

A Carnot's engine may be defined as a reversible engine operating between two reservoirs.

If a Carnot cycle is performed in opposite direction as discussed above, it becomes a *Carnot's refrigerator*.

Consider a Carnot's cycle of a fluid as shown in Fig. 1.20.

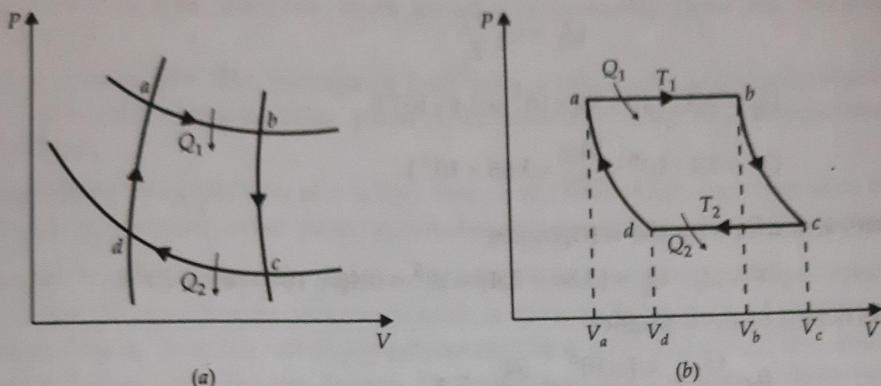


Fig. 1.20 Carnot cycle a gas (a) P-V diagram, (b) T-V diagram.

If the directions of the arrows are reversed cycle becomes $adcba$ instead of $abcda$. Then the cycles are reversible because each process is reversible, the magnitudes of the quantities Q_1 , Q_2 and W remain the same but their signs are reversed. Thus, heat Q_2 is absorbed by the system from the lower temperature reservoir and heat Q_1 is rejected to the higher temperature reservoir while work W in the cycle represents workdone on the system as shown in Fig. 1.21.

The features common to all refrigeration cycles are absorption of heat at a low temperature, rejection of amount of workdone on the system. In a domestic refrigerator heat is pumped out of the interior of the refrigerator, which is at a temperature lower than that of the surroundings, a larger quantity of heat is rejected to the surroundings and workdone by the motor driving the refrigerator.

In this case the input is the workdone on the system W , and output is the heat Q_2 removed from the lower temperature reservoir. A refrigerator is therefore rated by its coefficient of performance (β), defined as

$$\beta = \frac{\text{Heat output}}{\text{Work input}} = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

The definition of coefficient of performance applies to any refrigerator whether it operates in Carnot cycle or not.

Example 1.7 A Carnot's refrigerator absorbs heat from water at 0°C and rejects it at the room temperature 37°C . Calculate the amount of work required to convert 10 kg water at 0°C into ice at same temperature [Latent heat of ice = $3.4 \times 10^5 \text{ J kg}^{-1}$]. Also find the coefficient of performance of the refrigerator.

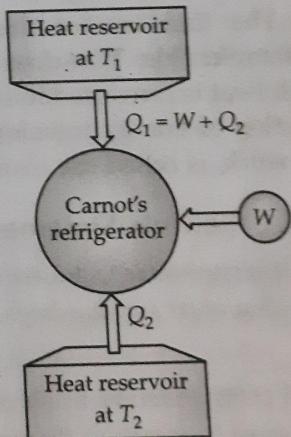


Fig. 1.21 A Carnot's refrigerator.

Solution. Given $m = 10 \text{ kg}$, $L = 3.4 \times 10^5 \text{ J kg}^{-1}$, $T_1 = 37^\circ\text{C} = 310 \text{ K}$, $T_2 = 0^\circ\text{C} = 273 \text{ K}$

Since we know that, for an ideal Carnot's cycle

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

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

Here $Q_2 = mL = 10 \times 3.4 \times 10^5 = 3.4 \times 10^6 \text{ J}$

Then $Q_1 = 3.4 \times 10^6 \times \frac{310}{273} = 3.86 \times 10^6 \text{ J}$

Therefore, workdone by the refrigerator

$$W = Q_1 - Q_2 = (3.86 - 3.4) \times 10^6 = 0.46 \times 10^6 = 4.6 \times 10^5 \text{ J}$$

Now coefficient of performance

$$\beta = \frac{Q_2}{W} = \frac{3.4 \times 10^6}{4.6 \times 10^5} = \frac{34}{4.6} = 7.4.$$

1.17 SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics establishes an exact relation between heat and work. It follows directly from this law, that it is impossible to get work from any machine without giving it an equivalent amount of energy in any form. In other words, this law is merely the generalization of the law of conservation of energy including heat energy and states that the *energy of the universe remains constant*.

The first law of thermodynamics tells us that heat and mechanical work both are interconvertible. This does not tell us the limitation and condition for this conversion i.e., how much heat is converted into work and whether the transformation itself can take place or not (the direction of energy transformation). The law specifying the condition of transformation of heat into work, is called the *second law of thermodynamics*.

1.17.1 Kelvin's Statement of Second Law of Thermodynamics

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

Or

A transformation, whose only final result is to transform into work the extracted from a source which is at the same temperature throughout is impossible.

1.17.2 Clausius Statement of Second Law of Thermodynamics

It is impossible for a self acting machine, unaided by any external agency to transfer heat from one body to another at a higher temperature.

Or

It is impossible for any cyclic machine to produce no other effect than to convey heat continuously from one body to another at a higher temperature.

Both statements of second law are equivalent. Violation of one automatically leads to violation of the other. They impart a direction for making the energy transformation. Let us take up, for the sake of illustration, the following examples of isolated system.

- (i) **Free expansion.** The free expansion of an ideal gas from a region of high pressure to a region of low pressure takes place spontaneously until the pressure becomes uniform.
- (ii) **Heat conduction.** The passage of heat from a region of high temperature to a region of low temperature takes place spontaneously until the temperature becomes uniform.
- (iii) **Diffusion.** The diffusion of a solute from a region of high concentration to a region of low concentration takes place spontaneously until concentration becomes uniform.

Thus we can conclude that every system, if left to itself (isolated), changes spontaneously at slow or rapid rate in such a way as to approach a definite final state of equilibrium. In such processes, according to first law of thermodynamics, the total energy of the system involved remains constant before and after the change. The important point to note in these processes is the direction *i.e.*, from high pressure to low pressure, from high temperature to low temperature. There is thus a direction which allows a system to come to equilibrium. However, if we imagine that after acquiring equilibrium, the process is reversed then obviously the system, at its own, will not move away from the state of equilibrium unless aided by some external agency. For example, two bodies at the same temperature, being in a state of thermal equilibrium will itself not create temperature difference between them provided one of them is not heated by some external sources.

