its centre of mass is equal to the total random kinetic energy of all its molecules ? (Molecular weight of hydrogen = 2)
[**Ans.** $1{\cdot}93\times10^{5}$ cm/s]

61. Calculate the temperature at which the r.m.s. velocity of a helium molecule will be equal to the speed of the earth's first satellite *i.e.*, $v = 8$ km/s. [**Ans.** $10{\cdot}28\times10^{3}$ K]

62. Calculate the mean kinetic energy of a molecule of a gas at 1,000°C. Given,

$$R = 8{\cdot}31\times10^{7} \text{ ergs/gram mol-K}$$
$$N = 6{\cdot}02\times10^{23}$$

(*Delhi 1969*) [**Ans.** $2{\cdot}07\times10^{-13}$ ergs]

63. If the density of nitrogen is 1·25 g/litre at N.T.P., calculate the R.M.S. velocity of its molecules.
[*Delhi 1972* ; *Delhi* (*Hons.*) *1973*] [**Ans.** $4{\cdot}95\times10^{4}$ cm/s]

64. At what temperature is the R.M.S. speed of oxygen molecules twice their R.M.S. speed at 27°C ?
(*Delhi 1973*) [**Ans.** 927°C]

65. Calculate the R.M.S. velocity of the molecules of hydrogen at 0°C. Molecular weight of hydrogen = 2·016 and

$$R = 8{\cdot}31\times10^{7} \text{ ergs/gram mole °C}$$

(*Delhi 1971*) [**Ans.** $18{\cdot}4\times10^{4}$ cm/s]

66. Calculate the R.M.S. velocity of the hydrogen molecules at room temperature, given that one litre of the gas at room temperature and normal pressure weighs 0·086 g.
(*Delhi 1976*) [**Ans.** $1{\cdot}88\times10^{5}$ cm/s)]

67. Write short notes on :

(*i*) Mean free path [*Agra 1962* ; *Delhi* (*Sub.*) *1966*]
(*ii*) Joule-Thomson Effect (*Agra 1962* ; *Delhi 1974, 75*)
(*iii*) Continuity of state
(*iv*) Rowland's experiment for finding J
(*v*) Van der Waals equation of state
(*vi*) Pressure exerted by an ideal gas
(*vii*) Critical constants
(*viii*) Degrees of freedom
(*ix*) Atomicity of gases
(*x*) Maxwell's law of distribution of velocity. (*Delhi 1975*)
(*xi*) Andrews' experiments
(*xii*) Amagat's experiments
(*xiii*) Halborn's experiments
(*xiv*) Behaviour of gases at high pressure
(*xv*) Critical point
(*xvi*) Corresponding states
(*xvii*) Intermolecular attraction
(*xviii*) Temperature of inversion
(*xix*) Reduced equation of state for a gas [*Delhi* (*Hons.*) *1976*]
(*xx*) Porous plug experiment.

6

Thermodynamics

6·1 Thermodynamic System

A thermodynamic system is one which can be described in terms of the thermodynamic co-ordinates. The co-ordinates of a thermodynamic system can be specified by any pair of quantities *viz.*, pressure (P), volume (V), temperature (T) and entropy (S). The thermodynamic systems in engineering are gas, vapour, steam, mixture of gasoline vapour and air, ammonia vapours and its liquid. In Physics, thermodynamics includes besides the above, systems like stretched wires, thermocouples, magnetic materials, electrical condenser, electrical cells, solids and surface films.

Examples : 1. Stretched wire. In a stretched wire, to find the Young's modulus of a wire by stretching, the complete thermodynamic co-ordinates are

(*a*) the stretching force F
(*b*) the length of the stretching wire and
(*c*) the temperature of the wire.

The pressure and volume are considered to be constant.

2. Surface Films. For liquid films, in the study of surface tension, the thermodynamic co-ordinates are

(*a*) the surface tension
(*b*) the area of the film and
(*c*) the temperature.

3. Reversible Cells. The thermodynamic coordinates to completely describe a reversible cell are

(*a*) the E.M.F. of the cell
(*b*) the charge that flows and
(*c*) the temperature.

6·2 Thermal equilibrium and Concept of Temperature [Zeroth Law of Thermodynamics]

A thermodynamic system is said to be in thermal equilibrium if any two of its independent thermodynamic co-ordinates X and Y remain constant as long as the external conditions remain unaltered. Consider a gas enclosed in a cylinder fitted with a piston. If the pressure and volume of the enclosed mass of gas are P and V at the temperature of the surroundings, these values of P and V will remain constant as long as the external conditions *viz.* temperature and pressure remain unaltered. The gas is said to be in thermal equilibrium with the surroundings.

The *zeroth law* of thermodynamics was formulated after the first and the second laws of thermodynamics have been enunciated. This law helps to define the term *temperature* of a system.

This law states that *if, of three systems, A, B and C, A and B are separately in thermal equilibrium with C, then A and B are also in thermal equilibrium with one another.*

Conversely the law can be stated as follows :

If three or more systems are in thermal contact, each to each, by means of diathermal walls and are all in thermal equilibrium together, then any two systems taken separately are in thermal equilibrium with one another.

Consider three fluids A, B and C. Let P_A, V_A represent the pressure and volume of A, P_B, V_B, the pressure and volume of B, and P_C, V_C are the pressure and volume of C.

If A and B are in thermal equilibrium, then

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B)$$

or $$F_1[P_A, V_A, P_B, V_B] = 0 \qquad \ldots(i)$$

Expression (i) can be solved, and

$$P_B = f_1[P_A, V_A, V_B] \qquad \ldots(ii)$$

If B and C are in thermal equilibrium

$$\phi_2(P_B, V_B) = \phi_3(P_C, V_C)$$

or $$F_2[P_B, V_B, P_C, V_C] = 0$$

Also $$P_B = f_2[V_B, P_C, V_C] \qquad \ldots(iii)$$

From equations (ii) and (iii) for A and C to be in thermal equilibrium separately,

$$f_1(P_A, V_A, V_B) = f_2[V_B, P_C, V_C] \qquad \ldots(iv)$$

If A and C are in thermal equilibrium with B separately, then according to the zeroth law, A and C are also in thermal equilibrium with one another.

$$\therefore \quad F_3[P_A, V_A, P_C, V_C] = 0. \qquad \ldots(v)$$

Equation (iv) contains a variable V_B, whereas equation (v) does not contain the variable V_B. It means

$$\phi_1(P_A, V_A) = \varphi_3(P_C, V_C) \qquad \ldots(vi)$$

numerical — সংখ্যাসূচক

In general,

$$\phi_1(P_A, V_A) = \phi_2(P_B, V_B) = \phi_3(P_C, V_C) \qquad \ldots(vii)$$

These three functions have the same numerical value though the parameters (P, V) of each are different. This numerical value is termed as *temperature* (T) of the body.

$$\therefore \qquad \phi(P, V) = T \qquad \ldots(viii)$$

This is called the equation of state of the fluid.

Therefore, the temperature of a system can be defined as the property that determines whether or not the body is in thermal equilibrium with the neighbouring systems. If a number of systems are in thermal equilibrium, this common property of the system can be represented by a single numerical value called the temperature. It means that if two systems are not in thermal equilibrium, they are at different temperatures.

Example. In a mercury in glass thermometer, the pressure above the mercury column is zero and volume of mercury measures the temperature. If a thermometer shows a constant reading in two systems A and B separately, it will show the same reading even when A and B are brought in contact.

6·3 Concept of Heat

Heat is defined as *energy in transit.* As it is not possible to speak of work in a body, it is also not possible to speak of heat in a body. Work is either done on a body or by a body. Similarly, heat can flow from a body or to a body. If a body is at a constant temperature, it has both mechanical and thermal energies due to the molecular agitations and it is not possible to separate them. So, in this case, we cannot talk of heat energy. It means, if the flow of heat stops, the word heat cannot be used. It is only used when there is transfer of energy between two or more systems.

Consider two systems A and B in thermal contact with one another and surrounded by adiabatic walls.

For the system A,

$$H = U_2 - U_1 + W \qquad \ldots(i)$$

where H is the heat energy transferred, U_1 is the initial internal energy, U_2 is the final internal energy and W is the work done.

Similarly for the system B,

$$H' = U_2' - U_1' + W' \qquad \ldots(ii)$$

Adding (i) and (ii)

$$\therefore \quad H + H' = (U_2 - U_1) + W + (U_2' - U_1') + W'$$

$$H + H' = [(U_2 + U_2') - (U_1 + U_1')] + (W + W') \qquad \ldots(iii)$$

The total change in the internal energy of the composite system

$$= [(U_2 + U_2') - (U_1 + U_1')]$$

The work done by the composite system $= W + W'$

It means that the heat transferred by the composite system $= H + H'$. But the composite system is surrounded by adiabatic walls and the net heat transferred is zero.

$$\therefore \quad H + H' = 0$$

$$H = -H' \qquad \ldots(iv)$$

Thus, for two systems A and B in thermal contact with each other, and the composite system surrounded by adiabatic walls, the heat gained by one system is equal to the heat lost by the other system.

6·4 Quasistatic Process

A system in thermodynamical equilibrium must satisfy the following requirements strictly :—

(*i*) **Mechanical Equilibrium.** For a system to be in mechanical equilibrium, there should be no unbalanced forces acting on any part of the system or the system as a whole.

(*ii*) **Thermal Equilibrium.** For a system to be in thermal equilibrium, there should be no temperature difference between the parts of the system or between the system and the surroundings.

(*iii*) **Chemical Equilibrium.** For a system to be in chemical equilibrium, there should be no chemical reaction within the system and also no movement of any chemical constituent from one part of the system to the other.

When a system is in thermodynamic equilibrium and the surroundings are kept unchanged, there will be no motion and also no work will be done. On the other hand, if the sum of the external forces is altered, resulting in a finite unbalanced force acting on the system, the condition for mechanical equilibrium will not be satisfied any longer. This results in the following :—

(*i*) Due to unbalanced forces within the system, turbulence, waves etc. may be set up. The system as a whole may possess an accelerated motion.

(*ii*) Due to turbulence, acceleration etc. the temperature distribution within the system may not be uniform. There may also exist a finite temperature difference between the system and the surroundings.

(*iii*) Due to the presence of unbalanced forces and difference in temperature, chemical reaction may take place or there may be movement of a chemical constituent.

From this discussion, it is clear that a finite unbalanced force may cause the system to pass through *non-equilibrium* states. If during a thermodynamic process, it is desired to describe every state of a system by thermodynamic coordinates referred to the system as a whole, the process should not be brought about by a finite unbalanced force.

A quasistatic process is defined as the process in which the deviation from thermodynamic equilibrium is infinitesimal and all the states through which the system passes during a quasistatic process can be considered as equilibrium states.

In actual practice, many processes closely approach a quasistatic process and may be treated as such with no significant error. Consider the expansion of a gas in a closed cylinder fitted with a piston. Initially weights are on the piston and the pressure of the gas inside the cylinder is higher than the atmospheric pressure. If the weights are small and are taken off slowly one by one, the process can be considered quasistatic. If, however, all the weights are removed at once, expansion takes place suddenly and it will be a non-equilibrium process. The system will not be in equilibrium at any time during this process.

A quasistatic process is an ideal concept that is applicable to all thermodynamic systems including electric and magnetic systems. It should be noted that conditions for such a process can never be satisfied rigorously in practice.

6·5 Heat—A Path Function

Heat is a path function. When a system changes from a state 1 to state 2, the quantity of heat transferred will depend upon the intermediate stages through which the system passes *i.e.*, its path. Hence heat is an **inexact differential** and is written as δH.

On integrating, we get

$$\int_{1A}^{2A} \delta H = H_{1A}^{2A}$$

Here, ${}_1H_2$ represents the heat transferred during the given process between the states 1 and 2 along a particular path A.

6·6 Work—A Path Function

Suppose that a system is taken from an initial equilibrium state 1 to a final equilibrium state 2 by two different paths A and B (Fig. 6·1). The processes are quasistatic.

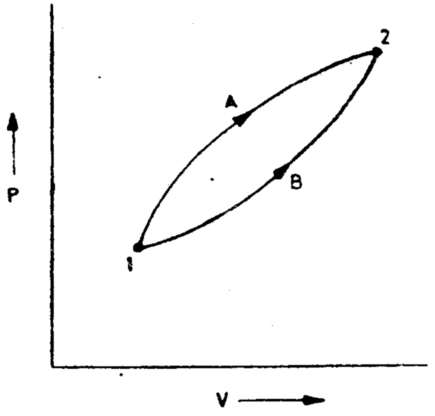

Fig. 6·1

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The areas under these curves are different and hence the quantities of work done are also different.

For the path A,

$$W_A = \int_{1A}^{2A} \delta W = \int_{1A}^{2A} P\,dV \qquad ...(i)$$

For the path B

$$W_B = \int_{1B}^{2B} \delta W = \int_{1B}^{2B} P\,dV \qquad ...(ii)$$

The values of W_A and W_B are not equal. Therefore work cannot be expressed as a difference between the values of some property of the system in the two states. *Therefore, it is not correct to represent*

$$W = \int_{W_1}^{W_2} \delta W = W_2 - W_1 \qquad ...(iii)$$

It may be pointed out that it is meaningless to say "work in a system or work of a system". Work cannot be interpreted similar to temperature or pressure of a system.

In terms of calculus δW is an inexact differential. It means that W is not a property of the system and $\int \delta W$ cannot be expressed as the difference between two quantities that depend entirely on the initial and the final states.

Hence, heat and work are **path functions** and they depend only on the process They are not point functions such as pressure or temperature. Work done in taking the system from state 1 to state 2 will be different for different paths.

6·7 Comparison of Heat and Work

There are many similarities between heat and work. These are :—

1. Heat and work are both transient phenomena. Systems do not possess heat or work.

2. When a system undergoes a change, heat transfer or work done may occur.

3. Heat and work are boundary phenomena. They are observed at the boundary of the system.

4. Heat and work represent the energy crossing the boundary of the system.

5. Heat and work are path functions and hence they are inexact differentials. They are written as δH and δW.

6. (*a*) *Heat* is defined as the form of energy that is transferred across a boundary by virtue of difference of temperature or temperature gradient.

(*b*) Work is said to be done by a system if the sole effect on things external to the system could be the raising of a weight.

It is customary to represent, work done by the system as +ve, work done on the system as —ve, heat flowing into the system as +ve, and heat flowing out of the system as —ve.

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6·8 First Law of Thermodynamics

Joule's law gives the relation between the work done and the heat produced. It is true when the whole of the work done is used in producing heat or *vice versa*. Here, $W = JH$ where J is the Joule's mechanical equivalent of heat. But in practice, when a certain quantity of heat is supplied to a system the whole of the heat energy may not be converted into work. Part of the heat may be used in doing external work and the rest of the heat might be used in increasing the internal energy of the molecules. ② Let the quantity of heat supplied to a system be δH, the amount of external work done be δW and the increase in internal energy of the molecules be dU. The term U represents the internal energy of a gas due to molecular agitation as well as due to the forces of inter-molecular attraction. Mathematically

$$\delta H = dU + \delta W \qquad ...(i)$$

1+2

Equation (*i*) represents the first law of thermodynamics. All the quantities are measured in heat units. ① The first law of thermodynamics states that the amount of heat given to a system is equal to the sum of the increase in the internal energy of the system and the external work done.

For a cyclic process, the change in the internal energy of the system is zero because the system is brought back to the original condition. Therefore for a cyclic process $\oint dU = 0$

and $$\oint \delta H = \oint \delta w \qquad ...(ii)$$

[Both are expressed in heat units].

This equation represents Joule's law.

For a system carried through a cyclic process, its initial and final internal energies are equal. From the first law of thermodynamics, for a system undergoing any number of complete cycles

$$U_2 - U_1 = 0$$

$$\oint \delta H = \oint \delta W$$

$$H = W \qquad \text{[Both are in heat units]}$$

6·9 First Law of Thermodynamics for a Change in State of a Closed System

For a closed system during a complete cycle, the first law of thermodynamics is written as

$$\oint \delta H = \oint \delta W$$

In practice, however, we are also concerned with a process rather than a cycle. Let the system undergo a cycle, changing its

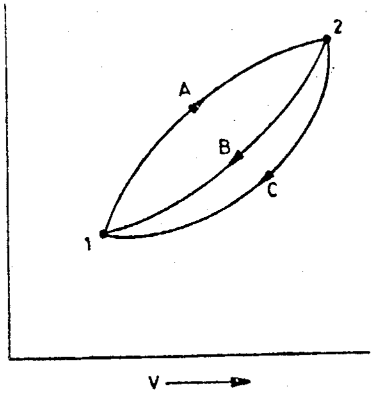

Fig. 6·2

state from 1 to 2 along the path A and from 2 to 1 along the path B. This cyclic process is represented in the P—V diagram (Fig. 6·2).

