Note: Area under curve ac is sum of abc and bcde while area under curve abc is only equal to rectangle bcde. Hence work done along ac is greater than work done along abc. This idea is the basis of examples 3.3 and 3.4.

Example 3.3

One mole of nitrogen is expanded isothermally from 20 to 60 liters against a constant pressure of 1 atm at 20 °C. Calculate the work done by the gas.

Solution

Initial volume = $V_1 = 20$ L

Final volume = $V_2 = 60$ L

Pressure = $P = 1$ atm

Work done = $W = ?$

We know that

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

Since pressure is constant. So

$$W = -P \int_{V_1}^{V_2} dV = -P(V_2 - V_1)$$

$$W = -1(60 - 20) = -40 \text{ atm L} = 4053 \text{ J}$$

Note: The value of work is negative because work is done by the system.

Example 3.4

One mole of a gas is expanded from 20 to 60 L isothermally and reversibly at 20 °C. Calculate work done by the gas.

Solution

$$\text{Initial volume} = V_1 = 20 \text{ L}$$

$$\text{Final volume} = V_2 = 60 \text{ L}$$

$$\text{No. of mole} = n = 1 \text{ mol}$$

$$\text{Temperature} = T = 20 \text{ }^\circ\text{C}$$

$$\text{Work done} = W = ?$$

For an isothermal and reversible expansion of a gas, we have

$$W = - \int_{V_1}^{V_2} P dV = -nRT \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$W = -nRT \ln \left(\frac{V_2}{V_1} \right)$$

$$W = -(1)(8.314)(293) \ln \left(\frac{60}{20} \right)$$

$$W = 2.676 \times 10^3 \text{ J}$$

3.6.4.1 Work Done in Adiabatic Process in Terms of Temperature

We know that in adiabatic process the value of PV^γ is constant but pressure, volume and temperature are variables. In the previous section, we have expressed work done in adiabatic process in terms of pressure and volume in equation (3.6). Work done in such process can also be expressed in terms of temperature. We can write for adiabatic process

$$(PV^\gamma) = \text{constant}$$

Taking differential on both sides, we get

$$d(PV^\gamma) = 0$$

$$Pd(V^\gamma) + V^\gamma d(P) = 0$$

$$P\gamma V^{\gamma-1} dV + V^\gamma dP = 0$$

$$\gamma PV^\gamma V^{-1} dV + V^\gamma dP = 0$$

$$V^\gamma (\gamma PV^{-1} dV + dP) = 0$$

$$(\gamma PV^{-1} dV + dP) = 0$$

Multiplying by V on both sides, we get

$$(\gamma PV + VdP) = 0$$

$$\gamma PV = -VdP \quad (3.7)$$

Equation of state for ideal gas system is

$$PV = nRT$$

On differentiation we get

$$PdV + VdP = nRdT \quad (3.8)$$

By putting the value of VdP from equation (3.7) into (3.8), we get

$$PdV - \gamma PdV = nRdT$$

Taking PdV common from left hand side of above equation

$$(1 - \gamma)PdV = nRdT$$

$$-\int_{V_1}^{V_2} PdV = -\frac{nR}{1 - \gamma} \int_{T_1}^{T_2} dT$$

$$W = -\frac{nR}{1 - \gamma} (T_2 - T_1)$$

$$W = \frac{nR}{\gamma - 1} (T_2 - T_1)$$

Where, W is work done in adiabatic process when system moves from state 1 to state 2 adiabatically. n is number of moles of gas present in a container, R is gas constant while T_1 and T_2 are temperatures of state 1 and 2 respectively, γ is ratio of C_p to C_v for ideal gases.

It is clear from final equation that work done in an adiabatic process depends upon temperature difference. When work is done on the system then temperature of the system increases such that $T_2 > T_1$ then work done will be positive because value of γ is greater than 1. When work is done by the system on surroundings such that $T_2 < T_1$ then work done will be negative.

3.7 APPLICATIONS OF FIRST LAW OF THERMODYNAMICS

3.7.1 Molar Heat Capacities of Ideal Gases

The heat absorbed by a system of ideal gas is directly proportional to increases in temperature of the system and number of gas molecules present in container. Mathematically it can be written as

$$Q \propto \Delta T$$

$$Q \propto n$$

$$Q \propto n \Delta T$$

$$Q = nC\Delta T \quad (3.9)$$

In this relation Q is heat added to the system which increases the temperature and increase in temperature of n mole of ideal gas is ΔT . The proportionality constant c in this relation is called molar heat capacity and it can be defined as heat energy required to raise the temperature of 1 mole of a gas through 1 °C. Mathematically it can be written as

$$C = \frac{Q}{n\Delta T}$$

Units of C are $\text{J mole}^{-1} \text{K}^{-1}$.

The heat energy added into ideal gas system is used to increase the internal energy of the system at constant volume but heat energy added into the system at constant pressure is used to increase the internal energy of the system as well as this heat is used to work done by the system at constant pressure. So there are two values of specific heat for gas phase system.