This principle which determines the 'direction for the process' to take place is second law of thermodynamics. For first law it does not matter how the equilibrium state has been attained because of before and after equilibrium state, energy of the system remains the same. Therefore, second law of thermodynamics cannot be derived from first law. It requires another thermodynamical parameter for the description and mathematical formulation. This parameter is known as **entropy**.

1.17.3 Entropy and Second Law of Thermodynamics

As said above, we require such a thermodynamical variable which has a different value for the initial and final states of an isolated system when the process has taken place even though the internal energy for the two states remains the same. We know that entropy is a variable. *It is a definite function of the thermal state of a body and is not affected in any way by the manner in which a particular state is reached.*

The change in entropy passing from one state A to another state B is given by

$$S_B - S_A = \int_A^B \frac{dQ}{T} \quad \dots(1.61)$$

where dQ is the quantity of heat absorbed or rejected at a temperature T is going from state A to state B, we also note that :

- (i) Entropy of a system remains constant during an adiabatic change.
- (ii) Entropy of a system remains constant during all reversible processes.
- (iii) Entropy of a system increases in all irreversible processes.

Since irreversible processes are continuously occurring in nature, the entropy of the universe is increasing.

Now on applying the concept of entropy for the explanation of the processes of free expansion, heat conduction and diffusion, we find that entropy of the system in final state (after attaining equilibrium) is greater than in initial state ($S_B > S_A$). Thus both the states are indistinguishable from point energy consideration (internal energy remains same) and hence from the view of the first law of thermodynamics, but entropy differentiates between the two. In other words, entropy characterizes the direction in which thermodynamical process can take place. That is all the thermodynamic processes take place in such a direction that the entropy of the system remains constant or increases. Second law of thermodynamics also stands for the same and therefore, the second law of thermodynamics in terms of entropy can be stated below :

A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus environment to increase.

If the two states A and B , as discussed above are infinitesimally close to each other, then change in entropy ($S_B - S_A = dS$) is going from state A to state B will be

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

or

$$dQ = TdS \quad \dots(1.62)$$

which is mathematical form of second law of thermodynamics.

1.18 CARNOT'S THEOREM

STATEMENT : A reversible engine operating between two given reservoirs i.e., Carnot's engine is most efficient that can operate between those reservoirs.

Or

No engine operating between two given temperature is more efficient than Carnot's engine.

Proof. Operate a Carnot's engine C and an arbitrary engine X (not necessarily reversible) between two reservoirs at temperature T_1 and T_2 with ($T_1 > T_2$). By first law of thermodynamics, the workdone by the engines (see Fig. 1.22).

$$(W)_C = (Q_1)_C - (Q_2)_C \quad \dots(1.63)$$

and

$$(Q)_x = (Q_1)_x - (Q_2)_x \quad \dots(1.64)$$

Let $\frac{(Q_1)_C}{(Q_1)_X} = \frac{N}{M}$, where N, M are two integers (can be satisfied to any desired accuracy).

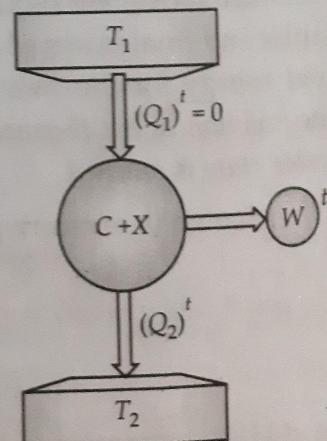


Fig. 1.22 Illustration for Carnot's theorem.

Now operate engine C, M cycles in reverse (as Carnot engines are reversible) and engine X, N cycles in forward direction. Consider (C + X) as an engine total, then

$$(W)_{\text{Total}} = N(W)_X - M(W)_C \quad \dots(1.65)$$

But $(Q_1)_{\text{Total}} = N(Q_1)_X - M(Q_1)_C = 0 \quad \dots(1.66)$

and $(Q_2)_{\text{Total}} = N(Q_2)_X - M(Q_2)_C \quad \dots(1.67)$

Hence $(W)_{\text{Total}} = -(Q_2)_{\text{Total}} = -[N(Q_2)_X - M(Q_2)_C]$

This is shown in Fig. 1.22.

However, Kelvin's statement says we cannot convert heat entirely to work – here we have extracted no heat from T_1 . Thus Kelvin's statement is broken unless $(W)_{\text{Total}} \leq 0$ or $(Q_2)_{\text{Total}} \geq 0$ i.e.,

$$N(Q_2)_X - M(Q_2)_C \geq 0$$

or $\frac{N}{M} \geq \frac{(Q_2)_C}{(Q_2)_X} \quad \dots(1.68)$

Therefore $\frac{(Q_1)_C}{(Q_2)_X} \geq \frac{(Q_2)_C}{(Q_2)_X}$

or $\frac{(Q_2)_C}{(Q_1)_C} \leq \frac{(Q_2)_X}{(Q_2)_X} \quad \dots(1.69)$

and $\eta_{CE} \left(= 1 - \frac{(Q_2)_C}{(Q_1)_C} \right) \geq \eta_X \left(= 1 - \frac{(Q_2)_C}{(Q_1)_C} \right)$
 $\eta_{CE} \geq \eta_X \quad \dots(1.70)$

This equality holds if X engine is also reversible. We therefore have the following corollary.

COROLLARY. All reversible engine (Carnot's engines) working between the same two heat reservoirs have identical efficiency.

This is a remarkable result. It means for reservoirs at temperature T_1 and T_2 , $\eta_{CE} = \eta_X(T_1 - T_2)$ only independent of working substance, for example, the working substance could be an ideal gas, real (non-ideal) gas, a paramagnet etc. We can evaluate for any one, and other will be same. So we prefer an ideal gas.

1.19 THE THERMODYNAMIC TEMPERATURE SCALE

Although we have evaluated the efficiency of an ideal gas Carnot's engine, one could easily imagine it might be more difficult for other working substances. We didn't have efficiency equal to 1. They are all the same (for given T_1, T_2). Indeed, we can now use this fact to define an *absolute temperature scale* i.e., independent of working substance. Since all Carnot's engines are equivalent the efficiency can be dependent on T_3, T_1 .