According to the first law of thermodynamics

$$\oint \delta H = \oint \delta W$$

For the complete cyclic process

$$\int_{1A}^{2A} \delta H + \int_{2B}^{1B} \delta H = \int_{1A}^{2A} \delta W + \int_{2B}^{1B} \delta W \qquad \ldots(i)$$

Now, consider the second cycle in which the system changes from state 1 to state 2 along the path A and returns from state 2 to state 1 along the path C. For this cyclic process

$$\int_{1A}^{2A} \delta H + \int_{2C}^{1C} \delta H = \int_{1A}^{2A} \delta W + \int_{2C}^{1C} \delta W \qquad \ldots(ii)$$

Subtracting (*ii*) from (*i*)

$$\int_{2B}^{1B} \delta H - \int_{2C}^{1C} \delta H = \int_{2B}^{1B} \delta W - \int_{2C}^{1C} \delta W$$

or

$$\int_{2B}^{1B} (\delta H - \delta W) = \int_{2C}^{1C} (\delta H - \delta W) \qquad \ldots(iii)$$

Here B and C represent arbitrary processes between the states 1 and 2. Therefore, it can be concluded that the quantity $(\delta H - \delta W)$ is the same for all processes between the states 1 and 2. The quantity

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$(\delta H - \delta W)$ depends only on the initial and the final states of the system and is independent of the path followed between the two states.

Let $$dE = (\delta H - \delta W)$$

From the above logic, it can be seen that

$$\int_1^2 dE = \text{constant and is independent of the path.}$$

This naturally suggests that E is a point function and dE is an exact differential.

The point function E is a property of the system.

Here dE is the derivative of E and it is an exact differential.

$$\therefore \quad \delta H - \delta W = dE \qquad \ldots(iv)$$

or $$\delta H = dE + \delta W \qquad \ldots(v)$$

Integrating equation (*v*), from the initial state 1 to the final state 2

$${}_1H_2 = (E_2 - E_1) + {}_1W_2$$

[**Note.** ${}_1H_2$ cannot be written as $(H_2 - H_1)$, because it depends upon the path].

Similarly, ${}_1W_2$ cannot be written as $(W_2 - W_1)$, because it also depends upon the path.

Here ${}_1H_2$ represents the heat transferred,

${}_1W_2$ represents the work done,

E_2 represents the total energy of the system in state 2,

E_1 represents the total energy of the system in state 1.

At this point, it is worthwhile discussing what this E can possibly mean. With reference to the system, the energies crossing the boundaries are all taken care of in the form of H and W. For dimensional stability of Eq. (*v*), this E must be energy and this must belong to the system. Therefore,

E_2 represents the energy of the system in state 2

E_1 represents the energy of the system in state 1

This energy E acquires a value at any given equilibrium condition by virtue of its thermodynamic state. The working substance, for example a gas, has molecules moving in all random fashion. The molecules have energy associated by virtue of mutual attraction and this part is similar to the potential energy of a body in macroscopic terms. They also have velocities and hence kinetic energy. This energy E therefore can be visualised as comprising of molecular potential and kinetic energies in addition to macroscopic potential and kinetic energies. The first part, which owes its existence to the thermodynamic nature is often called the internal energy which is completely dependent on the thermodynamic state and the other two depend on mechanical or physical state of the system.

$E = U+KE+PE+$Others which depend upon chemical nature etc.

For a closed system (non-chemical) the changes in all others except U are insignificant and

$$dE = dU$$

∴ From equation (v)

$$\delta H = dU+\delta W \qquad ...(vi)$$

Here all the quantities are in consistent units

Example 6·1. *When a system is taken from the state A to the state B, along the path ACB,* 80 joules *of heat flows into the system, and the system does* 30 joules *of work (Fig. 6·3).*

(*a*) *How much heat flows into the system along the path ADB, if the work done is 10* joules.

(*b*) *The system is returned from the state B to the state A along the curved path. The work done on the system is 20* joules. *Does the system absorb or liberate heat and how much ?*

(*c*) *If* $U_A = 0$, $U_D = 40$ joules, *find the heat absorbed in the process AD and DB.*

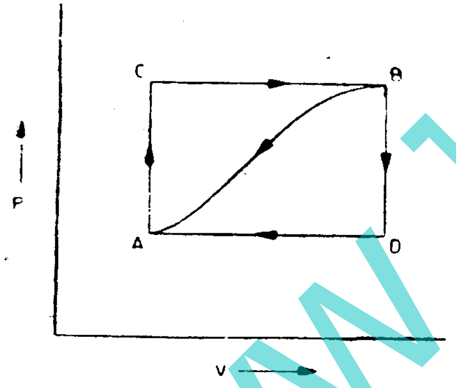


Fig. 6·3

Along the path ACB,

$$H_{ACB} = U_B - U_A + W$$

Here $H = +80$ joules

$W = +30$ joules

∴ $+80 = U_B - U_A + 30$

$U_B - U_A = 80-30 =$ **50 joules**

(a) Along the path ADB,

$W = +10$ joules

$$H_{ADB} = U_B - U_A + W$$

$H = 50+10 =$ **60 joules**

(b) For the curved path from B to A,

$W = -20$ joules

$H = (U_A - U_B)+W$

$= -50-20 =$ **−70 joules**

(—ve sign shows that heat is liberated by the system)

(c) $U_A = 0$, $U_D = 40$ joules

$U_B - U_A = 50$

∴ $U_B = 50$ joules

In the process ADB, 10 joules of work is done. Work done from A to D is +10 joules and from D to B is zero.

For AD,

$$H_{AD} = (U_D - U_A)+W$$

$= 40+10 = 50$ joules

For DB

$$H_{DB} = U_C - U_D + W$$

$= 50-40+0 =$ **10 joules**

6·10 Applications of First Law of Thermodynamics

Specific Heat of a Gas (T and V Independent)

The internal energy of a system is a single valued function of the state variables *viz.*, pressure, volume, temperature etc. In the case of a gas, any two of the variables P, V, T are sufficient to define completely its state. If V and T are chosen as the independent variables,

$$U = f(V, T) \qquad ...(i)$$

Differentiating equation (i)

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

If an amount of heat δH is supplied to a thermodynamical system, say an ideal gas and if the volume increases by dV at a constant pressure P, then according to the first law of thermodynamics

$$\delta H = dU + \delta W$$

Here $\delta W = P.dV$

∴ $\delta H = dU + P.dV$

Substituting the value of dU from equation (ii)

$$\delta H = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + PdV \qquad ...(iii)$$

Dividing both sides by dT

$$\frac{\delta H}{dT} = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \frac{dV}{dT} + \frac{P.dV}{dT}$$

or $$\left(\frac{\delta H}{dT}\right) = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\frac{dV}{dT} \qquad \ldots(iv)$$

If the gas is heated at constant volume,

$$\left(\frac{\delta H}{\partial T}\right)_V = C_V$$

and $$\frac{dV}{dT} = 0$$

$$\therefore \left(\frac{\delta H}{dT}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = C_V \qquad \ldots(v)$$

When the gas is heated at constant pressure,

$$\left(\frac{\delta H}{dT}\right)_P = C_P$$

$\therefore$ From equation (*iv*),

$$C_P = \left(\frac{\partial U}{\partial T}\right)_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

$$\therefore \quad C_P = C_V + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P$$

or $$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right]\left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(vi)$$

From Joule's experiment, for an ideal gas on opening the stop-cock, no work was done and no heat transfer took place.

So $\delta H = 0 = dU + 0$. Therefore, $dU = 0$. Even though the volume changed while the temperature is constant, there is no change in internal energy.

$$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

From the ideal gas equation

$$PV = RT$$

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

$$\therefore \quad C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$$

But $$\left(\frac{\partial U}{\partial V}\right)_T = 0$$

$$\therefore \quad C_P - C_V = P\left(\frac{\partial V}{\partial T}\right)_P = R$$

$$\therefore \quad C_P - C_V = R \qquad \ldots(viii)$$

Here C_P, C_V and R are expressed in the same units.

From equation (*iii*)

$$\delta H = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV \qquad \ldots(ix)$$

For a process at constant temperature

$$dT = 0$$

$$\therefore \quad (\delta H)_T = P(dV)_T + \left(\frac{\partial U}{\partial V}\right)_T (dV)_T \qquad \ldots(x)$$

This equation represents the amount of heat energy supplied to a system in an isothermal reversible process and is equal to the sum of the work done by the system and the increase in its internal energy.

For a reversible adiabatic process

$$\delta H = 0,$$

Therefore, from equation (*ix*),

$$0 = C_V\, dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

or $$C_V dT = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

Dividing throughout by dV,

$$C_V\left(\frac{\partial T}{\partial V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad \ldots(xii)$$

The isobaric volume coefficient of expansion

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

$$\therefore \quad \alpha V = \left(\frac{\partial V}{\partial T}\right)_P$$

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

$$\therefore \quad \frac{C_P - C_V}{\alpha V} = P$$

But $$\left(\frac{\partial U}{\partial V}\right)_T = 0 = P - P$$

or $$\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{C_P - C_V}{\alpha V}\right) - P \qquad \ldots(xiii)$$

or $$-\left(\frac{C_P - C_V}{\alpha V}\right) = -\left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \qquad \ldots(xiv)$$

From equations (*xii*) and (*xiv*)

$$C_V\left(\frac{\partial T}{\partial V}\right)=-\left(\frac{C_P-C_V}{\alpha V}\right)$$

or

$$\left(\frac{\partial T}{\partial V}\right)=\frac{C_V-C_P}{\alpha V C_V} \qquad \ldots(xv)$$

This expression holds good for an adiabatic reversible process.

6·11 Isothermal Process

If a system is perfectly conducting to the surroundings and the temperature remains constant throughout the process, it is called an isothermal process. Consider a working substance at a certain pressure and temperature and having a volume represented by the point A (Fig. 6·4).

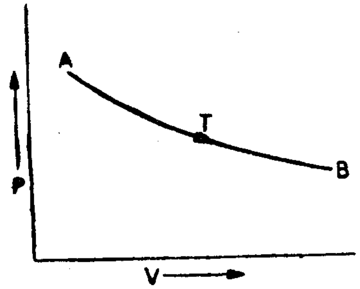


Fig. 6·4

Pressure is decreased and work is done by the working substance at the cost of its internal energy and there should be fall in temperature. But, the system is perfectly conducting to the surroundings. It absorbs heat from the surroundings and maintains a constant temperature. Thus from A to B the temperature remains constant. The curve AB is called the *isothermal* curve or *isothermal*.

Consider the working substance at the point B and let the pressure be increased. External work is done on the working substance and there should be rise in temperature. But the system is perfectly conducting to the surroundings. It gives extra heat to the surroundings and its temperature remains constant from B to A.

Thus, during the isothermal process, the temperature of the working substance remains constant. It can absorb heat or give heat to the surroundings. The equation for an isothermal process is

$PV = RT =$ constant [For one gram molecule of a gas.]

For n gram molecules of a gas $PV = nRT$

6·12 Adiabatic process

During an adiabatic process, the working substance is perfectly insulated from the surroundings It can neither give heat nor take heat from the surroundings. When work is done on the working substance, there is rise in temperature because the external work done on the working substance increases its internal energy. When work is done by the working substance, it is done at the cost of its internal energy. As the system is perfectly insulated from the surroundings, there is fall in temperature.

Thus, during an adiabatic process, the working substance is perfectly insulated from the surroundings. All along the process, there is change in temperature. A curve between pressure and volume during the adiabatic process is called an adiabatic curve or an adiabatic.

Examples. 1. The compression of the mixture of oil vapour and air during compression stroke of an internal combustion is an adiabatic process and there is rise in temperature.

2. The expansion of the combustion products during the working stroke of an engine is an adiabatic process and there is fall in temperature.

3. The sudden bursting of a cycle tube is an adiabatic process.

Apply the first law of thermodynamics to an adiabatic process, $\delta H = 0$,

$$\delta H = dU+\delta W$$

or

$$0 = dU+\delta W \qquad \ldots(i)$$

The processes that take place *suddenly* or *quickly* are adiabatic processes.

6·13 Isochoric Process

If the working substance is taken in a non-expanding chamber, the heat supplied will increase the pressure and temperature. The volume of the substance will remain constant. Such a process is called an *isochoric process*. The work done is zero because there is no change in volume. The whole of the heat supplied increases the internal energy. Therefore, during the isochoric process $\delta W = 0$.

$$\delta H = dU \qquad \ldots(i)$$

The heat transferred in such a process

$$\delta H = C_v dT$$

$$\therefore \quad C_v dT = dU \qquad \ldots(ii)$$

Hence C_v is the specific heat for one gram-molecule of a gas at constant volume.

6·14 Isobaric Process

If the working substance is taken in an expanding chamber kept at a constant pressure, the process is called an isobaric process. Here, the temperature and volume change. If an amount of heat δH is given to the working substance, it is partly used in increasing the temperature of the working substance by dT and partly used in doing external work. Considering one gra [illegible] working substance,

$$\delta H = 1 \times C_v dT + \frac{P\,.\,dV}{J} \qquad \ldots(i)$$

But $$\delta H = C_p.dT \qquad \ldots(ii)$$

$$P.dV = r.dT$$

$$\therefore \quad C_p dT = C_v.dT + \frac{r.dT}{J}$$

$$C_p - C_v = \frac{r}{J} \qquad \ldots(iii)$$

Here C_p and C_v represent the specific heats for 1 gram of a gas and r is the ordinary gas constant.

If C_p and C_v are the gram-molecular specific heats of gas, then

$$C_p - C_v = \frac{R}{J} \qquad \ldots(iv)$$

Here R is the universal gas constant.

6·15 Gas Equation During an Adiabatic Process

Consider 1 gram of the working substance (ideal gas) perfectly insulated from the surroundings. Let the external work done by the gas be δW.

Applying the first law of thermodynamics

$$\delta H = dU + \delta W$$

But $$\delta H = 0$$

and $$\delta W = P.dV$$

where P is the pressure of the gas and dV is the change in volume.

$$\therefore \quad 0 = dU + \frac{P.dV}{J} \qquad \ldots(i)$$

As the external work is done by the gas at the cost of its internal energy, there is fall in temperature by dT.

$$dU = 1 \times C_v \times dT$$

$$C_v.dT + \frac{P.dV}{J} = 0 \qquad \ldots(ii)$$

For an ideal gas

$$PV = rT \qquad \ldots(iii)$$

Differentiating,

$$P.dV + V.dP = r\cdot dT$$ $\therefore dT = \frac{pdv + v\,dp}{r}$

Substituting the value of dT in equation (ii),

$$C_v\left[\frac{P.dV + V.dP}{r}\right] + \frac{P.dV}{J} = 0$$

$$C_v[P.dV + V.dP] + r.\frac{P.dV}{J} = 0$$

But, $$\frac{r}{J} = C_p - C_v$$

$$\therefore \quad C_v.P.dV + C_v.V.dP + C_p.PdV - C_vPdV = 0$$

$$C_p.P.dV + C_v.V.dP = 0$$

Dividing by $C_v.PV$,

$$\frac{C_p}{C_v}\cdot\frac{dV}{V} + \frac{dP}{P} = 0$$

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

$$\therefore \quad \frac{dP}{P} + \gamma\,\frac{dV}{V} = 0$$

Integrating, $\log P + \gamma \log V = \text{const.}$ $\Rightarrow \log p + \log v^\gamma = c$

$$\log PV^\gamma = \text{const.}$$

or $$PV^\gamma = \text{const.}$$ ✓

This is the equation connecting pressure and volume during adiabatic process.