- (i) Specific heat at constant volume (C_v)
- (ii) Specific heat at constant pressure (C_p)

First law of thermodynamic can be applied to derive an expression between C_p and C_v for an ideal gas system. First law of thermodynamics is

$$\Delta E = Q + W$$

At constant volume, pressure-volume work is zero.

$$\Delta E = Q_v \tag{3.10}$$

Where Q is heat supplied to the system at constant volume which is being used to raise the internal energy of the system. In other words increase in internal energy will be equal to heat supplied to the system in the form of heat energy.

From expression (3.9), we have

$$Q_v = nC_v\Delta T \tag{3.11}$$

By putting this value in equation (3.10), we get

$$\Delta E = nC_v\Delta T \tag{3.12}$$

Using equation (3.12), we can determine the increase in internal energy of the system by knowing the values of temperature at two states of system and specific heat at constant volume. First law of thermodynamics at constant pressure can be written as

$$\Delta E = Q_p + W$$

Since heat supplied to the system at constant pressure, Q_p is used to increase the internal energy and in doing work. This heat energy will be equal to $nC_p\Delta T$ and work done by the system will be $-P\Delta V$. So

$$\Delta E = nC_p\Delta T - P\Delta V$$

$$C_v = \left(\frac{dE}{dT} \right)_V \quad C_p = \left(\frac{dH}{dT} \right)_P$$

Since pressure is constant, so

$$\Delta E = nC_p\Delta T - \Delta(PV) \quad (3.13)$$

According to equation of state of ideal gas, we have

$$PV = nRT \quad (3.14)$$

By putting the values of PV from equation (3.14) into equation (3.13), we get

$$\Delta E = nC_p\Delta T - \Delta(nRT)$$

$$\Delta E = nC_p\Delta T - nR(\Delta T)$$

When increase in temperature in both cases (at constant volume and at constant pressure) is same then ΔE will be same, so

$$\Delta E_v = nC_p\Delta T - nR(\Delta T)$$

$$nC_v\Delta T = nC_p\Delta T - nR\Delta T$$

$$nC_v = nC_p - nR$$

$$R = C_p - C_v \quad (3.15)$$

Hence heat capacity of an ideal gas at constant pressure is greater than that heat capacity which is at constant volume because R is a positive number whose value is always greater than 1.

3.7.2 Relation between Pressure and Volume in Adiabatic Process

In adiabatic process, either system does work on cost of internal energy or surrounding does work on the system and internal energy of the system increases. Thus pressure, volume and temperature of system change as a result of this work done. First law of thermodynamics for such process is

$$dE = dQ + dW$$

$$dE = 0 - PdV$$

$$dE = -PdV \quad (3.16)$$

dE can be expressed in terms of C_v according to equation (3.12), so

$$dE = nC_v dT \quad (3.17)$$

By putting the value of dE from equation (3.17) into (3.16), we get

$$-PdV = nC_v dT \quad (3.18)$$

The temperature (dT) can be obtained from equation of state for ideal gases as

$$PV = nRT$$

$$T = \frac{PV}{nR}$$

Taking differential, we get

$$dT = \frac{1}{nR} [PdV + VdP] \quad (3.19)$$

By putting the value of dT from equation (3.19) into (3.18), we get

$$-PdV = \frac{nC_v}{nR} [PdV + VdP]$$

$$-PdV = \frac{C_v}{R} [PdV + VdP]$$

Multiplying by R/C_v on both sides, we get

$$-\left(\frac{R}{C_v}\right)PdV = [PdV + VdP]$$

$$PdV + VdP + \frac{R}{C_v}PdV = 0 \quad (3.20)$$

By putting the value of R from equation (3.15) into (3.20), we get

$$PdV + VdP + \frac{C_p - C_v}{C_v}PdV = 0$$

$$PdV + VdP + \left(\frac{C_p}{C_v} - 1\right)PdV = 0$$

$$PdV + VdP + (\gamma - 1)PdV = 0$$

$$PdV + VdP + \gamma PdV - PdV = 0$$

$$VdP + \gamma PdV = 0$$

Separating variables and integrating, we get

$$VdP = -\gamma PdV$$

$$\int_{P_1}^{P_2} \frac{1}{P} dP = -\gamma \int_{V_1}^{V_2} \frac{1}{V} dV$$

$$[\ln P]_{P_1}^{P_2} = -\gamma [\ln V]_{V_1}^{V_2}$$

$$\ln P_2 - \ln P_1 = -\gamma (\ln V_2 - \ln V_1)$$

$$\ln \frac{P_2}{P_1} = -\gamma \ln \frac{V_2}{V_1}$$

$$\ln \frac{P_2}{P_1} + \gamma \ln \frac{V_2}{V_1} = 0$$

$$\ln \left(\frac{P_2 \left(\frac{V_2}{V_1} \right)^\gamma}{P_1} \right) = 0$$

Taking antilog on both sides

$$\frac{P_2 \left(\frac{V_2}{V_1} \right)^\gamma}{P_1} = 1$$

$$P_2 V_2^\gamma = P_1 V_1^\gamma$$

Hence

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

This expression can be used to work done in adiabatic expansion.

3.7.3 Isochoric Process

In isochoric process, volume is constant, thus work done is zero and first law of thermodynamics for such process can be written as

$$dE = dQ_v$$

Hence heat supplied to the system is used to increase the internal energy of the system. The above equation can be written as

$$dE = nC_v dT$$

$$nC_v = \left(\frac{\partial E}{\partial T} \right)_v$$

$$C_v = \frac{1}{n} \left(\frac{\partial E}{\partial T} \right)_v$$

For one mole of gas, C_v is

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v$$

Hence C_v is the rate of change of internal energy with respect to temperature per mole of gas at constant volume.