So we define

$$\frac{Q_3}{Q_1} = f(T_3, T_1) \quad \dots(1.71)$$

So,

$$\eta_{CE} = 1 - f(T_3 - T_1)$$

It is on unspecified temperature scale. Where $f(T_3 - T_1)$ is unknown. We will show, by considering Carnot's engines working in series, what the form $f(T_3 - T_1)$ must be?

Consider the Carnot's engine as shown in Fig. 1.23.

Clearly, the two engines in series on the left are completely equivalent to the single engine on the right (both the compound engine) and single engine draw Q_1 from the hot reservoir at temperature T_1 and reject Q_3 to the cool reservoir at temperature T_3 .

For compound engine

$$\frac{Q_2}{Q_1} = f(T_3, T_1);$$

$$W_1 = W_2 = Q_1 - Q_2 = [1 - f(T_2, T_1)] Q_1 \quad \dots(1.72)$$

$$\text{and } \frac{Q_3}{Q_2} = f(T_3, T_1);$$

$$W_2 = [1 - f(T_3, T_2)] Q_2 \\ = [1 - f(T_3 - T_2)] f(T_2, T_1) Q_1 \quad \dots(1.73)$$

[Using Eq. (1.72)]

Combine Eqs. (1.72) and (1.73)

$$W_1 + W_2 = [1 - f(T_3, T_2)] f(T_2, T_1) Q_1 \quad \dots(1.74)$$

Hence, the efficiency of the composite engine is

$$\eta_{CE} = \frac{W_1 + W_2}{Q_1} = 1 - f(T_3, T_2) f(T_2, T_1) \quad \dots(1.75)$$

which must be identical to Eq. (1.71), since $W = W_1 + W_2$, therefore

$$f(T_3, T_2) f(T_2, T_1) = f(T_3, T_1)$$

But from Eq. (1.71), $f(T_1, T_2) = \frac{1}{f(T_2, T_1)}$ by definition, hence

$$f(T_3, T_1) = \frac{f(T_3, T_2)}{f(T_1, T_2)} \quad \dots(1.76)$$

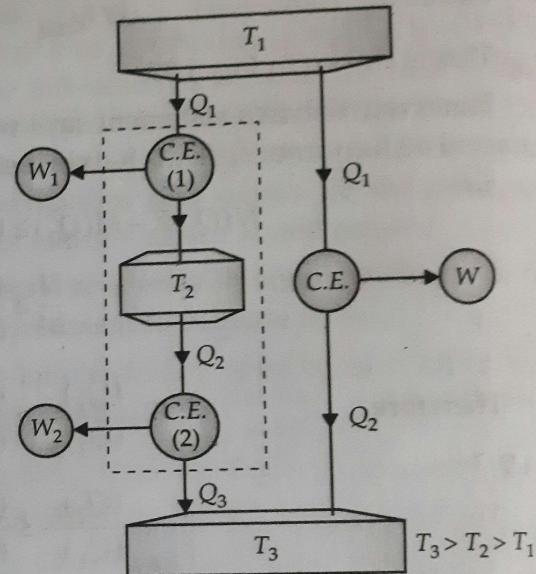


Fig. 1.23 Illustration for thermodynamic temperature scale.

Hence the R.H.S. must be independent of T_2 . Hence, this can only be true if $f(T_1, T_2)$ factorizes into a product of functions of T_1 and T_2 .

$$f(T_3, T_1) = \frac{t(T_3)}{t(T_1)} \quad \dots(1.77)$$

where $t(T)$ is any function of T . We have

$$\eta_{CE} = 1 - \frac{t(T_3)}{t(T_2)} \quad \dots(1.78)$$

and any function $t(T)$ defines a temperature scale (for example, we could define linear scale or logarithmic scale etc.).

The Kelvin absolute scale chooses a linear scale $t(T) = T$

$$\text{Kelvin scale} \quad \eta_{CE} = 1 - \frac{T_3}{T_1} \quad \dots(1.79)$$

Here T on this absolute scale is equal, by comparison with Eq. (1.70) of Carnot cycle $\eta_{CE} = 1 - \frac{T_3}{T_1}$ to KT , where T is the ideal gas (absolute) temperature and K is a constant. Clearly $K=1$,

if we define $T_{\text{triple}} = 273.16$ K.

1.19.1 Zero of Absolute or Thermodynamic Scale

The efficiency of carnot reversible heat engine is given by

$$\eta = \frac{Q_1 - Q_3}{Q_1} = 1 - \frac{Q_3}{Q_1} \quad \dots(1.80)$$

on the thermodynamics scale

$$\frac{Q_3}{Q_1} = \frac{T_3}{T_1} \quad \dots(1.81)$$

$$\text{Then,} \quad \eta = 1 - \frac{T_3}{T_1} \quad \dots(1.82)$$

Suppose $T_3 = 0$, $\eta = 1$ (from Eq. 1.82) and $Q_3 = 0$.

Thus,

Zero of absolute or thermodynamic scale is defined as that temperature of the sink at which the reversible heat engine underlying Carnot's cycle rejects no heat to it.

1.19.2 Negative Temperature is not Possible

The zero of absolute or thermodynamic scale is that temperature at which reversible heat engine undergoing Carnot's cycle rejects no heat to the sink. A negative temperature on this means that the heat engine extracts heat from the sink (at a lower temperature) and gives back to the source (at a higher temperature) which is against the second law of thermodynamics.

1.19.3 Thermodynamic Scale is Independent of Working Substance

The thermodynamic scale has been derived on the basis of the efficiency of a reversible Carnot's heat engine, which depends only on the temperature of the source and sink but is independent of the working substance. Hence the thermodynamic scale of temperature is also independent of the properties of the working substance.

1.20 ENTROPY

We know that in isothermal process, temperature of the system does not vary but in adiabatic process, no exchange of heat takes place between the body and the surroundings and so temperature changes. If gas is compressed adiabatically, the work is done on the gas and temperature, and internal energy of the gas increases. On the other hand, if the gas expands adiabatically, temperature and internal energy of the gas decreases. Thus in adiabatic process, neither the internal energy nor the temperature remains constant, rather they increase or decrease simultaneously.

Clausius concept was applied for the second law of thermodynamics, which led to believe that as in isothermal process temperature remains constant, a heat in an adiabatic process. This property of the gas which remains constant during adiabatic process is known as *entropy of the substance*. Hence *entropy is a physical quantity which remains constant in an adiabatic process*.

The concept of entropy can be best understood from P-V indicator diagram (Fig. 1.24) at the temperatures T_1 , T_2 and T_3 .

Let E_1 and E_2 are two adiabatics, which intersect the isothermal at the points (A_1, A_2) , (B_1, B_2) and (C_1, C_2) . This is shown in Fig. 1.24.