Taking $$PV = rT$$

or $$P = \frac{rT}{V}$$

$$\left(\frac{rT}{V}\right).V^\gamma = \text{const.}$$

But r is const.

$$rTV^{\gamma-1} = \text{const.}$$

$$\therefore \quad TV^{\gamma-1} = \text{const.}$$

Also $$V = \frac{rT}{P}$$

$$P\left[\frac{rT}{P}\right]^\gamma = \text{const.}$$

or $$\frac{r^\gamma T^\gamma}{P^{\gamma-1}} = \text{const.}$$

or $$\frac{P^{\gamma-1}}{T^\gamma} = \text{const.}$$

Thus, during an adiabatic process

(i) $PV^\gamma = \text{const.}$

(ii) $TV^{\gamma-1} = \text{const.}$ and

(iii) $\frac{P^{\gamma-1}}{T^\gamma} = \text{const.}$

Example 6·2. *A motor car tyre has a pressure of 2 atm pheres at the room temperature of 27°C. If the tyre suddenly burs find the resulting temperature.*

Here,

$$P_1 = 2 \text{ atmospheres}$$
$$T_1 = 273+27$$
$$= 300 \text{ K}$$
$$P_2 = 1 \text{ atmosphere}$$
$$T_2 = ?$$
$$\gamma = 1{\cdot}4$$
$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}}$$
$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$
$$\left(\frac{1}{2}\right)^{0{\cdot}4} = \left(\frac{T_2}{300}\right)^{1{\cdot}4}$$
$$0{\cdot}4 \log (0.5) = 1{\cdot}4 [\log T_2 - \log 300]$$
$$-0{\cdot}1204 = 1{\cdot}4 \log T_2 - 3{\cdot}4680$$
$$1{\cdot}4 \log T_2 = 3{\cdot}4680 - 0{\cdot}1204$$
$$= 3{\cdot}3476$$
$$\log T_2 = \frac{3{\cdot}3476}{1{\cdot}4}$$
$$= 2{\cdot}3911$$
$$T_2 = 246{\cdot}1 \text{ K}$$
$$= -26{\cdot}9^\circ\text{C}$$

Example 6·3. *A quantity of air at 27°C and atmospheric pres- suddenly compressed to half its original volume. Find the (i) pressure and (ii) temperature.*

(i) $P_1 = 1$ atmosphere ; $P_2 = ?,\quad \gamma = 1{\cdot}4$

$V_1 = V\,;\qquad V_2 = \dfrac{V}{2}$

During sudden compression, the process is adiabatic

$$P_1V_1^{\gamma} = P_2V_2^{\gamma}$$
$$P_2 = P_1\left[\frac{V_1}{V_2}\right]^{\gamma}$$
$$= 1[2]^{1{\cdot}4}$$
$$= 2{\cdot}636 \text{ atmospheres}$$

(ii) $V_1 = V\,;\qquad V_2 = \dfrac{V}{2}$

$$T_1 = 300 \text{ K}\,;\ T_2 = ?$$
$$\gamma = 1{\cdot}4$$
$$T_1(V_1)^{\gamma-1} = T_2\,(V_2)^{\gamma-1}$$
$$T_2 = T_1[2]^{1{\cdot}4-1}$$
$$= 300[2]^{0{\cdot}4}$$
$$= 395{\cdot}9 \text{ K}$$
$$= 122{\cdot}9^\circ\text{C}$$

Example 6·4. *Air is compressed adiabatically to half its volume. Calculate the change in its temperature.* (*Delhi 1969*)

Let the initial temperature be T_1 K and the final temperature T_2 K.

$$\text{Initial volume} = V_1$$
$$\text{Final volume} = V_2$$
$$= \frac{V_1}{2}$$

During an adiabatic process

$$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$$
$$T_2 = T_1\left[\frac{V_1}{V_2}\right]^{\gamma-1}$$
$$T_2 = T_1[2]^{\gamma-1}$$

But

$$\gamma \text{ for air} = 1{\cdot}40$$
$$T_2 = T_1[2]^{1{\cdot}40-1}$$
$$T_2 = T_1[2]^{0{\cdot}40}$$
$$T_2 = 1{\cdot}319\,T_1$$

Change in temperature

$$= T_2 - T_1$$
$$= 1{\cdot}319\,T_1 - T_1$$
$$= \mathbf{0{\cdot}319\,T_1\ K}$$

✓ **Example 6·5.** *1 gram molecule of a monoatomic ($\gamma = 5/3$) perfect gas at 27°C is adiabatically compressed in a reversible process from an initial pressure of 1 atmosphere to a final pressure of 50 atmospheres. Calculate the resulting difference in temperature.* [*Delhi (Hons.) 1973*]

In a reversible adiabatic process

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}}$$

or

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

Here,

$$P_2 = 50,$$
$$P_1 = 1,$$
$$T_1 = 273+27$$
$$= 300 \text{ K}$$
$$T_2 = ?$$
$$\gamma = \frac{5}{3}$$

$$\therefore\quad (50)^{2/3} = \left(\frac{T_2}{300}\right)^{5/3}$$

or

$$\frac{2}{3} \log (50) = \frac{5}{3} [\log T_2 - \log 300]$$
$$T_2 = \mathbf{1{,}434\ K}$$
$$= \mathbf{1{,}161^\circ C}$$

Example 6·6. *A quantity of dry air at 27°C is compressed (i) slowly and (ii) suddenly to 1/3 of its volume. Find the change in temperature in each case, assuming γ to be 1·4 for dry air.*

[Agra 1969 ; Delhi 71, 75]

(1) When the process is slow, the temperature of the system remains constant. Therefore, there is no change in temperature.

(2) When the compression is sudden, the process is adiabatic.

Here $V_1 = V, \quad V_2 = \frac{V}{3}$

$T_1 = 300 \text{ K}, \quad T_2 = ?$

$\gamma = 1{\cdot}4$

$$T_2 (V_2)^{\gamma-1} = T_1 [V_1]^{\gamma-1}$$

$$T_2 = T_1\left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

or $$T_2 = 300\left[\frac{3V}{V}\right]^{\gamma-1}$$

$$= 300\,[3]^{1\cdot4-1}$$

or $$T_2 = 465{\cdot}5 \text{ K}$$

$$= 192{\cdot}5\ ^\circ\text{C}$$

The temperature of air increases by

$192{\cdot}5-27 =$ **165·5 °C** or **165·5 K**

Example 6·7. *A certain mass of gas at* NTP *is expanded to three times its volume under adiabatic conditions. Calculate the resulting temperature and pressure.* γ *for the gas is 1·40.*

[Delhi (Hons.) 75]

(1) Here, $V_1 = V, \quad V_2 = 3V$

$T_1 = 273 \text{ K} \quad T_2 = ?$

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

or $$T_2 = T_1\left[\frac{V_1}{V_2}\right]^{\gamma-1}$$

$$T_2 = 273\left[\frac{1}{3}\right]^{1.4-1}$$

$$\mathbf{T_2 = 176 \text{ K} = -97°C}$$

(2) Here, $V_1 = V, \quad V_2 = 3V$

$P_1 = 1$ atmosphere, $\quad P_2 = ?$

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

$$P_2 = P_1\left[\frac{V_1}{V_2}\right]^{\gamma}$$

or $$P_2 = 1\left(\frac{1}{3}\right)^{1.4}$$

$P_2 =$ **0·2148 atmosphere**

6·16 Slopes of Adiabatics and Isothermals

In an isothermal process

$$PV = \text{const.}$$

Differentiating,

$$PdV + VdP = 0 \quad \Rightarrow v\,dp = -p\,dv$$

or $$\frac{dP}{dV} = -\frac{P}{V} \quad \ldots(i)$$

In an adiabatic process

$$PV^{\gamma} = \text{const.}$$

Differentiating,

$$P\gamma V^{\gamma-1} dV + VdP = 0 \quad \Rightarrow v^{\gamma} dp = p\gamma\, v^{\gamma-1} dv$$

$$\frac{dP}{dV} = -\frac{\gamma P}{V} \quad \ldots(ii)$$

Therefore, the slope of an adiabatic is γ times the slope of the isothermal.

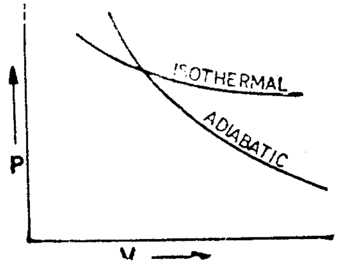


Fig. 6·5

Hence, the adiabatic curve is steeper than the isothermal curve (Fig. 6·5) at a point where the two curves intersect each other.

6·17 Work Done During an Isothermal Process

N

When a gas is allowed to expand isothermally, work is done by it.

Let the initial and final volumes be V_1 and V_2 respectively. In Fig. 6·6, the area of the shaded strip represents the work done for a small change in volume dV. When the volume changes from V_1 to V_2,

$$\text{Work done} = \int_{V_1}^{V_2} P\,.\,dV = \text{area } ABba \quad \ldots(i)$$

Fig. 6·6 represents the indicator diagram. Considering one gram molecule of the gas

$$PV = RT$$

or $$P = \frac{RT}{V}$$

$$\therefore \quad W = RT\int_{V_1}^{V_2}\frac{dV}{V}$$

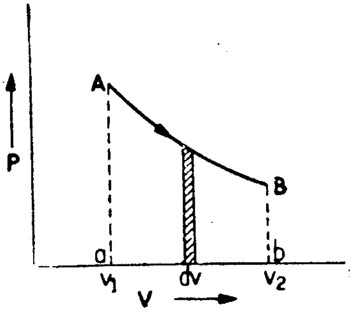


Fig. 6·6

$$= RT\log_e\frac{V_2}{V_1} \qquad \text{... (ii)}$$

$$W = RT\times 2.3026\ \log_{10}\frac{V_2}{V_1} \qquad \text{... (iii)}$$

Also $\quad P_1V_1 = P_2V_2$

or $\quad \dfrac{V_2}{V_1} = \dfrac{P_1}{P_2}$

$$\therefore \quad W = RT\times 2.3026\times\log_{10}\frac{P_1}{P_2} \qquad 4 \quad \text{... (iv)}$$

Here, the change in the internal energy of the system is zero (because the temperature remains constant). So the heat transferred is equal to the work done.

② 6.18 Work Done During an Adiabatic Process

During an adiabatic process, the gas expands from volume V_1 to V_2. As shown by the indicator diagram (Fig. 6.7) the work done for an increase in

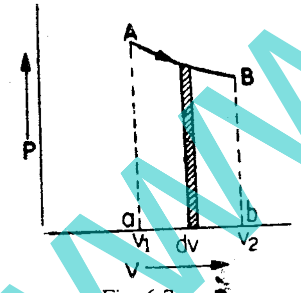


Fig. 6.7.

volume $dV = P.dV$. Work done when the gas expands from V_1 to V_2 is given by,

$$W = \int_{V_1}^{V_2} PdV = \text{Area } ABba$$

During an adiabatic process,

$$PV^{\gamma} = \text{const} = K$$

or

$$P = \frac{K}{V^{\gamma}}$$

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

$$= \frac{1}{1-\gamma}\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right] \qquad \text{...(i)}$$

Since A and B lie on the same adiabatic

$$P_1V_1^{\gamma} = P_2V_2^{\gamma} = K$$

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

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

$$= \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right] \qquad \text{...(ii)}$$

Taking T_1 and T_2 as the temperatures at the points A and B respectively and considering one gram molecule of the gas

$$P_1V_1 = RT_1$$

and

$$P_2V_2 = RT_2$$

Substituting these values in equation (ii)

$$W = \frac{1}{1-\gamma}\left[RT_2 - RT_1\right] \qquad \text{...(iii)}$$

Here, heat transferred is zero because the system is thermally insulated from the surroundings. The decrease in the internal energy of the system (due to fall in temperature) is equal to the work done by the system and *vice versa*.

(11) e 6·19. Relation Between Adiabatic and Isothermal Elasticities

1. Isothermal Elasticity

During an isothermal process

$$PV = \text{const}$$

Differentiating,

$$PdV + VdP = 0 \quad \Rightarrow V\,dP = P\,dV$$

or

$$\frac{V.dP}{-dV} = P \qquad \text{...(i)}$$

From the definition of elasticity of a gas

$$E_{iso} = \frac{dP}{-dV/V}$$

$$= \frac{VdP}{-dV} \qquad \text{...(ii)}$$

From (*i*) and (*ii*)

$$E_{iso} = P \qquad \text{...(iii)}$$

2. Adiabatic Elasticity

During an adiabatic process

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

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

or

$$\frac{VdP}{-dV} = \gamma P \qquad \text{...(iv)}$$

From the definition of elasticity of a gas

$$E_{adi} = \frac{dP}{-dV/V}$$

$$= \frac{V.dP}{-dV} \qquad \text{...(v)}$$

From (*iv*) and (*v*),

$$E_{adi} = \gamma P \qquad \text{...(vi)}$$

Comparing (*iii*) and (*vi*)

$$E_{adi} = \gamma E_{iso}$$

Thus, the adiabatic elasticity of a gas is γ times the isothermal elasticity.

6·20 Clement and Desormes Method—Determination of γ

Clement and Desormes in 1819 designed an experiment to find γ, the ratio between the two specific heats of a gas.

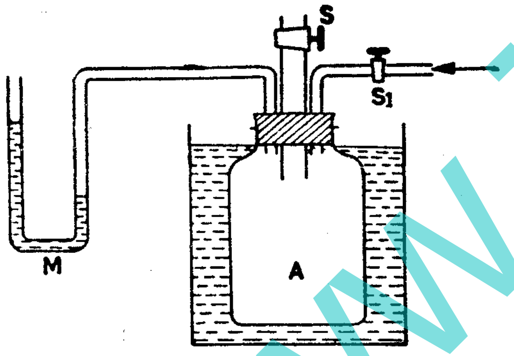


Fig. 6·8

The vessel *A* has a capacity of 20 to 30 litres and is fitted in a box containing cotton and wool. At the top end, three tubes are fitted as shown in Fig. 6·8. Through S_1, dry air is forced into the vessel *A*. The stop cock S_1 is closed when the pressure inside *A* is slightly greater than the atmospheric pressure. Let the difference in level on the two sides of the manometer be *H* and the atmospheric pressure be P_0. The pressure of air inside the vessel is P_1.

The stop-cock *S* is suddenly opened and closed just at the moment when the levels of the liquid on the two sides of the manometer are the same. Some quantity of air escapes to the atmosphere. The air inside the vessel expands adiabatically. The temperature of air inside the vessel falls due to adiabatic expansion. The air inside the vessel is allowed to gain heat from the surroundings and it finally attains the temperature of the surroundings. Let the pressure at the end be P_2 and the difference in levels on the two sides of the manometer be *h*.

Theory. Consider a fixed mass of air left in the vessel in the end. This mass of air has expanded from volume V_1 (less than the volume of the vessel) at pressure P_1 to volume V_2 at pressure P_0. The process is adiabatic as shown by the curve *AB* (Fig. 6·9).

$$P_1V_1^{\gamma} = P_0V_2^{\gamma}$$

$$\frac{P_1}{P_0} = \left(\frac{V_2}{V_1}\right)^{\gamma} \qquad \text{...(i)}$$

Finally the point *C* is reached. The points *A* and *C* are at the room temperature. Therefore *AC* can be considered as an isothermal.

$$P_1V_1 = P_2V_2$$

$$\frac{V_2}{V_1} = \frac{P_1}{P_2} \qquad \text{...(ii)}$$

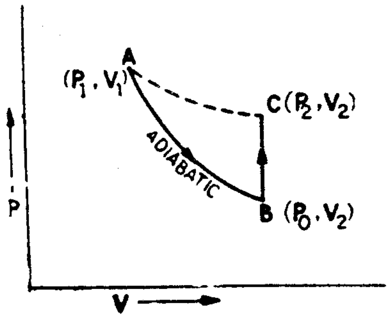


Fig. 6·9

Substituting the value of $\frac{V_2}{V_1}$ in equation (*i*),

$$\frac{P_1}{P_0} = \left(\frac{P_1}{P_2}\right)^{\gamma}$$

Taking logarithms,

$$\log P_1 - \log P_0 = \gamma[\log P_1 - \log P_2]$$

$$\gamma = \frac{\log P_1 - \log P_0}{\log P_1 - \log P_2} \qquad \text{...(iii)}$$

But $$P_1 = P_0+H \text{ and } P_2 = P_0+h$$

$$\therefore \quad \gamma = \frac{\log(P_0+H)-\log P_0}{\log(P_0+H)-\log(P_0+h)}$$

$$\gamma = \frac{\log\left(\frac{P_0+H}{P_0}\right)}{\log\left(\frac{P_0+H}{P_0+h}\right)}$$

$$= \frac{\log\left(1+\frac{H}{P_0}\right)}{\log\left(1+\frac{H-h}{P_0+h}\right)}$$

Approximately, $$\gamma = \frac{\frac{H}{P_0}}{\frac{H-h}{P_0}} = \frac{H}{H-h}$$

Hence $$\gamma = \frac{H}{H-h} \qquad ...(iv)$$

Similarly, γ for any gas can be determined by this method.

Drawbacks. When the stop-cock is opened, a series of oscillations are set up. This is shown by the up and down movement of the liquid in the manometer. Therefore, the exact moment when the stopcock should be closed is not known. The pressure may not be equal to the atmospheric pressure when the stop-cock is closed. It may be higher or less than the atmospheric pressure. Thus the result obtained will not be accurate.

6·21 Partington's Method

Lummer, Pringsheim and Partington designed an apparatus to determine the value of γ. In this method, the pressure and temperature are measured accurately before and after the adiabatic expansion.