3.7.4 Isobaric Process (Concept of Enthalpy)

First law of thermodynamics for an isobaric process, in which pressure is kept constant, can be written as

$$\Delta E = Q_p + W$$

$$\Delta E = Q_p - P\Delta V$$

$$Q_p = \Delta E + P\Delta V$$

$$Q_2 = (H_2 - H_1) + P(V_2 - V_1)$$

$$Q_2 = (H_2 - H_1) + P(V_2 - V_1)$$

$$Q_2 = H_2 + P(V_2) - (H_1 + P(V_1))$$

$H + PV$ is a new quantity called enthalpy of system and is denoted by H . It is also called total heat content of the system. It is also a state function because H , P and V are state functions. This physical quantity is very important in Chemistry. So above equation can be written as

$$Q_2 = \Delta H = H_2 - H_1 \quad (3.21)$$

Hence heat supplied to the system is equal to enthalpy change of the system. Q_2 in terms of enthalpy can be written as

$$nC_p \Delta T = \Delta H$$

$$nC_p = \left(\frac{\Delta H}{\Delta T} \right)_P$$

$$C_p = \frac{1}{n} \left(\frac{\Delta H}{\Delta T} \right)_P$$

For one mole of gas,

$$C_p = \left(\frac{\Delta H}{\Delta T} \right)_P$$

Hence specific heat at constant pressure is equal to rate of change of enthalpy of system with respect to temperature per mole of gas.

3.8 HEAT ENGINE

A device which converts heat energy into mechanical work is called heat engine. The heat engine which completely converts heat into mechanical work is called a perfect heat engine or an ideal heat engine. The heat engine which cannot do this is called real heat engine. A real heat engine takes heat energy from a hot body and converts a part of this heat into work and rejects remaining part to a cold body.

Construction of a real heat engine is shown in Fig. 3.8. A real heat engine consists of following parts.

- (i) A high temperature reservoir called source.
- (ii) A low temperature reservoir called sink.
- (iii) A working substance or system.

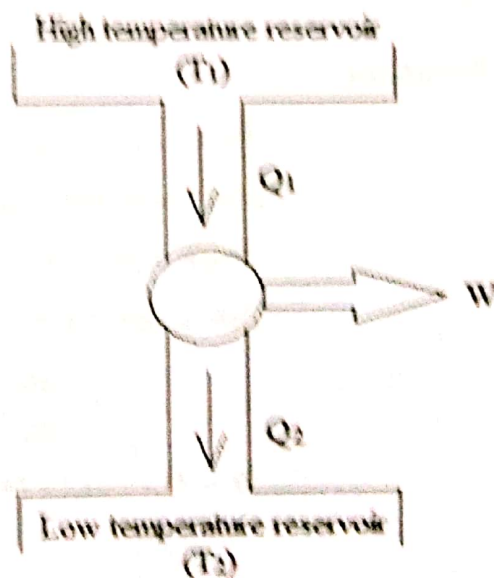


Fig. 3.8 Working of real heat engine

Working principle of heat engine is shown in Fig. 3.8. It takes heat Q_1 from a high temperature reservoir at temperature T_1 and converts a part of it into mechanical work W . Heat Q_2 is rejected by the system to low temperature reservoir at temperature T_2 . The efficiency of heat engine can be defined as the ratio of work done to input energy. Mathematically

$$\eta = \frac{W}{|Q_1|}$$

Since heat rejected by the system is taken as negative, therefore we write absolute values of heat energies to express efficiency of heat engine. Hence

$$\eta = \frac{|Q_1| - |Q_2|}{|Q_1|}$$

$$\eta = \frac{|Q_1|}{|Q_1|} - \frac{|Q_2|}{|Q_1|}$$

$$\eta = 1 - \frac{|Q_2|}{|Q_1|}$$

The percentage efficiency of heat engine can be written as

$$\% \text{age } \eta = \left(1 - \frac{|Q_2|}{|Q_1|} \right) \times 100$$

When $|Q_2|$ is equal to zero, then η will be 100 % which is not possible.

Example 3.5

A heat engine takes 60 kJ of heat energy from a hot body and rejects 40 kJ to cold body in a cycle. Calculate its efficiency and work done by the engine during the cycle.

Solution

$$\text{Heat input} = Q_1 = 60 \text{ kJ}$$

$$\text{Heat rejected} = Q_2 = 40 \text{ kJ}$$

$$\text{Work done} = W = ?$$

$$\text{Efficiency} = \eta = ?$$

$$\% \text{age } \eta = \left(1 - \frac{40}{60} \right) \times 100 = 33.33\%$$

$$W = |Q_1| - |Q_2| = 60 - 40 = 20 \text{ kJ}$$

3.9 CARNOT HEAT ENGINE

In 1824, Sadi Carnot proposed a heat engine free from all imperfections of actual engines. This heat engine has maximum possible efficiency but less than 100%. He claimed that no heat engine can beat my proposed heat engine.