We consider the Carnot cycle $A_1 A_2 B_2 B_1$. If the working substance passes from state A_1 to state A_2 along isothermal $A_1 A_2$, it absorbs Q_1 amount of heat at temperature T_1 and when it passes from B_2 to B_1 , it rejects heat Q_2 at temperature T_2 .

According to Carnot's theorem, we then have

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

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \dots(1.83)$$

If we consider Carnot's cycle bounded by other isothermals and the adiabatics, we may get similar results.

We may write this

$$\frac{Q_2}{T_2} = \frac{Q_3}{T_1} \quad \dots(1.84)$$

$$\therefore \frac{Q_1}{T_1} = \frac{Q_2}{T_2} = \frac{Q_3}{T_3} = \text{constant} \quad \dots(1.85)$$

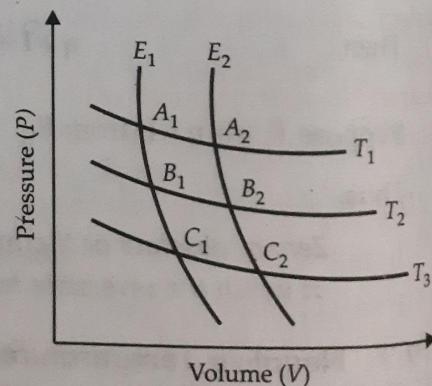


Fig. 1.24 P-V indicator diagram.

Thus, when going from one adiabatic to another if Q units of heat are absorbed or rejected, then

$$\frac{Q}{T} = \text{constant } (S) \quad \dots(1.86)$$

The constant S is the change of entropy between two states of the working substance as represented by the two adiabatics.

If the two adiabatics are very close so that heat absorbed or given out by the working substance is small and equal to dQ , then small change in entropy is given by

$$dS = \frac{dQ}{T} \quad \dots(1.87)$$

Thus the change in entropy is passing from an adiabatic A to another adiabatic B

$$S = \int_A^B dS = \int_A^B \frac{dQ}{T} \quad \dots(1.88)$$

Under adiabatic process $\frac{dQ}{T} = 0$, as during adiabatic process no heat is absorbed or given out by the working substance. Thus in an adiabatic process change in entropy becomes zero, i.e., *entropy remains constant in an adiabatic process*. For this reason, the adiabatic curves are called *isentropic curves*.

When there is any gain or loss of heat by a body, the entropy of the body alters. If such gain or loss of heat takes place reversibly, change of entropy of a body is given by $dS = \frac{dQ}{T}$, where T is the absolute temperature of the body. The entropy of a body alters from one adiabatic to another and in such transition, the change is independent of the path followed by the substance.

1.20.1 Physical Significance of Entropy

The role of entropy is highly significant in thermodynamics. Like pressure, volume, temperature etc. the entropy of a body is a real physical quantity. Its value depends only on the perfect state of the body. Change in entropy of a body depends on its initial and final states whatever be the way followed by the body in going from the initial state to the final state. This means *entropy is a function of state*. It is a single valued function which means that it allows only one value for a particular state and thus it is a perfect differential.

1.20.2 Second Law of Thermodynamics in Terms of Entropy

In terms of entropy the second law of thermodynamics may be stated in following way :

Every physical or chemical process in nature occurs in such a way that the sum of entropy of all bodies taking part in process increases. In the limiting case of a reversible process, the sum of entropies remains constant.

1.20.3 Entropy Change of Heat and Work Reservoirs

A heat reservoir is a system of infinite source of energy and the finite transfers of heat into or out of the reservoir does not affect its temperature.

If dQ' is the heat drawn from a heat reservoir at temperature T , decreases in entropy of heat reservoir is given by

$$(dS)_{\text{heat reservoir}} = \frac{dQ'}{T} \quad \dots(1.89)$$

$$(\Delta S)_{\text{heat reservoir}} = \int -\frac{dQ'}{T} = -\frac{Q'}{T} \quad \dots(1.90)$$

where $Q' = \text{Total heat abstracted from the heat reservoir.}$

In case of work reservoirs, since the heat transfers are zero i.e., $dQ' = 0$, it follows

$$(dS)_{\text{work reservoir}} = \left(\frac{dQ'}{T} \right) = 0 \quad \dots(1.91)$$

1.20.4 Temperature-Entropy (**T-S**) Diagram

We have used *P-V* diagrams to represent various processes because any two properties of a pure substance existing in a single phase could define the state of the system and these properties are easily measurable. The area under the curve $\int PdV$ on *abscissa* represent the workdone during any reversible process of a closed system, thus provides on additional information.

Similarly, the processes could also be represented on *T-S* diagram where T is taken in absolute units.

This diagram has the following advantages :

- (i) A reversible adiabatic process will be represented by a vertical line on *T-S* diagram, since entropy during the process remains constant. Process (a-b) represents a reversible adiabatic expansion process as shown in Fig. 1.25.
- (ii) A reversible isothermal process is represented by a horizontal line on *T-S* diagram, since temperature during the process constant. The process (c-d) represents an isothermal heating process as shown in Fig. 1.25.
- (iii) A compression process on *T-S* diagram following same law of process is represented by curve (1 → 2) in Fig. 1.25.

$$\therefore dS = \frac{dQ}{T} \quad \dots(1.92)$$

It follows that $dQ = TdS$

$$\text{or } Q_{1 \rightarrow 2} = \int_1^2 TdS \quad \dots(1.93)$$

Therefore, the area under the process curve on *T-S* diagram represents the heat transfer during a reversible process as shown in Fig. 1.25.

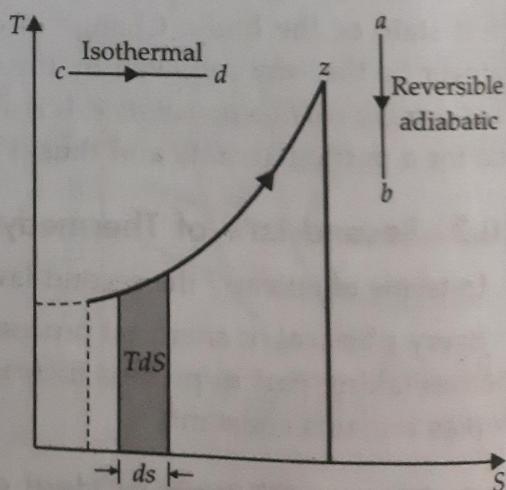


Fig. 1.25 *T-S* diagram.