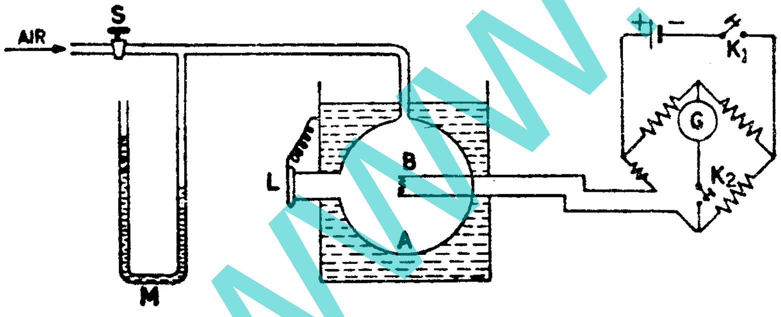


Fig. 6·10

The apparatus consists of a vessel A having a capacity between 130 and 150 litres. The valve L can be opened and closed suddenly. It is controlled by a spring arrangement (Fig. 6·10). Dry air (or gas) at a pressure higher than the atmospheric pressure is forced into the vessel A and the stop-cock S is closed. The oil manometer M is used to measure the pressure of air inside the vessel A. The bolometer B (a platinum wire) and a sensitive galvanometer are used in the Wheatstone's bridge arrangement.

The vessel is surrounded by a constant temperature bath. Let the initial pressure and temperature be P_1 and T_1 (room temperature). The bridge is kept slightly disturbed from the balanced position. The valve L is suddenly opened and closed. The Wheatstones bridge is at once adjusted for balanced position. The temperature of air inside A has decreased due to adiabatic expansion of air. Let the temperature inside be T_0 and the atmospheric pressure P_0. If the apparatus is allowed to remain as such for some time, it will gain heat from the surroundings and the balance point gets disturbed. In order that the balance point remains undisturbed, some pieces of ice are added into the water surrounding the vessel A. When the temperature of water bath is the same as that of air just after adiabatic expansion, the bridge will remain balanced.

The temperature T_0 of the bath represents the temperature of air after the adiabatic expansion.

$$\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_0^{\gamma-1}}{T_0^{\gamma}}$$

$$\left(\frac{P_1}{P_0}\right)^{\gamma-1} = \left(\frac{T_1}{T_0}\right)^{\gamma}$$

$$(\gamma-1)(\log P_1-\log P_0) = \gamma\,[\log T_1-\log T_0]$$

$$\gamma = \frac{\log P_1-\log P_0}{(\log P_1-\log P_0)-(\log T_1-\log T_0)}$$

As P_1, P_0, T_1 and T_0 are known, γ can be calculated. The value of γ for air at 17°C is found to be 1·4034.

Advantages. (1) Due to the large volume of the vessel, the expansion is adiabatic.

(2) The temperatures are measured accurately just before and after the adiabatic expansion.

Drawbacks. This method cannot be used to find the value of γ at higher temperatures because it is not possible to determine the cooling correction accurately.

6·22 Ruchhardt's Experiment

In 1929, Ruchhardt designed an apparatus to find the value of γ. It is based on the principle of mechanics. Air (or gas) is enclosed in a big jar (Fig. 6·11). A tube of uniform area of cross section is fitted and a ball of mass m fits in the tube just like a piston. In the equilibrium position, the ball is at the point A. The pressure P of air inside the vessel, is given by

$$P = P_0+\frac{mg}{A}$$

6·23 Irreversible Process

The thermodynamical state of a system can be defined with the help of the thermodynamical coordinates of the system. The state of a system can be changed by altering the thermodynamical coordinates. Changing from one state to the other by changing the thermodynamical coordinates is called a *process*.

Consider two states of a system *i.e.*, state A and state B. Change of state from A to B or *vice versa* is a process and the direction of the process will depend upon a new thermodynamical coordinate called **entropy**. All processes are not possible in the universe.

Consider the following processes :

(1) Let two blocks A and B at different temperatures T_1 and T_2 $(T_1 > T_2)$ be kept in contact but the system as a whole is insulated from the surroundings. Conduction of heat takes place between the blocks, the temperature of A falls and the temperature of B rises and thermodynamical equilibrium will be reached.

(2) Consider a flywheel rotating with an angular velocity ω. Its initial kinetic energy is $\frac{1}{2}I\omega^2$. After some time the wheel comes to rest and kinetic energy is utilised in overcoming friction at the bearings. The temperature of the wheel and the bearings rises and the increase in their internal energy is equal to the original kinetic energy of the fly wheel.

(3) Consider two flasks A and B connected by a glass tube provided with a stop cock. Let A contain air at high pressure and B is evacuated. The system is isolated from the surroundings. If the stop cock is opened, air rushes from A to B, the pressure in A decreases and the volume of air increases.

All the above three examples though different, are thermodynamical processes involving change in thermodynamical coordinates. Also, in accordance with the first law of thermodynamics, the principle of conservation of energy is not violated because the total energy of the system is conserved. It is also clear that, with the initial conditions described above, the three processes will take place.

Let us consider the possibility of the above three processes taking place in the reverse direction. In the first case, if the reverse process is possible, the block B should transfer heat to A and initial conditions should be restored. In the second case, if the reverse process is possible, the heat energy must again change to kinetic energy and the fly wheel should start rotating with the initial angular velocity ω. In the third case, if the reverse process is possible the air in B must flow back to A and the initial condition should be obtained.

But, it is a matter of common experience, that none of the above conditions for the reverse processes are reached. It means that the direction of the process cannot be determined by knowing the thermodynamical coordinates in the two end states. To determine the direction of the process a new thermodynamical coordinate has been devised by Clausius and this is called the entropy of the system. Similar to internal energy, entropy is also a function of the

state of a system. For any possible process, the entropy of an isolated system should increase or remain constant. The process in which there is a possibility of decrease in entropy cannot take place.

If the entropy of an isolated system is maximum, any change of state will mean decrease in entropy and hence that change of state will not take place.

To conclude, *processes in which the entropy of an isolated system decreases do not take place or for all processes taking place in an isolated system the entropy of the system should increase or remain constant.* It means a process is irreversible if the entropy decreases when the direction of the process is reversed. A process is said to be irreversible if it cannot be retraced back exactly in the opposite direction. During an irreversible process, heat energy is always used to overcome friction. Energy is also dissipated in the form of conduction and radiation. This loss of energy always takes place whether the engine works in one direction or the reverse direction. Such energy cannot be regained. In actual practice all the engines are irreversible. If electric current is passed through a wire, heat is produced. If the direction of the current is reversed, heat is again produced. This is also an example of an irreversible process. All chemical reactions are irreversible. In general, all natural processes are irreversible.

6·24 Reversible Process

From the thermodynamical point of view, a reversible process is one in which an infinitesimally small change in the external conditions will result in all the changes taking place in the direct process but exactly repeated in the reverse order and in the opposite sense. The process should take place at an extremely slow rate. In a reversible cycle, there should not be any loss of heat due to friction or radiation. In this process, the initial conditions of the working substance can be obtained.

Consider a cylinder, containing a gas at a certain pressure and temperature. The cylinder is fitted with a frictionless piston. If the pressure is decreased, the gas expands slowly and maintains a constant temperature (isothermal process). The energy required for this expansion is continuously drawn from the source (surroundings). If the pressure on the piston is increased, the gas contracts slowly and maintains constant temperature (isothermal process). The energy liberated during compression is given to the sink (surroundings). This is also true for an adiabatic process provided the process takes place infinitely slowly.

The process will not be reversible if there is any loss of heat due to friction, radiation or conduction. If the changes take place rapidly, the process will not be reversible. The energy used in overcoming friction cannot be retraced.

The conditions of reversibility for any heat engine or process can be stated as follows :—

(1) The pressure and temperature of the working substance

Reservior – যে কোন জিনিস রাখার পাত্র।

must not differ appreciably from those of the surroundings at any stage of the cycle of operation.

(2) All the processes taking place in the cycle of operation must be infinitely slow.

(3) The working parts of the engine must be completely free from friction.

(4) There should not be any loss of energy due to conduction or radiation during the cycle of operation.

It should be remembered that the complete reversible process or cycle of operation is only an ideal case. In an actual process, there is always loss of heat due to friction, conduction or radiation. The temperature and pressure of the working substance differ appreciably from those of the surroundings.

Q 6.25 Second Law of Thermodynamics

A heat engine is chiefly concerned with the conversion of heat energy into mechanical work. A refrigerator is a device to cool a certain space below the temperature of its surroundings. The first law of thermodynamics is a qualitative statement which does not preclude the possibility of the existence of either a heat engine or a refrigerator. The first law does not contradict the existence of a 100% efficient heat engine or a self-acting refrigerator.

In practice, these two are not attainable. These phenomena are recognized and this led to the formulation of a law governing these two devices. It is called second law of thermodynamics.

A new term reservoir is used to explain the second law. A **reservoir** is a device having infinite thermal capacity and which can absorb, retain or reject unlimited quantity of heat without any change in its temperature.

Kelvin-Planck statement of the second law is as follows :

"It is impossible to get a continuous supply of work from a body (or engine) which can transfer heat with a single heat reservoir. This is a negative statement. According to this statement, a single reservoir at a single temperature cannot continuously transfer heat into work. It means that there should be two reservoirs for any heat engine. One reservoir (called the source) is taken at a higher temperature and the other reservoir (called the sink) is taken at a lower temperature.

According to this statement, zero degree absolute temperature is not attainable because no heat is rejected to the sink at zero degree Kelvin. If an engine works between any temperature higher than zero degree Kelvin and zero degree Kelvin, it means it uses a single reservoir which contradicts Kelvin-Planck's statement of the second law. Similarly, no engine can be 100% efficient.

In a heat engine, the engine draws heat from the source and after doing some external work, it rejects the remaining heat to the sink. The source and sink are of infinite thermal capacity and they maintain constant temperature.

First Part. According to Kelvin, the second law can also be stated as follows :

"It is impossible to get a continuous supply of work from a body by cooling it to a temperature lower than that of its surroundings".

In a heat engine the working substance does some work and rejects the remaining heat to the *sink*. The temperature of the source must be higher than the surroundings and the engine will not work when the temperatures of the source and the sink are the same. Take the case of a steam engine. The steam (working substance) at high pressure is introduced into the cylinder of the engine. Steam expands, and it does external work. The contents remaining behind after doing work are rejected to the surroundings. The temperature of the working substance rejected to the surroundings is higher than the temperature of the surroundings.

If this working substance rejected by the first engine is used in another engine, it can do work and the temperature of the working substance will fall further.

It means that the working substance can do work only if its temperature is higher than that of the surroundings.

Second Part. According to Clausius :

"It is impossible to make heat flow from a body at a lower temperature to a body at a higher temperature without doing external work on the working substance."

This part is applicable in the case of ice plants and refrigerators. Heat itself cannot flow from a body at a lower temperature to a body at a higher temperature. But, it is possible, if some external work is done on the working substance. Take the case of ammonia ice plant. Ammonia is the working substance. Liquid ammonia at low pressure takes heat from the brine solution in the brine tank and is converted to low pressure vapour. External work is done to compress the ammonia vapours to high pressure. This ammonia at high pressure is passed through coils over which water at room temperature is poured. Ammonia vapour gives heat to water at room temperature and gets itself converted into liquid again. This high pressure liquid ammonia is throttled to low pressure liquid ammonia. In the whole process ammonia (the working substance) takes heat from brine solution (at a lower temperature) and gives heat to water at room temperature (at a higher temperature). This is possible only due to the external work done on ammonia by the piston in compressing it. The only work of electricity in the ammonia ice plant is to move the piston to do external work on ammonia. If the external work is not done, no ice plant or refrigerator will work. Hence, it is possible to make heat flow from a body at a lower temperature to a body at a higher temperature by doing external work on the working substance.

Thus, the second law of thermodynamics plays an important part for practical devices *e.g.*, heat engines and refrigerators. The first law of thermodynamics only gives the relation between the work done and the heat produced. But the second law of thermodynamics gives the conditions under which heat can be converted into work.

6·26 Carnot's Reversible Engine

Heat engines are used to convert heat into mechanical work. Sadi Carnot (French) conceived a theoretical engine which is free from all the defects of practical engines. Its efficiency is maximum and it is an ideal heat engine.

For any engine, there are three essential requisites :

(1) **Source.** The source should be at a fixed high temperature T_1 from which the heat engine can draw heat. It has infinite thermal capacity and any amount of heat can be drawn from it at constant temperature T_1.

(2) **Sink.** The sink should be at a fixed lower temperature T_2 to which any amount of heat can be rejected. It also has infinite thermal capacity and its temperature remains constant at T_2.

(3) **Working Substance.** A cylinder with non-conducting sides and conducting bottom contains the perfect gas as the *working substance.*

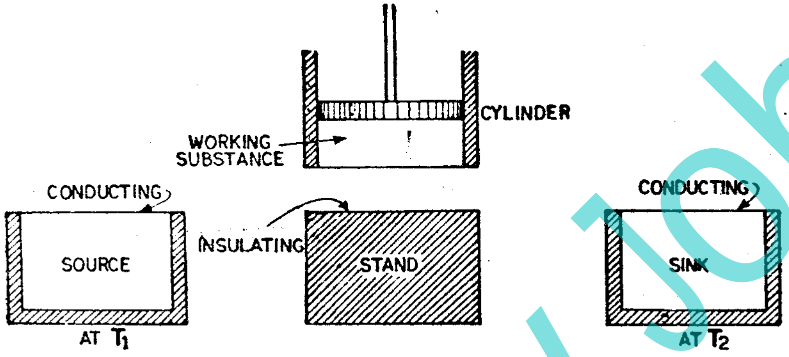


Fig. 6·12.

A perfect non-conducting and frictionless piston is fitted into the cylinder. The working substance undergoes a complete cyclic operation (Fig. 6·12).

A perfectly non-conducting stand is also provided so that the working substance can undergo adiabatic operation.

② Carnot's Cycle

12 b and C
Step 1

(1) Place the engine containing the working substance over the source at temperature T_1. The working substance is also at a temperature T_1. Its pressure is P_1 and volume is V_1 as shown by the point A in Fig. 6·13. Decrease the pressure. The volume of the working substance increases. Work is done by the working substance. As the bottom is perfectly conducting to the source at temperature T_1, it absorbs heat. The process is completely isothermal. The temperature remains constant. Let the amount of heat absorbed by the working substance be H_1 at the temperature T_1. The point B is obtained.

Consider one gram molecule of the working substance.

Work done from A to B (isothermal process)

$$W_1 = \int_{V_1}^{V_2} P.\,dV = RT_1 \log\frac{V_2}{V_1}$$

$$= \text{area } ABGE \qquad \ldots(i)$$

(2) Place the engine on the stand having an insulated top. Decrease the pressure on the working substance. The volume increases. The process is completely adiabatic. Work is done by the working substance at the cost of its internal energy. The temperature falls. The working substance undergoes adiabatic change from B to C. At C the temperature is T_2 (Fig. 6·13).

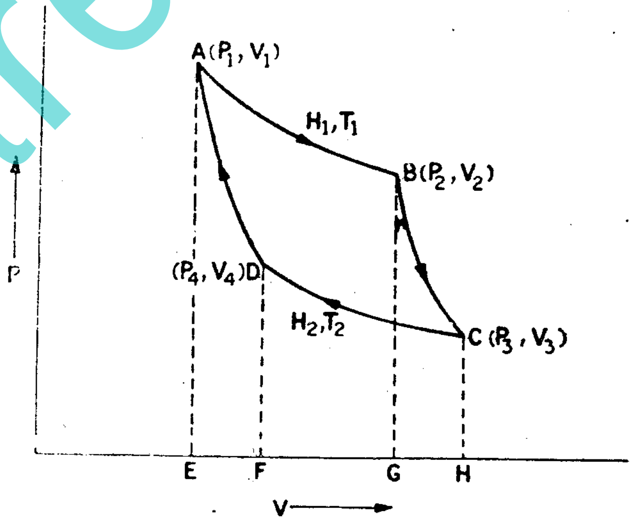


Fig. 6·13

Work done from B to C (adiabatic process)

$$W_2 = \int_{V_2}^{V_3} P.\,dV$$

$$= \int_{V_2}^{V_3} \frac{dV}{V^\gamma}$$

$$= \frac{KV_3^{1-\gamma} - KV_2^{1-\gamma}}{1-\gamma}$$

But PV^γ = constant = K

$P_2V_2 = RT_1$

$P_3V_3 = RT_2$

$P_3V_3^\gamma = P_2V_2^\gamma = K$

$$= \frac{P_3V_3 - P_2V_2}{1-\gamma}$$

$$= \frac{R[T_2 - T_1]}{1-\gamma} = \frac{R[T_1 - T_2]}{\gamma - 1}$$

$$W_2 = \text{Area } BCHG \qquad \ldots(ii)$$

(3) Place the engine on the sink at temperature T_2. Increase the pressure. The work is done on the working substance. As the base is conducting to the sink, the process is isothermal. A quantity of heat H_2 is rejected to the sink at temperature T_2. Finally the point D is reached.