3.9.1 Construction of Heat Engine

Carnot heat engine consists of a cylinder with perfect insulating walls, ideal constructing base, frictionless moveable piston and ideal gas as a working substance as shown in Fig. 3.9.

3.9.2 Working

The Carnot engine works in following four different thermodynamic processes in a cycle reversibly.

- (i) Isothermal expansion
- (ii) Adiabatic expansion
- (iii) Isothermal compression
- (iv) Adiabatic compression

The cycle is known as Carnot cycle. The above all processes are shown in PV diagram in Fig. 3.10.

(i) Isothermal Process

The cylinder is placed on a high temperature reservoir. System absorbs heat Q_1 from high temperature reservoir at temperature T_1 and gas works on surrounding causing expansion. The work done by the gas will be equal to heat absorbed by the system according to first law of thermodynamic as given below

$$\Delta E = Q_{11} + W_{AB}$$

Since change in temperature is zero, so $\Delta E=0$. Thus above equation will be

$$Q_{11} = -W_{AB}$$

The work done in isothermal reversible expansion is

$$W_{AB} = - \int_{v_A}^{v_B} PdV$$

$$\text{Hence, } |Q_1| = \int_{v_A}^{v_B} PdV$$

Since working substance is an ideal gas, so

$$PV = nRT_1$$

$$P = \frac{nRT_1}{V}$$

By putting value of P in above equation, we get

$$|Q_1| = \int_{V_A}^{V_B} \frac{nRT_1}{V} dV$$

$$|Q_1| = nRT_1 \int_{V_A}^{V_B} \frac{1}{V} dV$$

$$|Q_1| = nRT_1 [\ln V]_{V_A}^{V_B}$$

$$|Q_1| = nRT_1 \ln \left(\frac{V_B}{V_A} \right) \quad (3.22)$$

(ii) Adiabatic Expansion

The second ideal process is shown in Fig. 3.10 by curve BC is adiabatic expansion of gas. In this process, cylinder is placed on an insulating material. No heat is added to or removed from the system. Therefore Q is zero and system does work on surrounding on consumption of internal energy. We know that during this process PV^γ is constant. Hence

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

$$(PV) V^{\gamma-1} = \text{constant}$$

$$(nRT) V^{\gamma-1} = \text{constant}$$

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

Therefore for process BC, we can write as

$$T_1 V_B^{\gamma-1} = \text{constant}$$

And $T_1 V_C^{\gamma-1} = \text{constant}$

So, $T_1 V_B^{\gamma-1} = T_1 V_C^{\gamma-1} \quad (3.23)$

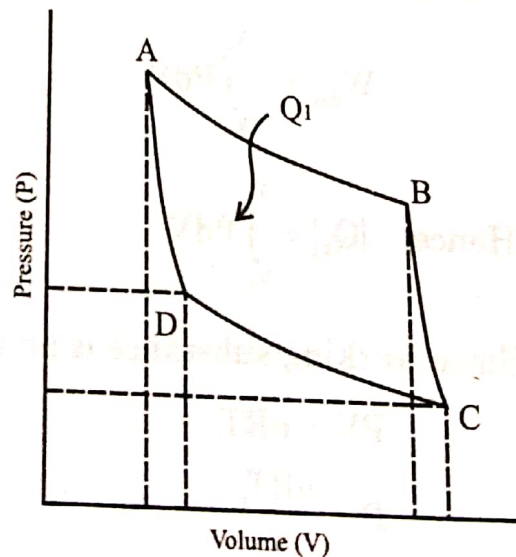
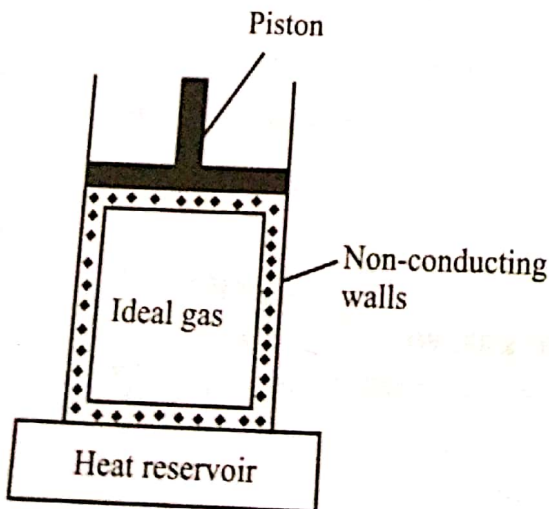


Fig. 3.9: Pictorial diagram of Carnot heat engine

Fig. 3.10: PV diagram of Carnot cycle

(iii) Isothermal Compression

The third process in a cycle shown by CD in PV diagram is isothermal compression. In this process heat Q_2 is rejected to cold body by the system and work is done on the system. Hence first law of thermodynamics is

$$\Delta E = Q_2 + W$$

$$0 = Q_2 + W_{CD}$$

$$Q_2 = -W_{CD}$$

But heat is rejected by the system, so it should be negative. Hence

$$Q_2 = nRT_2 \ln\left(\frac{V_C}{V_D}\right) \quad (3.24)$$

(iv) Adiabatic Compression

The fourth process shown by DA curve in PV diagram of Fig. 3.10 is an adiabatic compression. In this process no heat is added or removed from the system.