Heat transfer

$$Q_{1 \rightarrow 2} = TdS = \text{Area}(1 - 2 - f - e) \quad \dots(1.94)$$

- (iv) According to first law of thermodynamics for a cyclic process

$$\oint dQ = \oint dW \quad \dots(1.95)$$

It follows that the area enclosed by the loop representing a reversible cycle either on T-S diagram or P-V diagram represents either the net heat transfer or net work during a cycle.

- (v) Irreversible processes are usually represented by dotted lines on P-V and T-S diagrams. However, area under the curve on T-S diagram representing the heat transfer will be greater than that of heat transfer during a reversible process.

For example, consider reversible irreversible adiabatic processes represented on T-S diagram by process curves $(1 \rightarrow 2)$ and $(1 \rightarrow 2')$ respectively. The entropy of an irreversible process shown in Fig. 1.26 is greater; we say its irreversibility.

- (vi) In quite number of cases it is convenient to represent the processes and cycle on T-S diagram. To illustrate this fact we shall take the case of Carnot's cycle.

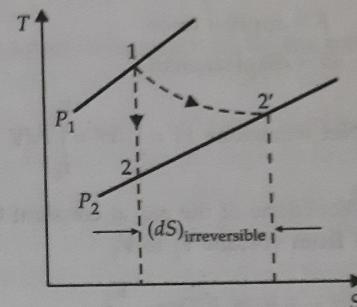


Fig. 1.26 Reversible and irreversible processes.

1.21 THIRD LAW OF THERMODYNAMICS (NERNST'S LAW)

The entropy of a system approaches a constant value as the temperature approaches absolute zero.

The third law is relatively easy to understand from a statistical point of view in which entropy is associated with disorder. As absolute zero is approached, all thermal motions cease, and any system must approach an ordered state in which the particle do not move. Hence, the entropy of a system is defined only for an arbitrary constant, and only changes in entropy have physical significance. The changes in entropy become negligibly small as absolute zero is approached.

The third law of thermodynamics states that "The entropy of all homogeneous crystalline substances in a state of equilibrium is zero at absolute zero of temperature".

Mathematically,

$$\lim_{T \rightarrow 0} S = 0 \quad \dots(1.96)$$

It implies that the entropy ceases, it is the function of state at absolute zero. However, many substances like alloys, all amorphous solids, chemical compounds like Co, Ni etc., the entropy does not tend to zero as $T \rightarrow 0$ but takes a finite value of entropy at absolute zero.

The third law provides an absolute base from which the entropy of each substance can be measured. Third law of thermodynamics is helpful in explaining the behaviour of solids at very low temperatures and is analysing the chemical phase equilibrium.

Formulae at a Glance

1.1 Specific volume $v = \frac{V}{m}$

1.2 $P\bar{v} = RT$

1.3 $W = JQ$

J = Joule's mechanical equivalent of heat
 W = workdone, Q = heat produced

1.4 $dW = F \cdot dx$

dW = workdone on the gas

F = applied force

dx = displacement

1.5 Net workdone $W = \int dW = \int_{V_1}^{V_2} PdV$

1.6 Workdone of the gas at constant temperature T from volume V_1 to V_2

$$W = 2.3026 RT \log_{10} \frac{V_2}{V_1}$$

1.7 In adiabatic process workdone

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

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

1.8 In isobaric process, workdone

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

1.9 In isochoric process

$$W = \int_{V_1}^{V_2} PdV = 0$$

1.10 According to first law of thermodynamics

$$dQ = dU + dW$$

dQ = heat supplied to the system,

dW = workdone by the system

dU = change in internal energy of the system

1.11 In isothermal process

$$dQ = dW$$

1.12 In adiabatic process

$$dW = -dU$$

1.13 In isochoric process

$$dQ = dU$$

1.14 In isobaric process

$$dQ = dU + PdV$$

1.15 In Carnot cycle

(a) Workdone by one mole of gas in isothermal expansion

$$W_1 = RT_1 \ln \frac{V_2}{V_1}$$

(b) Workdone during adiabatic expansion

$$W_2 = \frac{R(T_2 - T_1)}{1-\gamma}$$

(c) Workdone during isothermal compression

$$W_3 = RT_2 \ln \frac{V_1}{V_2}$$

(d) Workdone during adiabatic compression

$$W_4 = -\frac{R(T_2 - T_1)}{(1-\gamma)}$$

Net workdone W

$$= W_1 + W_2 - W_3 - W_4 \quad W_2 = W_4$$

$$W = W_1 - W_3 = R_1 - R_2$$

$$= RT_1 \ln \frac{V_2}{V_1} - RT_2 \ln \frac{V_2}{V_1}$$

1.16 Efficiency of Carnot's engine

$$\eta = \frac{W}{Q} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

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

1.17 Entropy

$$\Delta S = \int_A^B \frac{dQ}{T}$$

Miscellaneous Solved Numerical Problems

Problem 1.1 A bullet moving with a velocity 40 m/s falls down after striking a target. If only half of the heat produced is absorbed by the bullet, find rise in its temperature. Specific heat of lead = $120 \text{ J kg}^{-1} \text{ deg C}^{-1}$.

Solution. Given $v = 40 \text{ m/s}$, $s = 120 \text{ J kg}^{-1} \text{ deg C}^{-1}$

Let the mass of the bullet be $m \text{ kg}$ and its velocity be v .

Then before striking the target, the kinetic energy of the bullet = $\frac{1}{2}mv^2 \text{ J}$

On striking the target this is converted into heat

$$Q = \frac{1}{2}mv^2 \text{ J}$$

As the bullet absorbs only half of the heat produced in the impact, heat received by the bullet.

$$Q' = 0.5, Q = \frac{1}{2} \times \frac{1}{2}mv^2 \text{ J}$$

If the increase in the temperature of the bullet is $\Delta T^\circ \text{C}$,

$$\text{Then } Q' = ms\Delta T \text{ cal}$$

$$\text{Hence } ms\Delta T = \frac{1}{2} \times \frac{1}{2}mv^2$$

$$\therefore \Delta T = \frac{v^2}{4s} = \frac{(40)^2}{4 \times 120} = 3.33^\circ \text{C.}$$

Problem 1.2 The volume of 1 g mole of a gas filled in a container at standard pressure ($1 \times 10^5 \text{ N/m}^2$) and temperature (0°C) is $22.4 \times 10^{-3} \text{ m}^3$. The volume of the gas is reduced to half its original value by increasing the pressure. (i) isothermally, (ii) adiabatically. In each case calculate the final pressure of the gas and the amount of workdone. [$\gamma = 1.4$, $R = 8.3 \text{ J mol}^{-1} \text{ K}^{-1}$].