Work done from C to D (isothermal process)

$$W_3 = \int_{V_3}^{V_4} PdV$$

$$= RT_2 \log \frac{V_4}{V_3}$$

$$= -RT_2 \log \frac{V_3}{V_4} \qquad \ldots(iii)$$

$$W_3 = \text{area } CHFD$$

(The —ve sign indicates that work is done on the working substance.)

(4) Place the engine on the insulating stand. Increase the pressure. The volume decreases. The process is completely adiabatic. The temperature rises and finally the point A is reached.

Work done from D to A (adiabatic process).

$$W_4 = \int_{V_4}^{V_1} PdV$$

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

$$W_4 = \text{Area } DFEA \qquad \ldots(iv)$$

[W_2 and W_4 are equal and opposite and cancel each other.] T 12 b end

The net work done by the working substance in one complete cycle

$$= \text{Area } ABGE + \text{Area } BCHG - \text{Area } CHFD - \text{Area } DFEA$$

$$= \text{Area } ABCD$$

The net amount of heat absorbed by the working substance

$$= H_1 - H_2$$

$$\text{Net work} = W_1 + W_2 + W_3 + W_4$$

$$= RT_1 \log \frac{V_2}{V_1} + \frac{R(T_1-T_2)}{\gamma-1} - RT_2 \log \frac{V_3}{V_4} - \frac{R[T_1-T_2]}{\gamma-1}$$

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_3}{V_4} \qquad \ldots(v)$$

The points A and D are on the same adiabatic

$$T_1V_1^{\gamma-1} = T_2V_4^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \qquad \ldots(vi)$$

The points B and C are on the same adiabatic

$$T_1V_2^{\gamma-1} = T_2V_3^{\gamma-1}$$

$$\frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{\gamma-1} \qquad \ldots(vii)$$

From (vi) and (vii)

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

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

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

From equation (v)

$$W = RT_1 \log \frac{V_2}{V_1} - RT_2 \log \frac{V_2}{V_1}$$

$$W = R\left[\log \frac{V_2}{V_1}\right]\left[T_1 - T_2\right]$$

$$\therefore \quad W = H_1 - H_2$$

Efficiency $\eta = \dfrac{\text{Useful output}}{\text{Input}} = \dfrac{W}{H_1}$

Heat is supplied from the source from A to B only.

$$H_1 = RT_1 \log \frac{V_2}{V_1}$$

$$\therefore \quad \eta = \frac{W}{H_1} = \frac{H_1-H_2}{H_1}$$

$$= \frac{R[T_1-T_2] \log\left(\frac{V_2}{V_1}\right)}{RT_1 \log\left(\frac{V_2}{V_1}\right)} = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

or
$$\eta = 1 - \frac{H_2}{H_1}$$

$$\eta = 1 - \frac{T_2}{T_1} \qquad \ldots(viii)$$

The Carnot's engine is perfectly reversible. It can be operated in the reverse direction also. Then it works as a refrigerator. The heat H_2 is taken from the sink and external work is done on the working substance and heat H_1 is given to the source at a higher temperature.

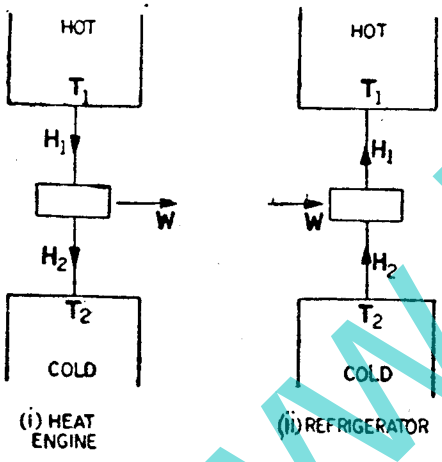
The isothermal process will take place only when the piston moves very slowly to give enough time for the heat transfer to take place. The adiabatic process will take place when the piston moves extremely fast to avoid heat transfer. Any practical engine cannot satisfy these conditions.

All practical engines have an efficiency less than the Carnot's engine.

6·27 Carnot's Engine and Refrigerator

Carnot's cycle is perfectly reversible. It can work as a heat engine and also as a refrigerator. When it works as a heat engine, it absorbs a quantity of heat H_1 from the source at a temperature T_1, does an amount of work W and rejects an amount of heat H_2 to the sink at temperature T_2. When it works as a refrigerator, it absorbs heat H_2 from the sink at temperature T_2. W amount of work is done on it by some external means and rejects heat H_1 to the source at a temperature T_1 (Fig. 6·14). In the second case heat flows from a body at a lower temperature to a body at a higher temperature, with the help of external work done on the working substance and it works as a refrigerator. This will not be possible if the cycle is not completely reversible.

Coefficient of Performance. The amount of heat absorbed at the lower temperature is H_2. The amount of work done by the external process (input energy) $= W$ and the amount of heat rejected $= H_1$. Here H_2 is the desired refrigerating effect.



(i) HEAT ENGINE (ii) REFRIGERATOR

Fig. 6·14

Coefficient of performance

$$= \frac{H_2}{W} = \frac{H_2}{H_1-H_2}$$

Suppose 200 joules of energy is absorbed at the lower temperature and 100 joules of work is done with external help. Then $200+100 = 300$ joules are rejected at the higher temperature.

The coefficient of preformance

$$= \frac{H_2}{W}$$

$$= \frac{H_2}{H_1-H_2}$$

$$= \frac{200}{300-200} = 2$$

Therefore the coefficient of performance of a refrigerator $= 2$.

In the case of a heat engine, the efficiency cannot be more than 100% but in the case of a refrigerator, the coefficient of performance can be much higher than 100%.

Example 6·8. *Find the efficiency of the Carnot's engine working between the steam point and the ice point.*

$$T_1 = 273+100 = 373 \text{ K}$$

$$T_2 = 273+0 = 273 \text{ K}$$

$$\eta = 1-\frac{T_2}{T_1}$$

$$= 1-\frac{273}{373} = \frac{100}{373}$$

$$\% \text{ efficiency} = \frac{100}{373}\times 100$$

$$= \mathbf{26{\cdot}81\%}$$

Example 6·9. *Find the efficiency of a Carnot's engine working between 127°C and 27°C.*

$$T_1 = 273+127 = 400 \text{ K}$$

$$T_2 = 273+27 = 300 \text{ K}$$

$$\eta = 1-\frac{T_2}{T_1}$$

$$= 1-\frac{300}{400} = 0{\cdot}25$$

$$\% \text{ efficiency} = \mathbf{25\%}$$

Example 6·10. *A Carnot's engine whose temperature of the source is 400 K takes 200 calories of heat at this temperature and rejects 150 calories of heat to the sink. What is the temperature of the sink? Also calculate the efficiency of the engine.*

$$H_1 = 200 \text{ cal}; \qquad H_2 = 150 \text{ cal}$$

$$T_1 = 400 \text{ K}; \qquad T_2 = ?$$

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

$$T_2 = \frac{H_2}{H_1}\times T_1$$

$$T_2 = \frac{150}{200}\times 400 = \mathbf{300\ K}$$

$$\eta = 1 - \frac{T_2}{T_1}$$

$$= 1 - \frac{300}{400} = 0{\cdot}25$$

$$\% \text{ efficiency} = \mathbf{25\%}$$

✓ **Example 6·11.** *A Carnot's engine is operated between two reservoirs at temperatures of 450* K *and 350* K. *If the engine receives 1000 calories of heat from the source in each cycle, calculate the amount of heat rejected to the sink in each cycle. Calculate the efficiency of the engine and the work done by the engine in each cycle.* (*1* calorie = *4·2* joules).

$$T_1 = 450 \text{ K}\ ; \qquad T_2 = 350 \text{ K}$$

$$H_1 = 1000 \text{ cal}\ ; \qquad H_2 = ?$$

$$\frac{H_2}{H_1} = \frac{T_2}{T_1}$$

$$H_2 = H_1 \times \frac{T_2}{T_1}$$

$$= \frac{1000 \times 350}{450} = \mathbf{777{\cdot}77 \text{ cals}}$$

$$\eta = 1 - \frac{T_2}{T_1}$$

$$= 1 - \frac{350}{450} = \frac{100}{450}$$

$$= 0{\cdot}2222$$

$$\% \text{ efficiency} = \mathbf{22{\cdot}22\%}$$

Work done in each cycle

$$= H_1 - H_2$$

$$= 1000 - 777{\cdot}77$$

$$= 222{\cdot}23 \text{ cal}$$

$$= 222{\cdot}23 \times 4{\cdot}2 \text{ joules}$$

$$= \mathbf{933{\cdot}33 \text{ joules}}$$

Example 6·12. *A Carnot's engine working as a refrigerator between 260* K *and 300* K *receives 500* calories *of heat from the reservoir at the lower temperature. Calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of work done in each cycle to operate the refrigerator.*

[*Delhi* (*Hons.*) *1974*]

$$H_1 = ? \qquad H_2 = 500 \text{ cal}$$

$$T_1 = 300 \text{ K} \qquad T_2 = 260 \text{ K}$$

$$\frac{H_1}{H_2} = \frac{T_1}{T_2}\ ;$$

$$H_1 = H_2 \cdot \frac{T_1}{T_2}$$

$$H_1 = \frac{500 \times 300}{260} = 576{\cdot}92 \text{ cal}$$

$$W = H_1 - H_2 = 76{\cdot}92 \text{ cal}$$

$$= 76{\cdot}92 \times 4{\cdot}2 \text{ joules}$$

$$= \mathbf{323{\cdot}08 \text{ joules}}$$

Example 6·13. *A Carnot's refrigerator takes heat from water at 0°*C *and discards it to a room at 27°*C. *1* kg *of water at 0°*C *is to be changed into ice at 0°*C. *How many calories of heat are discarded to the room ? What is the work done by the refrigerator in this process ? What is the coefficient of performance of the machine ?*

[*Delhi 1974*]

$$H_1 = ?$$

$$H_2 = 1000 \times 80 = 80{,}000 \text{ cal}$$

$$T_1 = 300 \text{ K}$$

$$T_2 = 273 \text{ K}$$

(1)

$$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

$$H_1 = \frac{H_2 T_1}{T_2}$$

$$= \frac{80{,}000 \times 300}{273}$$

$$H_1 = \mathbf{87{,}900 \text{ Cal}}$$

(2) Work done by the refrigerator

$$= W = J\,(H_1 - H_2)$$

$$W = 4{\cdot}2\ (87{,}900 - 80{,}000)$$

$$W = 4{\cdot}2 \times 7900$$

or

$$W = \mathbf{3{\cdot}183 \times 10^4 \text{ joules}}$$

(3) Coefficient of performance,

$$= \frac{H_2}{H_1 - H_2}$$

$$= \frac{80{,}000}{87{,}900 - 80{,}000}$$

$$= \frac{80{,}000}{7900}$$

$$= \mathbf{10{\cdot}13}$$

Example 6·14. *A carnot engine whose low temperature reservoir is at 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the high temperature reservoir be increased ?* (*Delhi 1971*)

In the first case

$$\eta = 50\% = 0{\cdot}5, \quad T_2 = 273+7 = 280 \text{ K.}$$

$$T_1 = ?$$

$$\eta = 1 - \frac{T_2}{T_1}$$

or
$$0{\cdot}5 = 1 - \frac{280}{T_1}$$

or
$$T_1 = 560\ K$$

In the second case

$$\eta' = 70\% = 0{\cdot}7,$$

$$T_2 = 280\ K,$$

$$T_1' = ?$$

$$\eta' = 1 - \frac{T_2}{T_1'}$$

$$0{\cdot}7 = 1 - \frac{280}{T_1'}$$

or
$$T_1' = 840\ K$$

Increase in temperature = 840—560 = **280 K**

6·28 Carnot's Theorem

The efficiency of a reversible engine does not depend on the nature of the working substance. It merely depends upon the temperature limits between which the engine works.

Carnot's theorem

120 Start

["All the reversible engines working between the same temperature limits have the same efficiency. No engine can be more efficient than a Carnot's reversible engine working between the same two temperatures."]

Consider two reversible engines A and B, working between the temperature limits T_1 and T_2 (Fig. 6·15). A and B are coupled. Suppose A is more efficient than B. The engine A works as a heat engine and B as a refrigerator. The engine A absorbs an amount of heat H_1 from the source at a temperature T_1. It does external work W and transfers it to B. The heat rejected to the sink is H_2 at a temperature T_2. The engine B absorbs heat H_2' from the sink at temperature T_2 and W amount of work is done on the working substance. The heat given to the source at temperature T_1 is H_1'.

Suppose the engine A is more efficient than B.

Efficiency of the engine A

$$= \eta = \frac{H_1 - H_2}{H_1} = \frac{W}{H_1}$$

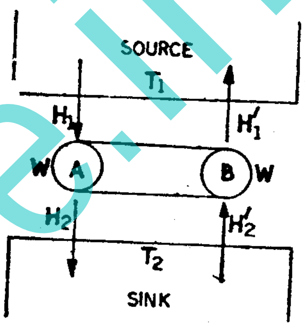


Fig. 6·15.

Efficiency of the engine B

$$= \eta' = \frac{H_1' - H_2'}{H_1'} = \frac{W}{H_1'}$$

Since $\quad \eta > \eta' \ ; \ H_1' > H_1$

Also, $\quad W = H_1 - H_2 = H_1' - H_2'$

$$\therefore \quad H_2' > H_2$$

Thus, for the two engines A and B working as a coupled system, $(H_2' - H_2)$ is the quantity of heat taken from the sink at a temperature T_2 and $(H_1' - H_1)$ is the quantity of heat given to the source at a temperature T_1. Both $(H_2' - H_2)$ and $(H_1' - H_1)$ are positive quantities. It means heat flows from the sink at a temperature T_2 (lower temperature) to the source at a temperature T_1 (higher temperature) *i.e.*, heat flows from a body at a lower temperature to a body at a higher temperature. But, no external work has been done on the system. This is contrary to the second law of thermodynamics. Thus, η cannot be greater than η'. The two engines (reversible) working between the same two temperature limits have the same efficiency. (Moreover, in the case of a Carnot's engine, there is no loss of heat due to friction, conduction or radiation (irreversible processes). Thus, the Carnot's engine has the maximum efficiency. Whatever may be the nature of the working substance, the efficiency depends only upon the two temperature limits.

In a practical engine there is always loss of energy due to friction, conduction, radiation etc. and hence its efficiency is always lower than that of a Carnot's engine.)]

120 finish end.

For the same compression ratio, the efficiency of an Otto engine is more than a diesel engine. In practice, the compression ratio for an Otto engine is from 7 to 9 and for a diesel engine it is from 15 to 20. Due to the higher compression ratio, an actual diesel engine has higher efficiency than the Otto (Petrol) engine. The cylinder must be strong enough to withstand very high pressure.

6·37 Multicylinder Engines

With an engine having one cylinder, the engine works only during the working stroke. The piston moves during the rest of the three strokes due to the momentum of the shaft. In a multicylinder engine (say 4-cylinder engine) the four cylinders are coupled. The working of each cylinder is given below :—

	First	*Second*	*Third*	*Fourth*
First quarter	Working	Exhaust	Compression	Charging
Second quarter	Exhaust	Charging	Working	Compression
Third quarter	Charging	Compression	Exhaust	Working
Fourth quarter	Compression	Working	Charging	Exhaust

In this way, the power of the engine increases and the shaft gets momentum during each quarter cycle.

6·38 Clapeyron Latent Heat Equation

Consider the isothermals *FBAE* at temperature $T+dT$ and *GCDH* at temperature T. Here *EA* and *HD* show the liquid state of the substance. At *A* and *D* the substance is purely in the liquid state (Fig. 6·23). From *A* to *B* or *D* to *C* the substance is in transition from the liquid to the gaseous state and *vice versa*. At *B* and *C* the substance is purely in the gaseous state. From *B* to *F* or *C* to *G* the substance is in the gaseous state. Join *A* to *D* and *B* to *C* by dotted lines.