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

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

$$\text{So } T_2 V_A^{\gamma-1} = T_2 V_D^{\gamma-1} \quad (3.25)$$

From equation (3.22) and (3.24) we get

$$-Q_2 = -W_{CD}$$

$$Q_2 = W_{CD}$$

$$Q_2 = - \int_{V_C}^{V_D} PdV$$

$$Q_2 = -nRT_2 \int_{V_C}^{V_D} \frac{1}{V} dV$$

$$Q_2 = -nRT_2 [\ln V]_{V_C}^{V_D}$$

$$Q_2 = -nRT_2 \ln\left(\frac{V_D}{V_C}\right)$$

$$\frac{|Q_1|}{|Q_2|} = \frac{nRT_1 \ln\left(\frac{V_B}{V_A}\right)}{nRT_2 \ln\left(\frac{V_C}{V_A}\right)}$$

$$\frac{|Q_1|}{|Q_2|} = \frac{nRT_1 \ln\left(\frac{V_B}{V_A}\right)}{nRT_2 \ln\left(\frac{V_C}{V_A}\right)}$$

$$\frac{|Q_1|}{|Q_2|} = \frac{T_1 \ln\left(\frac{V_B}{V_A}\right)}{T_2 \ln\left(\frac{V_C}{V_A}\right)} \quad (3.26)$$

From equation (3.23) and (3.25), we get

$$\begin{aligned} \frac{T_1 V_B^{\gamma-1}}{T_2 V_A^{\gamma-1}} &= \frac{T_1 V_C^{\gamma-1}}{T_2 V_D^{\gamma-1}} \\ \left(\frac{V_B}{V_A}\right)^{\gamma-1} &= \left(\frac{V_C}{V_D}\right)^{\gamma-1} \\ \left(\frac{V_B}{V_A}\right) &= \left(\frac{V_C}{V_D}\right) \end{aligned}$$

By putting this value in equation (3.26), we get

$$\begin{aligned} \frac{|Q_1|}{|Q_2|} &= \frac{T_1 \ln\left(\frac{V_C}{V_D}\right)}{T_2 \ln\left(\frac{V_C}{V_A}\right)} \\ \frac{|Q_1|}{|Q_2|} &= \frac{T_1}{T_2} \\ \frac{|Q_2|}{|Q_1|} &= \frac{T_2}{T_1} \end{aligned}$$

Hence efficiency of Carnot heat engine is

$$\begin{aligned} \eta &= 1 - \frac{|Q_2|}{|Q_1|} \\ \eta &= 1 - \frac{T_2}{T_1} \end{aligned} \quad (3.27)$$

3.10 CARNOT THEOREM

The efficiency of heat engine is independent of nature of working substance. It depends upon temperature of hot body and cold body only. This theorem is called Carnot theorem as shown in equation (3.27).

According to equation (3.27), η depends on the ratio of T_2 to T_1 . The efficiency will be hundred percent when T_2 is equal to zero which is not possible. So Carnot heat engine has maximum efficiency but less than 100%.

Example 3.6

Calculate heat efficiency of Carnot heat engine working between high temperature reservoir at 150°C and low temperature reservoir at 60°C .

Solution

Temperature of hot reservoir = $T_1 = 150^\circ\text{C}$

Temperature of cold reservoir = $T_2 = 60^\circ\text{C}$

Efficiency = $\eta = ?$

$$\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100 = \left(1 - \frac{60}{150}\right) \times 100 = 60\%$$

3.11 CONCEPT OF ENTROPY

An important thermodynamic function called entropy was introduced by Clausius in 1850 on the basis of Carnot cycle. According to Carnot cycle, we have following relation

$$\frac{|Q_1|}{|Q_2|} = \frac{T_1}{T_2}$$

Where Q_1 is heat added into the system and Q_2 is heat removed from the system. So it is taken as negative. Hence above expression can be written as

$$-\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

$$-\frac{Q_1}{T_1} = \frac{Q_2}{T_2}$$

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

$$\sum \frac{Q}{T} = 0$$

In integral form, it can be written as

$$\oint \frac{dQ}{T} = 0$$

The new variable dQ/T is called entropy.

Entropy is also a state function and it is independent of path. Therefore entropy change of a cyclic process as given above is zero.

3.12 CALCULATION OF ENTROPY CHANGE IN AN IDEAL GAS SYSTEM

According to first law of thermodynamics, we know that

$$dE = dQ + dW$$

$$nC_v dT = -PdV + dQ$$

$$dQ = nC_v dT + PdV$$

Dividing by T on both sides, we get

$$\frac{dQ}{T} = \frac{PdV}{T} + \frac{nC_v dT}{T}$$

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

So $\frac{dQ}{T} = \frac{nRTdV}{VT} + \frac{nC_v dT}{T}$

$$\frac{dQ}{T} = \frac{nRdV}{V} + \frac{nC_v dT}{T}$$

Integrating the above equation within limits

$$\int_1^2 \frac{dQ}{T} = nR \int_{V_1}^{V_2} \frac{dV}{V} + nC_v \int_{T_1}^{T_2} \frac{dT}{T}$$

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) + nC_v \ln \left(\frac{T_2}{T_1} \right) \quad (3.28)$$

Since ΔS depends upon temperature and volume of initial and final states of system. So entropy is a state function. The above expression is for entropy change for an ideal gas with temperature and volume. This shows entropy change of an ideal gas system with change in temperature and volume.