Solution. Given $P_1 = 1.0 \times 10^5 \text{ N/m}^2$, $T_1 = 0^\circ \text{C} = 273 \text{ K}$,

$$V_1 = 22.4 \times 10^{-3} \text{ m}^3 \quad \text{and} \quad V_2 = \frac{1}{2}V_1 = 11.2 \times 10^{-3} \text{ m}^3$$

(i) In a isothermal process $P_1 V_1 = P_2 V_2$

$$\text{or } P_2 = \frac{P_1 V_1}{V_2} = 1.0 \times 10^3 \times \frac{V_1}{V_1/2} = 2 \times 10^5 \text{ N/m}^2$$

Workdone in this process

$$W = 2.3026 RT \log_{10} \left(\frac{V_2}{V_1} \right) = 2.3026 \times 8.3 \times 273 \log_{10} \left(\frac{V_1}{2V_1} \right)$$

$$= 2.3026 \times 8.3 \times 273 \times \log_{10} \left(\frac{1}{2} \right) = 2.3026 \times 8.6 \times 273 \times (-0.3010)$$

$$= -1.57 \times 10^3 \text{ J.}$$

(ii) In the adiabatic process

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

Final temperature of the gas

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

or

$$T_2 = T_1 \left(\frac{V_1}{V_2} \right)^{\gamma-1} = 273 \times \left[\frac{V_1}{V_1/2} \right]^{1.4-1} = 273 \times [2]^{0.4} = 360.2 \text{ K}$$

$$\begin{aligned} \text{Workdone} \quad W &= \frac{R}{\gamma-1} (T_1 - T_2) = \frac{8.3 \times (273 - 360.2)}{1.4 - 1} \\ &= \frac{8.3 \times (-87.2)}{0.4} = -1.81 \times 10^3 \text{ J} \end{aligned}$$

Problem 1.3 A person consumes a diet of 10^4 J/day and spends total energy of $1.2 \times 10^4 \text{ J/day}$. Determine the daily change in the internal energy. If the net energy spent comes from sucrose at the rate of $1.6 \times 10^4 \text{ J/kg}$, in how many days will the person reduce his mass by 1 kg?

Solution. Given $dQ = 10^4 \text{ J/day}$, $dW = 1.2 \times 10^4 \text{ J/day}$

From the first law of thermodynamics

$$\begin{aligned} dU &= dQ - dW = (1.0 \times 10^4) - (1.2 \times 10^4) \\ &\approx -2.0 \times 10^3 \text{ J/day} \end{aligned}$$

This decrease corresponds to loss of sucrose. Therefore, sucrose lost per day

$$= \frac{2.0 \times 10^3}{1.6 \times 10^4} \text{ kg} = 0.125 \text{ kg/day}$$

∴ Number of days required for the loss of 1 kg

$$= \frac{1}{0.125} = 8 \text{ days.}$$

Problem 1.4 At normal temperature (0°C) and at normal pressure ($1.013 \times 10^6 \text{ N/m}^2$), when one gm of water freezes its volume increases by $0.09/\text{cm}^3$. Calculate the change in its internal energy (Latent heat of melting ice = 80 cals/gm, 1 cal = 4.2 J).

Solution. $P = 1.013 \times 10^5 \text{ N/m}^2 = 1.013 \times 10^6 \text{ dynes/cm}^2$,

$$m = 1 \text{ gm}, \quad V_1 = 1 \text{ cm}^3, \quad V_2 = 0.091 \text{ cm}^3$$

Workdone $dW = PdV = -1.013 \times 10^6 \times 0.091 = -9.2 \times 10^4 \text{ erg}$

$$dQ = 80 \text{ cal} = 80 \times 4.2 \times 10^7 \text{ erg} = 336 \times 10^7 \text{ erg}$$

According to first law of thermodynamics

$$dQ = dU + dW$$

$$dU = dQ - dW = (336 \times 10^7 + 9.2 \times 10^4) \text{ erg}$$

$$= (336 + 0.0092) \times 10^7 \text{ erg} = 336.0092 \times 10^7 \text{ erg} = 336 \text{ J.}$$

Conceptual Questions

1.1 What do you understand by thermodynamic system ?

Ans. A system consisting of very large number of particles such as gaseous molecules in a vessel is known as thermodynamic system.

1.2 State the zeroth law of thermodynamics.

Ans. If two thermodynamic systems are in thermal equilibrium with third system, then all the three systems are in thermal equilibrium with each other.

1.3 What do mean by (a) isothermal process, (b) adiabatic process, (c) isochoric process, (d) isobaric process ?

Ans. (a) Isothermal Process. Temperature of the system remains constant throughout the process. This process is very slow and container (containing the system) must be perfectly conducting.

(b) Adiabatic process. Heat of the system remains constant throughout the process. The process is very fast and container must be perfectly insulating in this process.

(c) Isochoric process. Volume of the system remains constant during the thermodynamical process.

(d) Isobaric process. Pressure of the system remains constant during the process.

1.4 What is internal energy ?

Ans. The internal energy is the microscopic energy possessed by the molecule due to their motion and arrangement in the system. Internal energy is a function of temperature of the system. For monotonic gas, internal energy is mainly due to molecular kinetic energy.

1.5 What do you understand by reversible and irreversible process ?

Ans. Reversible process. Consider a thermodynamic process in which a system undergoes from its initial to final position. If system returned back to its initial position without any other changes in the surrounding, then process is called reversible. Example : Carnot's engine.

Irreversible process. In which the system is not in equilibrium at all instants during the change.

Example : Workdone against friction.

1.6 State the Carnot's theorem.

Ans. All the reversible engines working between the same temperatures are equally efficient. Efficiency is only depends on temperature of source and sink and independent of the nature of the material (working substances) used in the engine.

1.7 State second law of thermodynamics.

Ans. According to Kelvin, "It is impossible to get continuous supply of work by cooling a body to lower than the surrounding temperature".

1.8 What is entropy ?

Ans. A property of a system that change during reversible process by an amount equal to the energy absorbed (dQ) by the system divided by thermodynamic temperature (T) i.e.,

$$\text{Change in entropy } dS = \frac{dQ}{T} \text{ or } \Delta S = \int_A^B \frac{dQ}{T}$$

where A and B are two states which are infinitesimal close to each other.

Above expression is also known as second law of thermodynamics. Entropy measures the randomness of system.