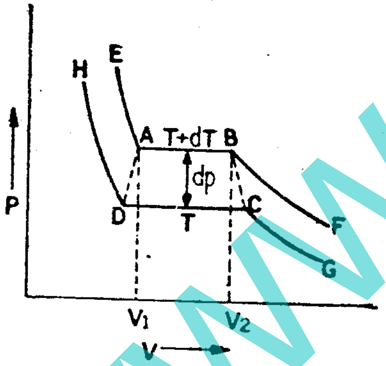


Fig. 6·23

The cycle *ABCD* represents a complete cycle and Carnot's theorem can be applied. Suppose the volume at the point *A* is V_1 and temperature is $T+dT$. The pressure is just below its saturation pressure and the liquid begins to evaporate and at the point *B* the volume is V_2. The substance is in the vapour state. Suppose the mass of the liquid at *B* is one gram. The amount of heat absorbed is H_1. Here $H_1=L+dL$, where $L+dL$ is the latent heat of the liquid at temperature $(T+dT)$.

At the point *B*, the pressure is decreased by dP. The vapour will expand and its temperature falls. The temperature at *C* is *T*. At this pressure and temperature *T*, the gas begins to condense and is converted into the liquid state. At the point *D*, the substance is in the liquid state. From *C* to *D*, the amount of heat rejected (given out) is H_2. Here $H_2 = L$ where *L* is the latent heat at temperature *T*. By increasing the pressure a little, the original point *A* is restored. The cycle *ABCDA* is completely reversible. Applying the principle of the Carnot's reversible cycle

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

or

$$\frac{H_1}{H_2} = \frac{T_1}{T_2}$$

$$\frac{H_1-H_2}{H_2} = \frac{T_1-T_2}{T_2}$$

Here,

$$H_1 = L+dL,\ H_2 = L,$$
$$T_1 = T+dT,\ T_2 = T$$
$$H_1-H_2 = L+dL-L = dL$$
$$T_1-T_2 = T+dT-T = dT$$

$$\therefore \quad \frac{dL}{L} = \frac{dT}{T}$$

The area of the figure

$$ABCD = H_1-H_2 = dL$$
$$= dP(V_2-V_1)$$

$$\therefore \quad \frac{dP\,(V_2-V_1)}{L} = \frac{dT}{T}$$

$$\frac{dP}{dT} = \frac{L}{T\,(V_2-V_1)} \qquad \text{...}(i)$$

This is called the Clapeyron's latent heat equation.

Applications. (1) *Effect of change of pressure on the melting point.*

When a solid is converted into a liquid, there is change in volume.

(*i*) If V_2 is greater than V_1

$\frac{dP}{dT}$ is a positive quantity. It means that the rate of change of

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pressure with respect to temperature is positive. In such cases, the melting point of the substance will increase with increase in pressure and *vice versa*.

(*ii*) If V_2 is less than V_1.

$\frac{dP}{dT}$ is a negative quantity. It means that the rate of change of pressure with respect to temperature is negative. In such cases, the melting point of the substance will decrease with increase in pressure and *vice versa*. In the case of melting ice, the volume of water formed is less than the volume of ice taken. Hence $V_2 < V_1$.

Therefore, the melting point of ice decreases with increase in pressure. Hence ice will melt at a temperature lower than zero degree centigrade at a pressure higher than the normal pressure.

Ice melts at 0°C only at a pressure of 76 cm of Hg.

(2) *Effect of change of pressure on the boiling point.*

When a liquid is converted into a gaseous state, the volume V_2 of the gas is always greater than the corresponding volume V_1 of the liquid *i.e.* $V_2 > V_1$.

Therefore, $\frac{dP}{dT}$ is a +ve quantity.

With increase in pressure, the boiling point of a substance increases and *vice versa*. The liquid will boil at a lower temperature under reduced pressure. In the case of water, the boiling point increases with increase in pressure and *vice versa*. Water boils at 100°C only at 76 cm of Hg pressure. In the laboratories, while preparing steam, the boiling point is less than 100°C because the atmospheric pressure is less than 76 cm of Hg. In pressure cookers, the liquid boils at a higher temperature because the pressure inside is more than the atmospheric pressure.

Example 6·17. *Calculate the depression in the melting point of ice produced by one atmosphere increase of pressure. Given latent heat of ice = 80* cal per gram *and the specific volumes of 1* gram *of ice and water at 0°C are 1·091* cm³ *and 1·000* cm³ *respectively.* (*Panjab 1963*)

Here

$$L = 80 \text{ cal} = 80 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$

$$T = 273 \text{ K}$$

$$dP = 1 \text{ atmosphere}$$

$$= 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$V_1 = 1{\cdot}091 \text{ cm}^3$$

$$V_2 = 1{\cdot}000 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP.T.(V_2 - V_1)}{L}$$

$$= \frac{76 \times 13{\cdot}6 \times 980 \times 273(1 - 1{\cdot}091)}{80 \times 4{\cdot}2 \times 10^7}$$

$$= -\mathbf{0{\cdot}0074 \text{ K}}$$

Therefore, the *decrease* in the melting point of ice with an increase in pressure of one atmosphere

$$= \mathbf{0{\cdot}0074 \text{ K}} = \mathbf{0{\cdot}0074°C}$$

Example 6·18. *Find the increase in the boiling point of water at 100°*C *when the pressure is increased by one atmosphere. Latent heat of vaporisation of steam is 540* cal/gram *and 1* gram *of steam occupies a volume of 1677* cm³.

$$dP = 76 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$T = 100 + 273$$

$$= 373 \text{ K}$$

$$L = 540 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$

$$V_1 = 1{\cdot}000 \text{ cm}^3$$

$$V_2 = 1677 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$dT = \frac{dP \times T(V_2 - V_1)}{L}$$

$$= \frac{76 \times 13{\cdot}6 \times 980 \times 373 \times 1676}{540 \times 4{\cdot}2 \times 10^7}$$

$$= \mathbf{27{\cdot}92°C}$$

Therefore, the *increase* in the boiling point of water with an increase in pressure of one atmosphere

$$= \mathbf{27{\cdot}92°C}$$

$$= \mathbf{27{\cdot}92 \text{ K}}$$

Example 6·19. *Calculate the change in temperature of boiling water when the pressure is increased by 27·12* mm *of* Hg. *The normal boiling point of water at atmospheric pressure is 100°*C.

Latent heat of steam = *537* cal/g

and specific volume of steam = *1674* cm³ (*Delhi 1974*)

$$dP = 2{\cdot}712 \times 13{\cdot}6 \times 980 \text{ dynes/cm}^2$$

$$T = 100 + 273 = 373 \text{ K}$$

$$L = 537 \times 4{\cdot}2 \times 10^7 \text{ ergs}$$

$$V_1 = 1{\cdot}000 \text{ cm}^3$$

$$V_2 = 1674 \text{ cm}^3$$

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)}$$

$$= \mathbf{2{\cdot}792\ K}$$
$$= \mathbf{2{\cdot}792°C}$$

Therefore, the *increase* in the boiling point of water with an increase of 0·1 atmosphere pressure

$$= \mathbf{2{\cdot}792\ K}$$
$$= \mathbf{2{\cdot}792°C}$$

Example 6·23. *Calculate the change in the melting point of ice when it is subjected to a pressure of 100 atmospheres.*

Density of ice = *0·917* g/cm³ *and*

Latent heat of ice = *336* J/g

(*Delhi 1972*)

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$
$$dP = 100-1$$
$$= 99 \text{ atmospheres}$$
$$dP = 99\times 76\times 13{\cdot}6\times 980 \text{ dynes/cm}^2$$
$$L = 336 \text{ J/g}$$
$$= 336\times 10^7 \text{ ergs/g}$$
$$T = 273 \text{ K}$$
$$(V_2-V_1) = 1-\frac{1}{0{\cdot}917}$$
$$= -\frac{0{\cdot}083}{0{\cdot}917}$$
$$= -0{\cdot}091 \text{ cm}^3$$
$$\therefore \quad dT = \frac{T\,dP(V_2-V_1)}{L}$$
$$dT = \frac{273\times 99\times 76\times 13{\cdot}6\times 980\times(-0{\cdot}091)}{336\times 10^7}$$
$$dT = -0{\cdot}7326 \text{ K}$$
$$= \mathbf{-0{\cdot}7326°C}$$

The decrease in the melting point of ice with a pressure of 100 atmospheres

$$= \mathbf{0{\cdot}7326°C}$$

Example 6·24 *Calculate the pressure required to lowc melting point of ice by 1°C.*

(*L = 79·6* cal/g, *specific volume of water at 0°C = 1·000* cm· *specific volume of ice at 0°C = 1 091* cm³ *and 1 atmosphere pressure = 1·013 × 10⁶* dynes/cm³).

(*Delhi 1973*)

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$

$$dT = -1 \text{ K}$$
$$T = 273 \text{ K}$$
$$V_2-V_1 = -0{\cdot}091 \text{ cm}^3$$
$$L = 79{\cdot}6 \text{ cal/g}$$
$$= 79{\cdot}6\times 4{\cdot}18\times 10^7 \text{ ergs/g}$$
$$dP = \frac{L\cdot dT}{T(V_2-V_1)}$$
$$dP = \frac{79{\cdot}6\times 4{\cdot}18\times 10^7\times 1}{273\times 0{\cdot}091} \text{ dynes/cm}^2$$

or

$$dP = \frac{79{\cdot}6\times 4{\cdot}18\times 10^7}{273\times 0\ 091\times 1\ 013\times 10^6} \text{ atmospheres}$$
$$dP = 135{\cdot}2 \text{ atmospheres}$$

∴ Pressure required

$$= 135{\cdot}2+1$$
$$= \mathbf{136{\cdot}2\ atmospheres}$$

Example 6·25. *Water boils at a temperature of 101°C at a pressure of 787* mm of Hg. *1 gram of water occupies 1,601* cm³ *on evaporation. Calculate the latent heat of steam. J = 4·2 × 10⁷* ergs/cal.

[*Delhi (Hons.) 1971*]

$$\frac{dP}{dT} = \frac{L}{T(V_2-V_1)}$$
$$dP = 787-760$$
$$= 27 \text{ mm of Hg}$$
$$= 2{\cdot}7 \text{ cm of Hg}$$
$$= 2{\cdot}7\times 13{\cdot}6\times 980 \text{ dynes/cm}^2$$
$$dT = 1°\text{C} = 1\text{K}$$
$$T = 373 \text{ K}$$
$$V_2-V_1 = 1{,}601-1 = 1{,}600 \text{ cm}^3$$
$$L = ?$$
$$L = \frac{T\,dP\,(V_2-V_1)}{dT}$$
$$L = \frac{373\times 2{\cdot}7\times 13{\cdot}6\times 980\times 1{,}600}{1} \text{ ergs/g}$$
$$L = \frac{373\times 2{\cdot}7\times 13{\cdot}6\times 980\times 1{,}600}{4{\cdot}2\times 10^7} \text{ cal/g}$$
$$L = \mathbf{511{\cdot}3\ cal/g}$$

Example 6·26. *When lead is melted at atmospheric pressure, (the melting point is 600* K) *the density decreases from 11·01 to 10·65* g/cm³ *and the latent heat of fusion is 24·5* J/g. *What is the melting point at a pressure of 100 atmospheres ?*

[*Delhi (Hons.) 1972*]

Here $H_1 = +1000$ joules

$H_2 = -800$ joules (since heat is rejected)

$T_1 = 500$ K

$T_2 = 300$ K

$$\sum \frac{H}{T} = \frac{1000}{500} + \frac{-800}{300}$$

$$= -\frac{2}{3} \text{ joule/degree}$$

(3) Consider a Carnots reversible engine working between the temperatures 500 K and 300 K. Suppose 1000 joules of heat energy is drawn from the high temperature reservoir.

Here $$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

$$\frac{1000}{500} = \frac{H_2}{300}$$

or $H_2 = 600$ joules

$$\sum \frac{H}{T} = \frac{H_1}{T_1} + \frac{H_2}{T_2}$$

Here $H_1 = +1000$ joules

$H_2 = -600$ joules

$T_1 = 500$ K

$T_2 = 300$ K

$$\therefore \quad \sum \frac{H}{T} = \frac{1000}{500} + \frac{(-600)}{300}$$

or $$\sum \frac{H}{T} = 0$$

This example shows $\sum \frac{H}{T} = 0$, only in the limiting case and in no case $\sum \frac{H}{T}$ is greater than zero.

6·42. Entropy and the Second Law of Thermodynamics

Consider a closed system undergoing a reversible process from state 1 to state 2 along the path A and from state 2 to state 1 along the path B (Fig. 6·25). As this is a reversible cyclic process

$$\oint \frac{\delta H}{T} = 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \qquad \ldots(i)$$

Now consider the reversible cycle from state 1 to state 2 along the path A and from state 2 to state 1 along the path C.

For this reversible cyclic process

$$\int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} = 0 \qquad \ldots(ii)$$

From equations (i) and (ii)

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2C}^{1C} \frac{\delta H}{T} \qquad \ldots(iii)$$

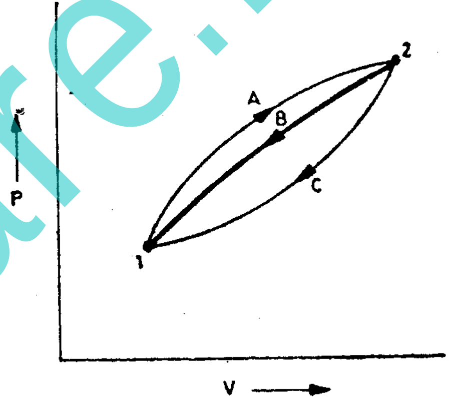

Fig. 6·25

This shows that $\int \frac{\delta H}{T}$ has the same value for all the reversible paths from state 2 to state 1. The quantity $\int \frac{\delta H}{T}$ is independent of the path and is a function of the end states only, therefore it is a property.

This property is called entropy. Entropy is a thermodynamical property and is defined by the relation

$$dS = \frac{\delta H}{T} \qquad \ldots(iv)$$

or $$S_2 - S_1 = \int_1^2 \frac{\delta H}{T} \qquad \ldots(v)$$

The quantity $S_2 - S_1$ represents the change in entropy of the system when it is changed from state 1 to state 2.

6·43 Entropy changes of a Closed System During an Irreversible Process

Consider a reversible cycle where the state is changed from 1 to 2 along the path A and 2 to 1 along the path B (Fig. 6·26).

For a reversible cyclic process

$$\oint \delta H = 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2B}^{1B} \frac{\delta H}{T} = 0 \qquad \text{...(i)}$$

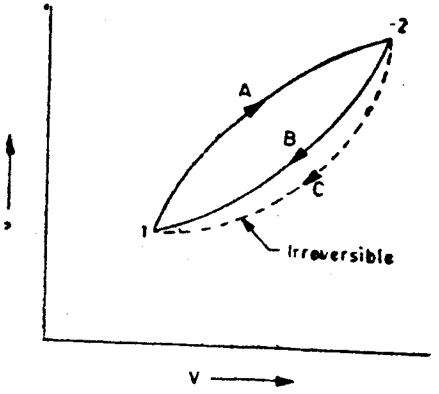

Fig. 6·26

Now consider an irreversible path C from state 2 to state 1.

Applying Clausius inequality for the cycle of processes A and C

$$\oint \frac{\delta H}{T} \leq 0$$

$$\therefore \quad \int_{1A}^{2A} \frac{\delta H}{T} + \int_{2C}^{1C} \frac{\delta H}{T} \leq 0 \qquad \text{...(ii)}$$

From equations (*i*) and (*ii*)

$$\int_{2B}^{1B} \frac{\delta H}{T} - \int_{2C}^{1C} \frac{\delta H}{T} \geq 0$$

Since path B is reversible and entropy is a property

$$\int_{2B}^{1B} \frac{\delta H}{T} = \int_{2B}^{1B} dS = \int_{2C}^{1C} dS$$

$$\therefore \quad dS \geq \frac{\delta H}{T} \qquad \text{...(iii)}$$

$$S_2 - S_1 \geq \int_1^2 \delta H \qquad \text{...(iv)}$$

To conclude,

For a reversible process

$$S_2 - S_1 = \int_1^2 \frac{\delta H}{T}$$

nd for an irreversible process

$$S_2 - S_1 > \int_1^2 \frac{\delta H}{T}$$

Equation (*iv*) shows that the effect of irreversibility is always to increase the entropy of a system.

6·44 Entropy

Consider adiabatics L and M on the $P-V$ indicator diagram (Fig. 6·27). All along the adiabatic L, with change in pressure there is change in volume and temperature. This shows that all along the adiabatics L or M, there is change of temperature. Consider the isothermals at temperatures T_1, T_2 and T_3. $ABCD$ represents the Carnot's reversible cycle. From A to B, heat energy H_1 is absorbed at temperature T_1. From C to D, heat energy H_2 is rejected at temperature T_2.