3.13 ENTROPY CHANGE FOR AN ISOTHERMAL REVERSIBLE PROCESS

For an isothermal process, $T_1 = T_2$. So, above expression can be written as

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) + nC_v \ln \left(\frac{T}{T} \right)$$

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) + nC_v \ln \left(\frac{1}{1} \right)$$

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right)$$

$$\Delta S = 2.303 \times nR \log \left(\frac{V_2}{V_1} \right)$$

When $V_2 > V_1$, then ΔS will be positive and when $V_2 < V_1$ then ΔS will be negative.

In terms of pressure, above equation can be written as

$$\Delta S = 2.303 \times nR \log \left(\frac{P_2}{P_1} \right)$$

Because $P_1V_1 = P_2V_2$. The increase in entropy of an ideal system in an isothermal reversible expansion is equal to decrease in entropy of surroundings. Thus total change in entropy of universe is zero.

3.14 ENTROPY CHANGE IN AN IDEAL GAS FOR ISOCHORIC PROCESS

For isochoric process, $V_2 = V_1$, so above equation becomes

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) + nC_V \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = nR \ln \left(\frac{V}{V} \right) + nC_V \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = nR \ln \left(\frac{1}{1} \right) + nC_V \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = nC_V \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = 2.303 \times nC_V \log \left(\frac{T_2}{T_1} \right)$$

When $T_2 > T_1$, then ΔS is positive while ΔS is negative for $T_2 < T_1$.

3.15 ENTROPY CHANGE IN AN IDEAL GAS FOR ISOBARIC PROCESS

From equation (3.28), we have

$$\Delta S = nR \ln \left(\frac{V_2}{V_1} \right) + nC_V \ln \left(\frac{T_2}{T_1} \right)$$

For an ideal gas, we have

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$\frac{V_2}{V_1} = \frac{P_1T_2}{P_2T_1}$$

By putting value of V_2/V_1 in equation (3.7), we get

$$\Delta S = nR \ln \left(\frac{P_1T_2}{P_2T_1} \right) + nC_V \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = nR \ln \left(\frac{P_1}{P_2} \right) + nR \ln \left(\frac{T_2}{T_1} \right) + nC_V \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = nR \ln \left(\frac{P_1}{P_2} \right) + n(R + C_V) \ln \left(\frac{T_2}{T_1} \right)$$

$$\Delta S = nR \ln\left(\frac{P_1}{P_2}\right) + nC_p \ln\left(\frac{T_2}{T_1}\right) \quad (3.29)$$

For isobaric process $P_1 = P_2 = P$, so

$$\Delta S = nR \ln\left(\frac{P}{P}\right) + nC_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = nR \ln\left(\frac{1}{1}\right) + nC_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = 2.303 \times nC_p \log\left(\frac{T_2}{T_1}\right)$$

Example 3.7

Calculate entropy change in an isothermal expansion of 3 moles of an ideal gas from 2 to 5 liter.

Solution

No. of moles = $n = 3$ mol

Initial volume = $V_1 = 2$ L

Final volume = $V_2 = 5$ L

Change in entropy = $\Delta S = ?$

We know that,

$$\Delta S = nR \ln\left(\frac{V_2}{V_1}\right)$$

$$\Delta S = 3 \times 8.314 \times \ln\left(\frac{5}{2}\right) = 22.85 \text{ J K}^{-1}$$

Example 3.8

Calculate the change in entropy when 2 moles of an ideal gas are heated from 25 to 75 °C at constant pressure. The value of molar heat capacity of the gas is 25 kJ mol⁻¹.

Solution

No. of moles = $n = 2$ mol

Initial temperature = $T_1 = 25$ °C

Final temperature = $T_2 = 75$ °C

Change in entropy = $\Delta S = ?$

We know that,

$$\Delta S = nC_p \ln\left(\frac{T_2}{T_1}\right)$$

$$\Delta S = 2 \times 25 \times 10^3 \times \ln\left(\frac{75}{25}\right) = 5.49 \times 10^4 \text{ JK}$$

3.16 ENTROPY OF MIXING

When two gases are mixed together, entropy changes occur. In this section we shall establish a mathematical relationship for entropy of mixing of two ideal gases A and B.

Suppose n_1 moles of gas A at its initial pressure P_1' and n_2 moles of gas B at its initial pressure P_2' . When these gases are mixed then partial pressure of gas A and B becomes P_1 and P_2 respectively. In case of isothermal process, change in entropy for gas A by using equation (3.29) can be written as

$$\Delta S_A = n_1 R \ln\left(\frac{P_1'}{P_1}\right) \tag{3.30}$$

The next term in equation (3.29) is zero because process is isothermal. Similarly entropy change for gas B is

$$\Delta S_B = n_2 R \ln\left(\frac{P_2'}{P_2}\right) \tag{3.31}$$

By adding equation (3.30) and (3.31), total entropy change can be calculated as

$$\begin{aligned} \Delta S_{\text{mixing}} &= \Delta S_A + \Delta S_B \\ \Delta S_{\text{mixing}} &= n_1 R \ln\left(\frac{P_1'}{P_1}\right) + n_2 R \ln\left(\frac{P_2'}{P_2}\right) \end{aligned} \tag{3.32}$$

According to Dalton's law of partial pressure, partial pressure of a gas is related to total pressure of the gas after mixing. Hence

$$\begin{aligned} P_1 &\propto x_1 \\ P_1 &= P_t x_1 \end{aligned} \tag{3.33}$$

Where P_1 is partial pressure of gas A and P_t is total pressure of mixing of gases and x_1 is mole fraction of gas A.