Theoretical Questions

- 1.1 What are fundamental ideals of thermodynamics ?
- 1.2 Discuss continuum model of thermodynamics ?
- 1.3 Define the following : (a) system (b) state (c) equilibrium (d) process.
- 1.4 Explain how first law of thermodynamics leads to concept of internal energy ?
- 1.5 Why does the temperature of a gas drop when it is subjected to adiabatic expansion ? Explain.
- 1.6 State First law of thermodynamics and prove that internal energy is a thermodynamical variable.
- 1.7 Write notes on following :
 - (a) Zeroth law of thermodynamics and concept of temperature
 - (b) Zeroth law of thermodynamics
 - (c) Concept of internal energy
 - (d) First law of thermodynamics
- 1.8 Explain in short first law of thermodynamics.
- 1.9 What do you mean by indicator diagram ? Draw indicator diagram for isochoric and isobaric processes.
- 1.10 What do you understand by internal energy of a system ?
- 1.11 What is zeroth law of thermodynamics ? State its importance ?
- 1.12 State first law of thermodynamics. What are its limitations ?
- 1.13 State the zeroth law of thermodynamics. How is mercury in thermometer able to find temperature of a body using the zeroth law of thermodynamics ?
- 1.14 Explain the first law of thermodynamics for the closed system undergoing a cyclic change.
- 1.15 Write the zeroth law of thermodynamics. On this basis explain the concept of temperature.
- 1.16 Explain the zeroth law of thermodynamics.
- 1.17 What is the concept of temperature ? Define temperature.
- 1.18 Prove that heat and work both are the path function.
- 1.19 State first law of thermodynamics. Show that for a cyclic process the heat supplied to a system is equal to the workdone by the system.
- 1.20 Define reversible and irreversible processes with one example of each process.
- 1.21 State zeroth law of thermodynamics and explain the concept of temperature on the basis of this law.
- 1.22 State the first law of thermodynamics. Discuss its significance.
- 1.23 Calculate workdone in an adiabatic expansion of a perfect gas.
- 1.24 State first law of thermodynamics and show that heat and work are path functions but their difference is a point function.
- 1.25 Write down the zeroth law of thermodynamics. Explain how it is introduces the temperature of a system as its function of state.
- 1.26 State the first law of thermodynamics and use it to derive a relation between the volume and temperature of a perfect gas undergoing an adiabatic change.

1.27 Show that workdone (W) for a perfect gas can be given by

$$(i) W = RT \log_e \frac{V_f}{V_i},$$

$$(ii) W = C_V(T_i - T_f) \text{ for adiabatic process.}$$

1.28 Explain the first law of thermodynamics. Explain the latent heat on the basis of it.

1.29 Derive the expression for the efficiency of a Carnot engine directly from a $T-S$ diagram.

1.30 What are the reversible processes ?

1.31 Write the Kelvin-Planck and Clausius statements of the second law of thermodynamics.

1.32 Between two given temperatures no ordinary engine can be more efficient than the Carnot engine and all Carnot's engines are equally efficient. Prove the statement.

1.33 State the essential conditions for a process to be reversible.

1.34 What do you understand by entropy ? State the second law of thermodynamics in the entropy.

1.35 What is Carnot's theorem ? Prove it.

1.36 Explain need of second law of thermodynamics. State its both statements and show the equivalence.

1.37 Prove that the efficiency of a Carnot's engine depends only upon the two temperature between which it works.

1.38 Differentiate between reversible and irreversible processes.

1.39 State two statements of second law of thermodynamics and show their equivalence.

1.40 State second law of thermodynamics.

1.41 A Carnot's engine and refrigerator work between same temperatures T_1 K and T_2 K. Write expressions for the efficiency η of Carnot's engine and coefficient of performance β , the refrigerator and inter relationship between η and β .

1.42 Write the expression for efficiency of a Carnot's reversible engine.

1.43 Establish a relation between the efficiency η of an ideal Carnot engine and the coefficient of performance β of an ideal refrigerator working between temperatures T_1 and T_2 .

1.44 Explain second law of thermodynamics.

1.45 What is significance of second law of thermodynamics ?

1.46 What is physical significance of entropy ?

1.47 'The entropy of a substance is a unique function of its state'. Explain.

1.48 Prove that the integral $\int_1^2 \frac{dQ}{T}$ does not depend on path for a reversible process.

1.49 Define and explain entropy. Explain why unavailable energy in the universe tends to increase ?

1.50 Show that entropy remains constant in a reversible process whether it increases for an irreversible process.

1.51 Define entropy and explain its physical significance ?

1.52 What is the absolute scale to temperature and how has it been derived ? Explain clearly why the scale is called absolute and why the zero of this scale is considered to be the lowest temperature possible ?

1.53 State and Prove Carnot's theorem.

- 1.54 Derive a relationship between the efficiency of a Carnot's engine and the coefficient of performance of the same engine when operated as a refrigerator. Is a Carnot's engine whose efficiency is very high particularly suited as a refrigerator? Give some reasons.
- 1.55 Discuss second law of thermodynamics. Derive an expression for the efficiency for the efficiency of Carnot's engine.
- 1.56 Derive an expression for the efficiency of a Carnot's cycle. In which case will the efficiency of Carnot cycle be higher when the temperature of the source is increased by ΔT or when the sink temperature is decreased by the same amount?
- 1.57 What is Carnot's engine? Explain Carnot's cycle and derive the expression for the efficiency of engine.
- 1.58 Explain how on the basis of second law of thermodynamics one can define a scale of temperature which does not depend upon the properties of working substance. How this scale can be realized in practice?
- 1.59 What is Carnot's cycle? Derive an expression for efficiency of Carnot engine in terms of temperatures T_1 and T_2 and adiabatic expansion ratio γ .
- 1.60 Explain the concept of entropy. Using the second law of thermodynamics as a postulate show that the entropy of universe always increases in any adiabatic process.
- 1.61 What do you mean by entropy of a substance? Prove that the total change in the entropy of a substance in a reversible cyclic process is zero. Why this statement is not true for an irreversible cycle? Explain.
- 1.62 Prove that the entropy of an ideal gas remains constant in a reversible process. But it increases in a irreversible process.
- 1.63 Define 'Entropy'. Show that in the process of equalisation of temperature, entropy increases but available energy decreases.
- 1.64 Define entropy and explain its physical significance. Show the working of Carnot' cycle on a T-S graph.
- 1.65 What are the processes involved in a Carnot's cycle? Derive an expression for thermal efficiency of the Carnot's cycle.
- 1.66 Draw T-S diagram and derive an expression for the efficiency of a Carnot's engine.
- 1.67 State and prove Carnot's theorem.
- 1.68 Describe the working of Carnot's reversible heat engine. Calculate the workdone per Carnot cycle of operation and from this obtain the expression for its efficiency.
- 1.69 Calculate the efficiency of a reversible engine working between temperature of ice and steam.
- 1.70 Describe Carnot's reversible heat engine and find an expression for the net workdone by the system in one cycle and its efficiency.