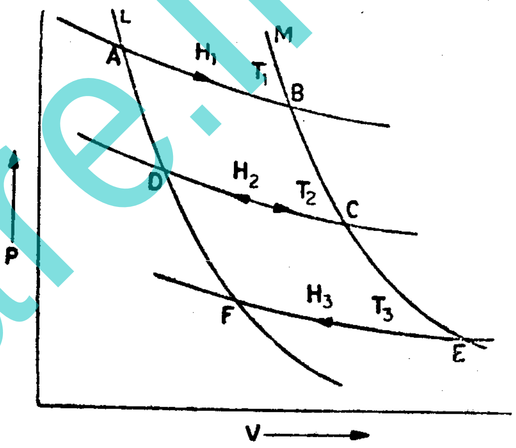

Fig. 6·27

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Similarly considering the cycle $DCEF$

$$\frac{H_2}{T_2} = \frac{H_3}{T_3}$$

$$\therefore \quad \frac{H_1}{T_1} = \frac{H_2}{T_2} = \frac{H_3}{T_3} = \text{constant}$$

From one adiabatic to the other adiabatic, heat energy is either absorbed or rejected. The quantity of heat absorbed or rejected is not constant but it depends upon the temperature. Higher the temperature, more is the heat energy absorbed or rejected and *vice versa*. The quantity H/T between two adiabatics is constant and this is called the change in entropy. Let the entropy for the adiabatics L and M be S_1 and S_2 respectively.

Here S_1 and S_2 are arbitrary quantities.

$$S_2 - S_1 = \frac{H}{T} \text{ constant.}$$

If the adiabatics are very close, and the heat absorbed or rejected is δH at a temperature T,

Change in entropy

$$dS = \frac{\delta H}{T} \qquad \ldots(1)$$

In general, the change in entropy

$$= \int_{S_1}^{S_2} dS = S_2 - S_1 = \int_A^B \frac{\delta H}{T} \qquad \ldots(2)$$

$\int_A^B \frac{\delta H}{T} = \int_{S_1}^{S_2} dS$ represents the thermodynamic co-ordinate of a system. This integral refers to the value of the function at the final state minus its value at the initial state. This function is called entropy and is represented by S. Moreover, dS is an exact differential since it is the differential of an actual function.

All along the adiabatic, $\delta H = 0$. Therefore, the change in entropy along an adiabatic is zero or the entropy all along the adiabatic is constant. *Thus entropy remains constant during an adiabatic reversible process. When heat is absorbed during a process there is increase in entropy and when heat is rejected during a process there is decrease in entropy.*

6·45 Change in Entropy in a Reversible Process (Carnot's Cycle)

Consider a complete reversible process [Carnot's cycle] *ABCDA* (Fig. 6·28). From A to B, heat energy H_1 is absorbed by the working substance at temperature T_1. The gain in entropy of the working substance from A to $B = H_1/T_1$. (H_1/T_1 is the decrease in entropy of the source from which the amount of heat H_1 is drawn at a temperature T_1). From B to C there is no change in entropy because BC is an adiabatic. From C to D, heat energy H_2 is rejected by the working substance at a temperature T_2. The loss in entropy of the working substance from C to $D = H_2/T_2$. (H_2/T_2 is also the gain in entropy of the sink to which the amount of heat H_2 is rejected at a temperature T_2). From D to A there is no change in entropy. Thus

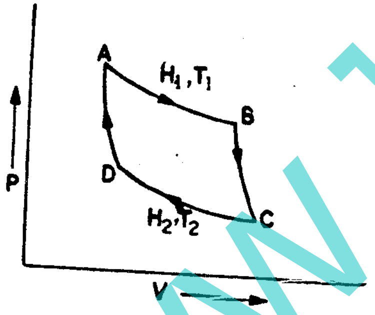

Fig. 6·28

the total gain in entropy by the working substance in the cycle *ABCDA*

$$= \frac{H_1}{T_1} \quad \frac{H_2}{T_2}$$

But for a complete reversible process

$$\frac{H_1}{T_1} = \frac{H_2}{T_2}$$

Hence the total change in entropy of the working substance in a complete reversible process

$$= \oint dS = \frac{H_1}{T_1} - \frac{H_1}{T_2} = 0.$$

6·46 Change in Entropy in an Irreversible Process

In an irreversible process like conduction or radiation, heat is lost by a body at a higher temperature T_1 and is gained by the body at a lower temperature T_2. Here T_1 is greater than T_2.

Let the quantity of heat given out by a body at a temperature T_1 be H and the heat gained by the body at a temperature T_2 be H. Consider the hot and the cold bodies as one system.

$$\text{Loss in entropy of the hot body} = \frac{H}{T_1}$$

$$\text{Gain in entropy of the cold body} = \frac{H}{T_2}$$

Therefore, the total increase in entropy of the system

$$= \frac{H}{T_2} - \frac{H}{T_1}$$

It is a positive quantity because T_2 is less than T_1. Thus the entropy of the system increases in all irreversible processes.

6·47 Third Law of Thermodynamics

In all heat engines, there is always loss of heat in the form of conduction, radiation and friction. Therefore, in actual heat engines

$$\frac{H_1}{T_1} \text{ is not equal to } \frac{H_2}{T_2} \ldots$$

$\therefore$ $\frac{H_1}{T_1} - \frac{H_2}{T_2}$ is not zero but it is a positive quantity. When cycle after cycle is repeated, the entropy of the system increases and tends to a maximum value. When the system has attained the maximum value, a stage of stagnancy is reached and no work can be done by the engine at this stage. In this universe the entropy is increasing and ultimately the universe will also reach a maximum value of entropy when no work will be possible. With the increase in entropy, the disorder of the molecules of a substance increases. The entropy is also a measure of the disorder of the system. With decrease in entropy, the disorder decreases. *At absolute zero temperature, the entropy tends to zero and the molecules of a substance or a system are in perfect order (well arrenged). This is the third law of thermodynamics.*

Example. The molecules are more free to move in the gaseous state than in the liquid state. The entropy is more in the gaseous state than in the liquid state. The molecules are more free to move in the liquid state than in the solid state. The entropy is more in the liquid state than in the solid. Thus when a substance is converted from a solid to a liquid and then from the liquid to the solid state, the entropy increases and *vice versa*. When ice is converted into water and then into steam, the entropy and disorder of the molecules increase. When steam is converted into water and then into ice, the entropy and disorder of the molecules decrease. *Hence entropy is a measure of the disorder of the molecules of the system.*

By any ideal procedure, it is impossible to bring any system to absolute zero temperature performing a finite number of operations. This is called the principle of unattainability of absolute zero. Thus according to Fowler and Guggenheim, the unattainability principle is called the third law of thermodynamics.

6·48 Temperature-Entropy Diagram

The temperature-entropy diagram is used in engineering and meteorology. Consider the Carnot's cycle *ABCDA* [Fig. 6·29 (*i*)]. From *A* to *B*, heat energy H_1 is absorbed at temperature T_1. The increase in entropy S_1 takes place from *A* to *B* [Fig. 6·29 (*ii*)]. From *B* to *C*, there is no change in entropy. The tempetature decreases at constant entropy. From *C* to *D*, there is decrease in entropy (S_2) at constant temperature T_2. From *D* to *A*, there is no change in entropy but the temperature increases.

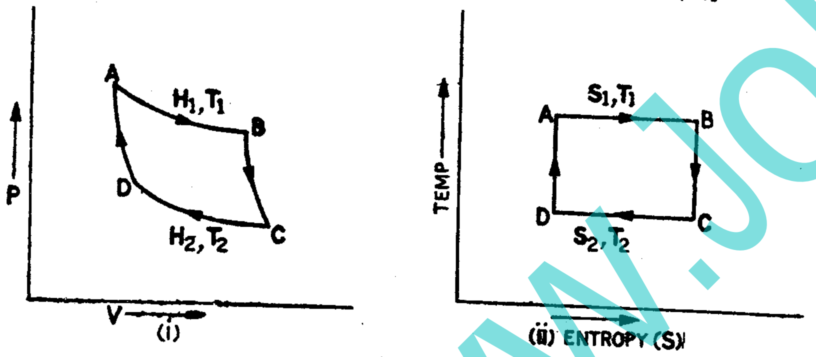

Fig. 6·29

The area *ABCD* in the temperature-entropy diagram represents the actual amount of energy converted into work [Fig. 6·29 (*ii*)].

$$\text{The area} \quad ABCD = S_1(T_1-T_2) = S_2(T_1-T_2)$$

$$\text{But} \quad S_1 = \frac{H_1}{T_1} \text{ and } S_2 = \frac{H_2}{T_2}$$

$$\text{Here} \quad S_1 = S_2 = \frac{H_1}{T_1} = \frac{H_2}{T_2} = \frac{H_1-H_2}{T_1-T_2}$$

$$\therefore \text{ Area} \quad ABCD = \frac{(H_1-H_2)(T_1-T_2)}{T_1-T_2} = H_1-H_2$$

Therefore, the area *ABCD* represents the energy converted to work

$$\text{Efficiency} = \frac{H_1-H_2}{H_1} = 1-\frac{H_2}{H_1} = 1-\frac{T_2}{T_1}$$

Here H_2 is the unavailable energy.

$$H_2 = \frac{H_1}{T_1} \times T_2 = S_1 \times T_2$$

The unavailable energy depends on the change in entropy at temperature T_1 and the temperature T_2.

6·49 Entropy of Perfect Gas

Consider one gram of a perfect gas at a pressure *P*, volume *V* and temperature *T*. Let the quantity of heat given to the gas be δH.

$$\delta H = dU + \delta W$$

$$\delta H = 1 \times C_V \times dT + \frac{PdV}{J} \quad \ldots(i)$$

$$\delta H = TdS$$

$$\therefore \quad TdS = C_V dT + \frac{PdV}{J} \quad \ldots(ii)$$

$$\text{Also} \quad PV = rT$$

$$\text{or} \quad P = \frac{rT}{V}$$

$$\therefore \quad TdS = C_V dT + \frac{rT.dV}{JV}$$

$$dS = C_V \frac{dT}{T} + \frac{r}{J}\frac{dV}{V}$$

$$\text{Integrating,} \quad \int_{S_1}^{S_2} dS = C_V \int_{T_1}^{T_2} \frac{dT}{T} + \frac{r}{J}\int_{V_1}^{V_2} \frac{dV}{V}$$

$$S_2-S_1 = C_V \log_e \frac{T_2}{T_1} + \frac{r}{J} \log_e \frac{V_2}{V_1} \quad \ldots(iii)$$

$$S_2-S_1 = C_v \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1} + \frac{r}{J} \times 2{\cdot}3026 \log_{10} \frac{V_2}{V_1} \quad \ldots(iv)$$

The change in entropy can be calculated in terms of pressure also.

$$PV = rT$$

Differentiating

$$PdV + VdP = rdT$$

$$\text{or} \quad PdV = rdT - VdP$$

Substituting the value of PdV in equation (*ii*)

$$TdS = C_V \times dT + \frac{rdT}{J} - \frac{VdP}{J}$$

$$TdS = \left(C_V + \frac{r}{J}\right) dT - \frac{VdP}{J}$$

But $$C_V + \frac{r}{J} = C_P$$

$\therefore$ $$dS = C_P \frac{dT}{T} - \frac{VdP}{JT}$$

Also $$PV = rT$$

or $$\frac{V}{T} = \frac{r}{P}$$

$\therefore$ $$dS = C_P \frac{dT}{T} - \frac{r}{J} \frac{dP}{P}$$

Integrating

$$\int_{S_1}^{S_2} dS = C_P \int_{T_1}^{T_2} \frac{dT}{T} - \frac{r}{J} \int_{P_1}^{P_2} \frac{dP}{P}$$

$$S_2 - S_1 = C_P \log_e \frac{T_2}{T_1} - \frac{r}{J} \log_e \frac{P_2}{P_1} \qquad \ldots(v)$$

$$S_2 - S_1 = C_P \times 2\cdot3026 \times \log_{10} \frac{T_2}{T_1} - \frac{r}{J} \times 2\cdot3026 \log_{10} \frac{P_2}{P_1} \qquad \ldots(vi)$$

Note. r is the ordinary gas constant and has to be taken in units of work, C_P represents the specific heat for 1 gram of a gas at constant pressure.

If C_P represents gram molecular specific heat of a gas at constant pressure and R the universal gas constant, then

$$S_2 - S_1 = C_P \times 2\cdot3026 \log_{10} \frac{T_2}{T_1} - \frac{R}{J} \times 2\cdot3026 \log_{10} \frac{P_2}{P_1} \qquad \ldots(vii)$$

Example 6·29. *Calculate the change in entropy when 10 grams of ice at 0°C is converted into water at the same temperature.*

(*Punjab 1963, Delhi 1975*)

Heat absorbed by 10 g of ice at 0°C when it is converted into water at 0°C = 10 × 80 = 800 cal

$\therefore$ $$\delta H = 800 \text{ cal}$$

$$T = 0°\text{C} = 273 \text{ K}$$

The gain in entropy

$$dS = \frac{\delta H}{T}$$

$$= \frac{800}{273} = \mathbf{2\cdot93\ cal/K}$$

Example 6·30. *Calculate the change in entropy when 5 kg of water at 100°C is converted into steam at the same temperature.*

Heat absorbed by 5 kg of water at 100°C when it is converted into steam at 100°C

$$= 5000 \times 540$$

$$= 2700000 \text{ cal}$$

$\therefore$ $$\delta H = 2700000 \text{ cal}$$

The gain in entropy

$$dS = \frac{\delta H}{T}$$

$$= \frac{2700000}{373} = \mathbf{7240\ cal/K}$$

Example 6·31. *Calculate the increase in entropy when 1 gram of ice at −10°C is converted into steam at 100°C. Specific heat of ice = 0·5, latent heat of ice = 80 cal/g, latent heat of steam = 540 cal/g.*

(*Bombay 1974 ; Delhi 1973*)

(1) Increase in entropy when the temperature of 1 gram of ice increases from −10°C to 0°C

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \int_{T_1}^{T_2} \frac{dT}{T}$$

$$= ms \log_e \frac{T_2}{T_1}$$

$$= ms \times 2\cdot3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1 \times 0\cdot5 \times 2\cdot3026 \log_{10} \frac{273}{263}$$

$$= 0\cdot01865 \text{ cal/K}$$

(2) Increase in entropy when 1 gram of ice at 0°C is converted into water at 0°C.

$$dS = \frac{\delta H}{T}$$

$$= \frac{80}{273} = 0\cdot293 \text{ cal/K}$$

(3) Increase in entropy when the temperature of 1 g of water is raised from 0°C to 100°C.

$$dS = \int_{T_1}^{T_2} \frac{\delta H}{T}$$

$$= ms \times 2{\cdot}3026 \log_{10} \frac{T_2}{T_1}$$

$$= 1 \times 1 \times 2{\cdot}3026 \log_{10} \frac{373}{273}$$

$$= 0{\cdot}312 \text{ cal/K}$$

(4) Increase in entropy when 1 g water at 100°C is converted into steam at 100°C

$$dS = \frac{\delta H}{T}$$

$$= \frac{540}{373} = 1{\cdot}447 \text{ cal/K}$$

Total increase in entropy

$$= 0{\cdot}01865 + 0{\cdot}293 + 0{\cdot}312 + 1{\cdot}447$$

$$= \mathbf{2{\cdot}07065\ cal/K}$$

Example 6·32. *One gram molecule of a gas expands isothermally to four times its volume. Calculate the change in its entropy in terms of the gas constant.*

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

But $PV = RT$

or $P = \frac{RT}{V}$

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

$$= RT \log_e \frac{V_2}{V_1}$$

Here $\frac{V_2}{V_1} = 4$

$$W = RT \times 2{\cdot}3026 \log_{10} (4)$$

Here, W and R are in the units of work

Gain in entropy $= \frac{\delta H}{T}$

$$= \frac{W}{JT} = \frac{RT \times 2{\cdot}3026 \log_{10} 4}{JT}$$

$$= \mathbf{1{\cdot}387 \frac{R}{J}\ cal/K}$$

Example 6·33. *50 grams of water at 0°C is mixed with an equal mass of water at 83°C. Calculate the resultant increase in entropy.* *(Punjab 1963)*

(*i*) $m_1 = 50$ g ; $T_1 = 273$ K

$m_2 = 50$ g ; $T_2 = 353$ K

Let the final temperature of the mixture be T K

$$m_1 s \times (T - T_1) = m_2 s (T_2 - T)$$

$$50 \times 1 \times (T - 273) = 50 \times 1 \times (353 - T)$$

$$T = 313 \text{ K}$$

(*ii*) Change in entropy by 50 g of water when its temperature rises from 273 K to 313 K.

$$= \frac{\delta H}{T}$$

$$= ms \int_{T_1}^{T} \frac{dT}{T}$$

$$= 50 \times 1 \times \log_e \frac{313}{273}$$

$$= 50 \times 2{\cdot}3026 \times \log_{10} \frac{313}{273}$$

$$= +6{\cdot}829 \text{ cal/K}$$

Here, the +ve sign indicates gain in entropy.