Similarly for gas B, we can write as

$$P_2 = P_t x_2 \tag{3.34}$$

Where P_2 is partial pressure of gas B and P_t is total pressure of mixing of gases and x_2 is mole fraction of gas B.

By putting the values of P_1 and P_2 from equations (3.33) and (3.34) respectively into equation (3.32), we get

$$\Delta S_{\text{mixing}} = n_1 R \ln \left(\frac{P_1}{P_1 x_1} \right) + n_2 R \ln \left(\frac{P_2}{P_1 x_2} \right)$$

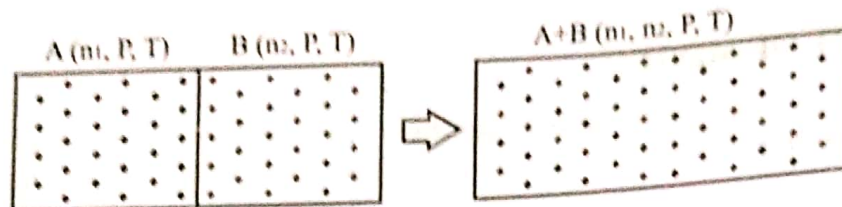


Fig. 3.11 Mixing of two gases

For special case shown in Fig. in which temperature and pressure both remains constant during mixing, then $P_1 = P_2 = P_1 = P$. Hence above equation becomes

$$\begin{aligned} \Delta S_{\text{mixing}} &= n_1 R \ln \left(\frac{1}{x_1} \right) + n_2 R \ln \left(\frac{1}{x_2} \right) \\ \Delta S_{\text{mixing}} &= -n_1 R \ln x_1 - n_2 R \ln x_2 \\ \Delta S_{\text{mixing}} &= -R [n_1 \ln x_1 + n_2 \ln x_2] \end{aligned}$$

This is the mathematical expression for calculation of entropy of mixing of two of two ideal gases when pressure and temperature of the system remains constant. The value of ΔS_{mixing} for the specified conditions is positive because values of x_1 and x_2 are less than unity. Therefore the term in bracket will give a negative answer. Hence entropy increases during mixing.

3.17 ENTROPY CHANGE IN UNIVERSE DURING REVERSIBLE PROCESS

During the reversible process, entropy of the universe (system + surrounding) remains constant. It means entropy change of universe in a reversible process should be zero. It can be verified as

When a system absorbs Q_{rev} heat at temperature T , then heat lost by surrounding will be equal to Q_{rev} . So we can write

$$\text{Entropy change of the system} = \Delta S_{\text{system}} = Q_{\text{rev}}/T$$

$$\text{Entropy change of the surrounding} = \Delta S_{\text{surrounding}} = -Q_{\text{rev}}/T$$

$$\text{Entropy change of universe} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$$\Delta S_{\text{Total}} = \frac{Q_{\text{rev}}}{T} - \frac{Q_{\text{rev}}}{T}$$

$$\Delta S_{\text{Total}} = 0$$

So, entropy change in the universe for reversible process is equal to zero.

$$\ln K_2 - \ln K_1 = \frac{\Delta H^\circ}{R} \left[-\frac{1}{T_2} + \frac{1}{T_1} \right]$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3.60)$$

Equation (3.60) can be used for determination of value of ΔH° .

Example 3.10

Calculate the enthalpy change for reaction $A + B \rightarrow C + D$ for which values of equilibrium constant at two different temperatures are given below.

Temperature (K)	1900	2200
Equilibrium constant	3×10^{-4}	8.6×10^{-4}

Solution

Initial temperature = $T_1 = 1900$ K

Final temperature = $T_2 = 2200$ K

Equilibrium constant at $T_1 = K_1 = 3 \times 10^{-4}$

Equilibrium constant at $T_2 = K_2 = 8.6 \times 10^{-4}$

Enthalpy change = $\Delta H^\circ = ?$

We know that

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\Delta H^\circ = \left(\frac{R T_1 T_2}{T_2 - T_1} \right) \ln \frac{K_2}{K_1}$$

$$\Delta H^\circ = \left(\frac{8.314 \times 1900 \times 2200}{2200 - 1900} \right) \ln \frac{8.6 \times 10^{-4}}{3 \times 10^{-4}} = 122 \text{ kJ/mol}$$

3.24 NERNST HEAT THEOREM

According to Gibbs – Helmholtz equation, we know that

$$F = H + T \left(\frac{\partial F}{\partial T} \right)_P$$

For finite change of a process, we can write

$$\Delta F = \Delta H + T \left(\frac{\partial(\Delta F)}{\partial T} \right)_P$$

$$\Delta F - \Delta H = T \left[\frac{\partial(\Delta F)}{\partial T} \right]_P$$

At 0 K, the right hand side of the above equation will become zero, i.e.