Numerical Problems

- 1.1 1 mole of a gas at 127°C expands isothermally until its volume is doubled. Calculate the workdone.

Hint : In isothermal process $W = RT \ln \frac{V_2}{V_1}$ $[\because V_2 = 2V_1]$

$$R = 8.3 \times 10^7, T = 127 + 273 = 400\text{K}$$

$$\Rightarrow W = 22.9 \times 10^9 \text{ ergs.}$$

- 1.2 A Carnot's engine whose low temperature reservoir is at 7°C has an efficiency of 40%. To increase the efficiency to 50% by how many degree should the temperature of the source be increased?

Hint : $\eta = 1 - \frac{T_2}{T_1}$ $\eta' = 1 - \frac{T_2}{T'_1}$ $T_2 = 280 \text{ K}$

$$T_1 = 466.67 \text{ K} \quad T'_1 = 560 \text{ K}$$

$$\Delta T = 560 - 466.67 = 93.33 \text{ K} = -179.67^\circ\text{C}$$

- 1.3 A Carnot's engine working between the temperatures 100°C and 0°C absorbs 10^4 calories of heat at higher temperature. What will be the workdone when the cycle of operation is over.

Hint : $\eta = 1 - \frac{T_2}{T_1} = \frac{W}{\text{Heat absorbed}}$

$$W = 1.126 \times 10^4 \text{ J}$$

- 1.4 One of the most efficiency engines ever developed operates between 2100 K and 700 K . Its actual efficiency is 40%. What percentage of its maximum possible efficiency is the actual efficiency?

Hint : $\eta = \frac{T_1 - T_2}{T_1} = \frac{200}{3} \%$

$$\frac{\text{Actual efficiency}}{\text{Maximum efficiency}} = \frac{40}{200/3} \times 100 = 60\%$$

- 1.5 Calculate the change in entropy when 2 g of ice melts into water at the same temperature. Latent heat of ice = 80 Cal/g .

Hint : $dQ = TdS$

$$dS = \frac{dQ}{T} = \frac{160}{273} = 0.58 \text{ Cal/K} = 0.58 \text{ Cal}/^\circ\text{C}$$

Multiple Choice Questions

- 1.1 The first law of thermodynamics is the conservation of

- (a) momentum
- (b) energy
- (c) both momentum and energy
- (d) temperature

- 1.2 In which process there is a change in internal energy of the system.

- (a) isothermal
- (b) adiabatic
- (c) free expansion
- (d) cyclic

- 1.3 Which one true

- (a) $dQ = dU + dW$
- (b) $dQ = dU + \frac{dV}{P}$
- (c) $dQ = \frac{dS}{T}$
- (d) $dQ = SdT$

- 1.4 In a cyclic process, the change in internal energy is

- (a) infinity
- (b) zero
- (c) equal to area of cycle
- (d) cannot be determined

- 1.5 A gas is compressed adiabatically till its temperature is doubled. The ratio of its final volume to initial volume will be

- (a) $\frac{1}{2}$
- (b) more than $\frac{1}{2}$
- (c) less than $\frac{1}{2}$
- (d) between 1 and 2

Answers

- | Answers | 1.2 (a) | 1.3 (a) | 1.4 (b) | 1.5 (c) | 1.6 (c) |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1.1 (b) | | | | | |
| 1.7 (b) | 1.8 (a) | 1.9 (a) | 1.10 (d) | 1.11 (a) | 1.12 (d) |
| 1.13 (b) | 1.14 (b) | 1.15 (a) | 1.16 (a) | 1.17 (c) | 1.18 (a) |
| 1.19 (b) | 1.20 (b) | 1.21 (c) | 1.22 (d) | 1.23 (b) | 1.24 (a) |
| 1.25 (c) | 1.26 (d) | 1.27 (c) | 1.28 (a) | 1.29 (d) | 1.30 (b) |
| 1.31 (b) | 1.32 (c) | | | | |

TUTORIAL

- 1.1 10 g of water at 100°C and pressure 10^5 N/m^2 is converted into steam at the same temperature. Calculate the increase in internal energy if latent heat of steam is 540 cal/g and its specific volume is 1671 cc. [Ans. 20990 J]
- 1.2 Calculate the change in internal energy when 1 gm mole of a perfect gas at normal pressure and temperature is compressed adiabatically to one eighth of its initial volume. The gram molecular specific heat of the gas at constant volume is $\frac{3}{2} R$. [Ans. 1150 J]
- 1.3 A Carnot's engine whose low temperature reservoir is fixed at 27°C has an efficiency of 50%. What should be the rise in temperature of high temperature reservoir such that its efficiency becomes 15% ? [Ans. 600 K]
- 1.4 The efficiency of a Carnot's engine is $\frac{1}{6}$. On decreasing the temperature of the sink by 65°C , the efficiency increases to $\frac{1}{3}$. Calculate the temperature of the source and sink. [Ans. 117°C and 52°C]
- 1.5 A Carnot's engine absorbs heat from a source at 900 K and rejects heat to a sink at $T\text{K}$. The heat given by this engine is absorbed by another engine which rejects heat to the sink at 400 K. Calculate T if the two engines have (i) equal work output, (ii) equal efficiency. [Ans. (i) 650 K (ii) 600 K]
- 1.6 The efficiency of a Carnot's engine is 50%. Temperature of sink is 27°C . By what amount the temperature of the source should be raised to have efficiency 60% ? [Ans. 150 K]
- 1.7 100 g steam at 100°C is converted into water at the same temperature. The latent heat of steam is 540 kilo cal/kg. Calculate the change in entropy. [Ans. 67.36 cal/K]
- 1.8 Calculate the change in entropy when 10 g mole of lead gets melted. [Given M.P. of lead = 600 K
Latent heat of fusion = 6 Cal/g. Molecular weight = 207] [Ans. 14.48 cal/K]
- 1.9 Calculate the change in entropy in melting 10 gram molecule of lead. Molecular weight of lead = 207, Latent heat of melting = 6, Melting point of lead = 600 K. [Ans. 8.6 cal/K]
- 1.10 What will be the change in entropy when 1 kg of water at 7°C mixed with 2 kg of water at 37°C ? [Ans. $\Delta S = 3.0 \text{ cal/K}$]