(*iii*) Change in entropy by 50 g of water when its temperature falls from 353 K to 313 K

$$= \frac{\delta H}{T} = ms \int_{T_2}^{T} \frac{dT}{T}$$

$$= 50 \times 1 \times \log_e \frac{313}{353}$$

$$= 50 \times 2{\cdot}3026 \times \log_{10} \frac{313}{353}$$

$$= -6{\cdot}023 \text{ cal/K}$$

Here, the –ve sign indicates loss in entropy.

Therefore, the total gain in entropy of the system

$$= 6{\cdot}829 - 6{\cdot}023$$

$$= \mathbf{0{\cdot}806\ cal/K}$$

Example 6·34. *Calculate the change in entropy when 50 grams of water at 15°C is mixed with 80 grams of water at 40°C. Specific heat of water may be assumed to be equal to 1.* *(Rajasthan 1961)*

(*i*) $m_1 = 50$ g

$T_1 = 15 + 273 = 288$ K

$m_2 = 10$ grams

$T_2 = 40 + 273 = 313$ K

Let the final temperature be T K.

$$m_1\times s\times(T-T_1) = m_2\times s\times(T_2-T)$$

$$50\times1\times(T-288) = 80\times1\times(313-T)$$

$$T = 303\cdot4\ \text{K}$$

(*ii*) Change in entropy when the temperature of 50 g of water rises from 288 K to 303·4 K

$$= \frac{\delta H}{T} = ms\int_{T_1}^{T}\frac{dT}{T}$$

$$= 50\times1\times2\cdot3026\times\log_{10}\frac{303\cdot4}{288}$$

$$= +2\cdot602\ \text{cal/K.}$$

(*iii*) Change in entropy when the temperature of 80 g of water decreases from 313 K to 303·4 K

$$= \frac{\delta H}{T} = ms\int_{T_2}^{T}\frac{dT}{T}$$

$$= 80\times1\times2\cdot3026\times\log_{10}\frac{303\cdot4}{313}$$

$$= -2\cdot487\ \text{cal/K}$$

Therefore, the net change in the entropy of the system

$$= +2\cdot602-2\cdot487$$

$$= +0\cdot115\ \text{cal/K}$$

Hence the net increase in the entropy of the system

$$= \mathbf{0\cdot115\ cal/K}$$

Example 6·35. *10 g of steam at 100°C is blown into 90 grams of water at 0°C, contained in a calorimeter of water equivalent 10 grams. The whole of the steam is condensed. Calculate the increase in the entropy of the system.* [*Delhi (Hons.) 1973*]

(*i*)

$$m_1 = 10\ \text{g}$$

$$T_1 = 100°\text{C} = 373\ \text{K}$$

$$m_2 = 90+10 = 100\ \text{g}$$

$$T_2 = 273\ \text{K}$$

Let the final temperature be T K

$$10\times540+10(373-T) = 100(T-273)$$

$$T = 331\cdot2\ \text{K}$$

(*ii*) Change in entropy when the temperature of water and calorimeter rises from 273 K to 331·2 K

$$= \frac{\delta H}{T} = ms\int_{T_2}^{T}\frac{dT}{T}$$

$$= 100\int_{273}^{331\cdot2}\frac{dT}{T}$$

$$= 100\times2\cdot3026\times\log_{10}\left(\frac{331\cdot2}{273}\right)$$

$$= +19\cdot32\ \text{cal/K}$$

(*iii*) Change in entropy when 10 grams of steam at 373 K is condensed to water at 373 K

$$= \left(\frac{\delta H}{T}\right) = -\frac{10\times540}{273}$$

$$= -14\cdot47\ \text{cal/K}$$

(—ve sign indicates decrease in entropy).

(*iv*) Change in entropy when 10 grams of water at 373 K is cooled to water at 331·2 K

$$\frac{\delta H}{T} = ms\int_{T_2}^{T}\frac{dT}{T}$$

$$= 10\times2\cdot3026\ \log_{10}\left(\frac{331\cdot2}{373}\right)$$

$$= -1\cdot188\ \text{cals/K}$$

Net change in entropy

$$= 19\cdot32-14\cdot47-1\cdot188$$

$$= \mathbf{+3\cdot662\ cal/K}$$

Hence the net increase in the entropy of the system

$$= \mathbf{3\cdot662\ cal/K}$$

Example 6·36. *1 g of water at 20°C is converted into ice at −10°C at constant pressure. Heat capacity for 1 g of water is 4·2 J/g-K and that of ice is 2·1 J/g-K. Heat of fusion of ice at 0°C = 335 J/g. Calculate the total change in the entropy of the system.*

(*i*) Change in entropy when the temperature of 1 g of water at 293 K falls to 273 K.

$$dS = \frac{\delta H}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T}$$

$$= 1\times4\cdot2\int_{293}^{273}\frac{dT}{T}$$

$$= 4\cdot2\times2\cdot3026\ \log_{10}\left(\frac{273}{293}\right)$$

$$= -0\cdot2969\ \text{J/K}$$

(*ii*) Change in entropy when 1 g of water at 273 K is converted into ice at 273 K

$$dS = \frac{\delta H}{T} = \frac{-1\times335}{273} = -1\cdot227\ \text{J/K}$$

(*iii*) Change in entropy when the temperature of 1 g of ice at 273 K falls to 263 K

$$dS = \frac{\delta H}{T} = ms\int_{T_1}^{T_2}\frac{dT}{T}$$

$$= 1\times 2{\cdot}1\times 2{\cdot}3026\,\log_{10}\left(\frac{263}{273}\right)$$

$$= -0{\cdot}07834\ \mathrm{J/K}$$

Total change in entropy of the system

$$= -0{\cdot}2969-1{\cdot}227-0{\cdot}07834$$

$$= \mathbf{-1{\cdot}60224\ J/K}$$

Negative sign shows that there is decrease in entropy of the system.

Example 6·37. *1 kg of water at 273 K is brought in contact with a heat reservoir at 373 K (1) what is the change in entropy of water when its temperature reaches 373 K ?*

(2) What is the change in entropy of (i) the reservoir and (ii) the universe.

(1) Increase in entropy when the temperature of 1000 g of water is raised from 273 K to 373 K

$$dS = \int_{T_1}^{T_2}\frac{\delta H}{T}$$

$$= ms\times 2{\cdot}3026\,\log_{10}\frac{T_2}{T_1}$$

$$= 1000\times 1\times 2{\cdot}3026\,\log_{10}\frac{373}{273}$$

$$= \mathbf{312\ cal/K}$$

(2) (*i*) Change in entropy of the reservoir,

$$dS = \frac{-\delta H}{T}$$

$$= -\frac{1000\times 1\times 100}{373} = \mathbf{-268{\cdot}1\ cal/K}$$

Negative sign shows decrease in entropy

(2) (*ii*) Change in entropy of the universe

$$= 312-268{\cdot}1$$

$$= \mathbf{43{\cdot}9\ cal/K}$$

Therefore, the net increase in entropy of the universe

$$= \mathbf{43{\cdot}9\ cal/K}$$

6·50 Zero Point Energy

According to Kinetic theory, the energy of a system at absolute zero should be zero. It means the molecules of the system do not possess any motion. But according to the modern concept, even at absolute zero, the molecules are not completely deprived of their motion and hence possess energy. The energy of the molecules at absolute zero temperature is called **zero point energy.**

6·51 Negative Temperatures

The specific heat of a substance decreases with increase in temperature. However, the specific heat does not tend to zero as the temperature tends to infinity. This shows that the temperature has a +ve sign only.

But recent experiments by Ramsey (1956) have shown that a part of a system *i.e.*, the nucleus of a solid, can have a negative temperature. This sub-system is considered isolated from the main system (*i.e.*, solid lattice). The specific heat of the sub-system tends to zero at high temperature. A small amount of heat energy tends to raise the temperature of the system to infinity. It is possible to add still more energy to the sub-system at infinity and it forces the sub-system into the negative temperature region. It has been shown by microscopic statistical analysis that there is no distinction between the temperature of $+\infty$ and $-\infty$. In thermodynamics, the parameter $1/T$ is more significant than T.

The *negative* temperatures are hotter than the positive temperatures and minus zero (−0) is the hottest temperature and plus zero (+0) is the coldest temperature.

The negative temperature is not possible with the system as a whole and is only an exception to the rule that only positive temperatures exist. The negative temperatures are possible only for isolable sub-systems. For all normal purposes the temperatures are always positive.

6·52 Maxwell's Thermodynamical Relations

From the two laws of thermodynamics, Maxwell was able to derive six fundamental thermodynamical relations. The state of a system can be specified by any pair of quantities *viz.* pressure (P), volume (V), temperature (T) and entropy (S). In solving any thermodynamical problem, the most suitable pair is chosen and the quantities constituting the pair are taken as independent variables.

From the first law of thermodynamics

$$\delta H = dU+\delta W$$

$$\delta H = dU+PdV$$

or

$$\delta U = \delta H-PdV$$

From the second law of thermodynamics,

$$dS = \frac{\delta H}{T}$$

or

$$\delta H = TdS$$

Substituting this value of δH in the first equation

$$dU = TdS - PdV \qquad \ldots(i)$$

Considering S, U and V to be functions of two independent variables x and y [here x and y can be any two variables out of P, V, T and S],

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dU = \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy$$

Substituting these values in equation (i)

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = T\left[\left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy\right]$$
$$-P\left[\left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{dy}\right)_x dy\right]$$

$$\left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy = \left[T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y\right]dx$$
$$+\left[T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x\right]dy$$

Comparing the coefficients of dx and dy, we get

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - P\left(\frac{\partial V}{\partial x}\right)_y \qquad \ldots(ii)$$

$$\left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - P\left(\frac{\partial V}{\partial y}\right)_x \qquad \ldots(iii)$$

Differentiating equation (ii) with respect to y and equation (iii) with respect to x

$$\frac{\partial^2 U}{\partial y \cdot \partial x} = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y\,\partial x}$$
$$-\left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y\partial x}$$

and

$$\frac{\partial^2 U}{\partial x\partial y} = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x\partial y}$$
$$-\left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x\partial y}$$

The change in internal energy brought about by changing V and T whether V is changed by dV first and T by dT later or *vice versa* is the same.

It means dU is a perfect differential

$$\therefore \qquad \frac{\partial^2 U}{\partial x\partial y} = \frac{\partial^2 U}{\partial x\partial y} \quad \text{and}$$

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\frac{\partial^2 S}{\partial y\partial x} - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - P\frac{\partial^2 V}{\partial y\partial x}$$
$$= \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\frac{\partial^2 S}{\partial x\partial y}$$
$$-\left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x - P\frac{\partial^2 V}{\partial x\partial y}$$

Simplifying,

$$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y$$
$$= \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x \qquad \ldots(iv)$$

Here x and y can be any two variables out of P, V, T and S.

Derivation of Relations

(1) Taking T and V as independent variables and

$$x = T$$

and

$$y = V$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial V}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial V}{\partial x} = 0$$

Substituting these values in equation (iv)

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(v)$$

But

$$dS = \frac{\partial H}{T}$$

$$\therefore \qquad \left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad \ldots(vi)$$

(2) Taking T and P as independent variables and

$$x = T$$

and

$$y = P$$

$$\frac{\partial T}{\partial x} = 1, \quad \frac{\partial P}{\partial y} = 1,$$

$$\frac{\partial T}{\partial y} = 0, \quad \frac{\partial P}{\partial x} =$$

78. Derive the following relations :

(*a*) $$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T$$

(*b*) $$TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$$

(*c*) $$\frac{(\partial P/\partial T)_S}{(\partial P/\partial T)_V} = \frac{\gamma}{\gamma - 1}.$$ [*Delhi* (*Hons.*), *1978*]

79. Write short notes on :

(*i*) Isothermal Process
(*ii*) Adiabatic Process
(*iii*) Isochoric Process
(*iv*) Carnot's engine
(*v*) Carnot's theorem [*Delhi*, *1975*]
(*vi*) Second Law of thermodynamics
(*vii*) Clement and Desormes' method
(*viii*) Ruchhardt's experiment for γ
(*ix*) Absolute gas scale
(*x*) Rankine cycle
(*xi*) Diesel engine
(*xii*) Steam engine
(*xiii*) Otto cycle
(*xiv*) Entropy is a measure of disorder
(*xv*) Entropy tends to a maximum
(*xvi*) Third Law of thermodynamics
(*xvii*) Absolute zero temperature
(*xviii*) Entropy of a perfect gas [*Delhi* (*Hons.*) *1977*]
(*xix*) Temperature-Entropy diagram
(*xx*) Thermodynamic system
(*xxi*) Thermal Equilibrium
(*xxii*) Concept of Temperature
(*xxiii*) Concept of Heat
(*xxiv*) Zeroth Law in Thermodynamics.
(*xxv*) Phase changes of the second order. [*Delhi* (*Hons.*) *75*]

80. A motor car tyre has a pressure of 3 atmospheres at the room temperature of 27°C. If the tyre suddenly bursts what is the resulting temperature ? [**Ans.** 218·6 K = –54·4°C]

81. A quantity of air (γ = 1·4) at 27°C is compressed suddenly to $\frac{1}{4}$ of its original volume. Find the final temperature. [**Ans.** 522·3 K = 249·3°C]

82. A quantity of air at 27°C and atmospheric pressure is suddenly compressed to $\frac{1}{5}$ of its original volume. Find (*i*) the final pressure and (*ii*) the final temperature.
[**Ans.** (*i*) 8·29 atmospheres (*ii*) 571·1 K = 298·1°C]

83. Find the efficiency of the Carnot's engine working between 150°C and 50°C. [**Ans.** 23·64%]

84. Find the efficiency of a Carnot's engine working between 227°C and 27°C. [**Ans.** 40%]

85. A Carnot's engine whose temperature of the source is 400 K takes 500 calories of heat at this temperature and rejects 400 calories of heat to the sink. What is the temperature of the sink ? Calculate the efficiency of the engine.
[**Ans.** (*i*) 320 K, (*ii*) 20%]

86. A Carnot's engine is operated between two reservoirs at temperatures of 500 K and 400 K. If the engine receives 2000 calories of heat from the source in each cycle, calculate (*a*) the amount of heat rejected to the sink in each cycle, (*b*) the efficiency of the engine and (*c*) the work done by the engine in each cycle in (*i*) joules (*ii*) kilo-Watt hours.
[**Ans.** (*a*) 1600 calories, (*b*) 20%, (*c*) (*i*) 1780 joules, (*ii*) $4{\cdot}944 \times 10^{-4}$ kWh]

87. A Carnot's engine working as a refrigerator between 250 K and 300 K receives 1000 calories of heat from the reservoir at the lower temperature. (*i*) Calculate the amount of heat rejected to the reservoir at the higher temperature. (*ii*) Calculate also the amount of work done in each cycle to operate the refrigerator.
[**Ans.** (*i*) 1200 cal, (*ii*) 840 joules]

88. Calculate the depression in the melting point of ice produced by 2 atmospheres increase of pressure. Given latent heat of ice = 80 cal/g and the specific volumes of 1 gram of ice and water at 0°C are 1·091 cm³ and 1·000 cm³ respectively.
[**Ans.** 0·0148 K or 0·0148°C]

89. Find the increase in the boiling point of water at 100°C when the pressure is increased by 2 atmospheres. Latent heat of vaporisation of steam is 540 cal/g and 1 g of steam occupies 1677 cm³ volume. [**Ans.** 55·84 K or 55·84°C]

90. Calculate the change in the melting point of naphthalene for 2 atmospheres rise in pressure, given that its melting point is 80°C. Latent heat of fusion is 4563 cal/mol and increase in volume on fusion is 18·7 cm³/mol. 1 cal = $4{\cdot}2 \times 10^7$ ergs.
[**Ans.** –0·06976 K or –0·06976°C]

91. Calculate the temperature at which ice will freeze if the pressure is increased by 135·2 atmospheres. The change in specific volume when 1 gram of water freezes into ice is 0·091 cm³. One atmospheric pressure = 10^6 dynes/cm². Latent heat of fusion of ice = 80 cal/g. and $J = 4{\cdot}2 \times 10^7$ ergs/cal. [**Ans.** –1·0°C]

92. Calculate the temperature at which water will boil if the pressure is increased by 1·814 atmospheres. Given that the change in specific volume when one gram of water is converted into steam is 1676 cm³. Latent heat of vaporization of steam = 540 cal/g. $J = 4{\cdot}2 \times 10^7$ ergs/cal and one atmosphere pressure = 10^6 dynes/cm².
[**Ans.** 150°C]