$$\Delta F - \Delta H = 0$$

So, when temperature approaches to zero, then the change in Gibbs energy of the process becomes equal to the change in enthalpy of that process, i.e.

$$\lim_{T \rightarrow 0} (\Delta F) = \lim_{T \rightarrow 0} (\Delta H)$$

Nernst found experimentally that the quantity $[\partial(\Delta F)/\partial T]_P$ decreases with the decrease in temperature asymptotically and becomes equal to zero at absolute zero. This statement is called Nernst Heat Theorem. Mathematically, it can be written as

$$\lim_{T \rightarrow 0} \left(\frac{\partial(\Delta F)}{\partial T} \right)_P = \lim_{T \rightarrow 0} \left(\frac{\partial(\Delta H)}{\partial T} \right)_P = 0 \tag{3.61}$$

Nernst Heat theorem can also be stated as "There is no change in entropy of the system when the process occurs in the vicinity of absolute zero". This statement can be proved using equation (3.38), i.e.

$$dF = VdP - SdT$$

At constant pressure, we have

$$\left(\frac{\partial F}{\partial T} \right)_P = -S$$

For a process, F and S can be replaced by ΔF and ΔS respectively, hence

$$\left(\frac{\partial(\Delta F)}{\partial T} \right)_P = -\Delta S$$

According to equation (3.61), the left hand side of the above equation will become zero at 0 K, hence

$$\lim_{T \rightarrow 0} \Delta S = 0$$

$$\lim_{T \rightarrow 0} (S_2 - S_1) = 0$$

This implies that, when $T \rightarrow 0$, then $S_1 = S_2$.

Nernst Heat theorem can be used for the study of variation in molar specific heat at constant pressure for the process occurring in the neighbourhood of absolute zero. The molar heat capacity at constant pressure can be defined as

$$C_p = \left(\frac{\partial H}{\partial T} \right)_p$$

For the change in H and C_p , the above equation can be written as

$$\Delta C_p = \left(\frac{\partial(\Delta H)}{\partial T} \right)_p$$

In the vicinity of absolute zero, the above expression can be written as

$$\lim_{T \rightarrow 0} (\Delta C_p) = \lim_{T \rightarrow 0} \left(\frac{\partial(\Delta H)}{\partial T} \right)_p$$

According to Nernst Heat theorem, the right hand side of the above equation is equal to zero. Therefore

$$\lim_{T \rightarrow 0} (\Delta C_p) = 0$$

$$\lim_{T \rightarrow 0} (C_{p_2} - C_{p_1}) = 0$$

$$\lim_{T \rightarrow 0} (C_{p_2}) = \lim_{T \rightarrow 0} (C_{p_1})$$

According to the above equation, the molar heat capacity at constant pressure during any transformation at absolute zero remains unchanged.

3.25 THIRD LAW OF THERMODYNAMICS

The value of entropy decreases with the decrease in temperature and for pure and perfect-crystalline substance. It becomes zero at absolute zero. This statement is called the third law of thermodynamics. Mathematically, it can be stated as

$$\lim_{T \rightarrow 0} S = 0 \quad (\text{For perfect crystalline solid})$$

The value of molar heat capacity at constant pressure decreases with the decrease in temperature and ultimately becomes zero at absolute zero. This statement is also called third law of thermodynamics. The above statement can be proved easily using the definition of molar heat capacity, i.e.

$$C_p = \left(\frac{dq}{dT} \right)_p \quad (3.62)$$

According to the second law of thermodynamics, we have

$$\frac{dq}{T} = dS$$

$$dq = TdS$$

Putting this value of dq in equation (3.62), we get

$$C_p = \left(\frac{TdS}{dT} \right)_p$$

Rearranging the above equation, we get

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

Integrating the above equation, we get

$$\int_{S_0}^{S_T} dS = \int_0^T C_p \frac{dT}{T}$$

$$S_T - S_0 = \int_0^T C_p \frac{dT}{T} \quad (3.63)$$

According to equation (3.63), for finite value of $S_T - S_0$, C_p must be zero at absolute zero. Hence 3rd law can be stated as

$$\lim_{T \rightarrow 0} C_p = 0$$

3.26 DETERMINATION OF ABSOLUTE ENTROPY OF A SUBSTANCE

The physical significance of 3rd law of thermodynamics is that this law can be used for determination of absolute entropy of a substance. Equation (3.57) is used for this purpose.

$$S_T - S_0 = \int_0^T \frac{C_p}{T} dT \quad (3.64)$$

According to 3rd law of thermodynamics, entropy of pure crystalline solid is zero at 0 K. So equation (3.64) becomes

$$S_T = \int_0^T \frac{C_p}{T} dT \quad (3.65)$$

Where S_T is absolute entropy of a substance at temperature T . The value of S_T can be determined using equation (3.65). We know that

$$\frac{d}{dT} (\ln T) = \frac{1}{T}$$

$$d \ln T = \frac{dT}{T} \quad (3.66)$$

Putting value of dT/T from equation (3.61) into (3.60)

$$S_T = \int_0^T C_p (d \ln T) = 2.303 \int_0^T C_p (d \log T)$$

The value of above definite integral can be obtained by measuring the area under a curve of C_p versus $\log T$ as shown in Fig. 3.12.