12.11.1 Entropy

The concept of entropy was introduced by Rudolph Clausius in 1865. *Entropy which is the measure of thermodynamic disorder of the system is used to describe the state of the system along with pressure, volume and temperature.* The second law of thermodynamics can also be stated in terms of entropy. The concept of entropy finds its significance when it was found that "Entropy of the universe increases in all natural processes". This is another statement of second law.

Change in entropy ΔS of a system during a process is given as

$\Delta S = S_f - S_i = \int_i^f \frac{\Delta Q}{T}$, where i - initial state and f - final state. Thus II law is stated as 'if a process occurs in a closed system, the entropy of the system increases in the case of an irreversible process and remains constant for reversible processes, but it never decreases.

12.12 Reversible and Irreversible Processes

i. Reversible process

*A **reversible process** is one in which the system can be sent back, so that the system and the surroundings pass through exactly the same intermediate states as in the direct process.*

e.g. i. Isochoric process, isothermal process, adiabatic process etc. can be performed in reversible manner.

ii. Slow compression and extension of a spring.

For the reversible process to take place the conditions to be satisfied are,

i. the process should be extremely at slow rate, so that the system remains in its mechanical, thermal and chemical equilibrium.

ii. the system should be free from dissipative forces - friction, viscosity etc. so that there is energy loss.

ii. Irreversible process

A process that does not satisfy the conditions of reversibility is called ***irreversible process.***

OR

A process that is not reversible is irreversible.

eg: For expansion of a gas, rusting of iron, most chemical reaction, decay of organic matter, mixing of two gases or liquids.

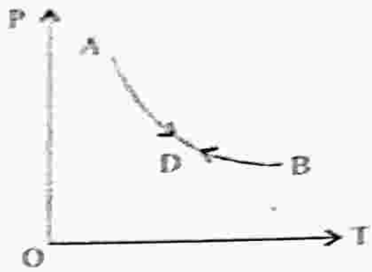


Fig. 12

12.13 Carnot Engine

A Carnot engine is a theoretical engine and an ideal engine. It was described by the French engineer Sadi Carnot in 1824. He showed that a heat engine operating in an ideal, reversible cycle, called carnot cycle between two heat reservoirs kept at different temperatures is the most efficient engine possible i.e., there is no engine more efficient than carnot engine.

The operation of carnot cycle is explained in the following paragraph and derived an expression is derived for the efficiency of carnot engine.

An ideal gas is enclosed in a cylindrical vessel filted with a frictionless, movable piston. The walls of the container and the piston are thermally non conducting.

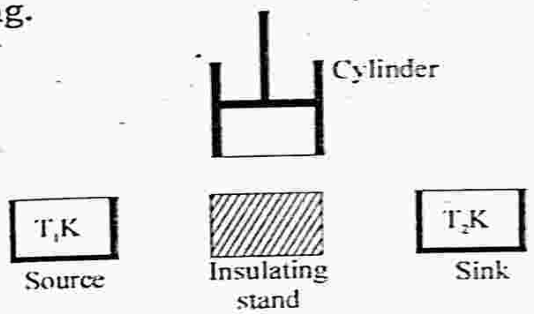


Fig.13

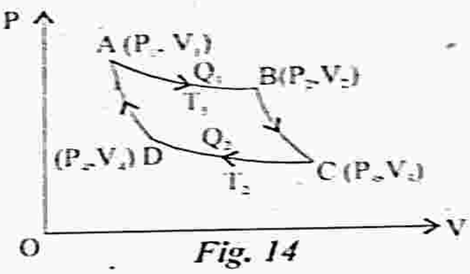


Fig. 14

The four stages of the cycle are given below.

i. Isothermal expansion (AB)

The cylinder containing the gas is placed in thermal contact with the source kept at high temperature (T_1). The gas absorbs, say Q_1 amount of heat from the source and expands. Since the temperature T_1 is constant, the expansion is isothermal. The initial pressure P_1 and volume V_1 of the gas change to P_2 and V_2. Thus the gas does a work W_{AB}.

ii. Adiabatic expansion (BC)

The gas is now placed on an insulating stand for the expansion to complete. Since now no heat enters or leaves the system, the expansion is adiabatic. Pressure and volume change from P_2 to P_3 and V_2 to V_3. During this process temperature falls to T_2. Work done by the gas is W_{BC}.

iii. Isothermal compression (CD)

The cylinder is then placed on the sink at temperature T_2. Gas is compressed to reject some heat, say Q_2 to the sink. Since temperature T_2 remains constant, the compression is isothermal. Pressure and volume change to P_4 and V_4. Work done on the gas is W_{CD}.

iv. Adiabatic compression (DA)

The cylinder is again placed on the insulating stand for the completion of the compression process. Since no heat transfers or leaves the system, the compression is adiabatic. The gas attains the original pressure P_1 and volume V_1 at the end of this. Work done now is W_{DA}.

Thus one cycle of operation gets completed and gas is now ready for a fresh cycle of operation.

Theory

$$W_{AB} = \mu RT_1 \log_e\left(\frac{V_2}{V_1}\right) \quad \text{............ (1)}$$

$$W_{BC} = \frac{\mu R(T_1 - T_2)}{\gamma - 1} \quad \text{............ (2)}$$

$$W_{CD} = -\mu RT_2 \log_e\left(\frac{V_3}{4}\right) \quad \text{............... (3)}$$

$$W_{DA} = -\mu R\frac{(T_1 - T_2)}{\gamma - 1} \quad \text{............ (4)}$$

Amount of heat absorbed during isothermal expansion = Q_1
Amount of heat absorbed during adiabatic expansion = 0
Amount of heat rejected during isothermal compression = Q_2
Amount of heat rejected during adiabatic compression = 0
Hence net heat absorbed = $Q_1 - Q_2 = W$ .... (5) and
Net work done, $W = W_{AB} + W_{BC} + W_{CD} + W_{DA}$ .... (6)
Since $W_{BC} = -W_{DA}$,

$$W = W_{AB} + W_{CD} = \mu RT_1 \log_e\left(\frac{V_2}{V_1}\right) - \mu RT_2 \log_e\left(\frac{V_3}{V_4}\right) \quad \text{.......... (7)}$$

But, $P_1V_1 = P_2V_2$ and $P_3V_3 = P_4V_4$ .... (8)

$P_2V_2^\gamma = P_3V_3^\gamma$ and $P_4V_4^\gamma = P_1V_1^\gamma$ .... (9)

Hence $\dfrac{P_2V_2^\gamma}{P_1V_1^\gamma} = \dfrac{P_3V_3^\gamma}{P_4V_4^\gamma}$

i.e., $\dfrac{P_2V_2V_2^{\gamma-1}}{P_1V_1V_1^{\gamma-1}} = \dfrac{P_3V_3V_3^{\gamma-1}}{P_4V_4V_4^{\gamma-1}}$ .... (10)

i.e., $\left(\dfrac{V_2}{V_1}\right)^{\gamma-1} = \left(\dfrac{V_3}{V_4}\right)^{\gamma-1}$ and $\therefore \dfrac{V_2}{V_1} = \dfrac{V_3}{V_4}$ .... (11) [from eq. 8]

$$W = \mu R\left[T_1 \log_e\left(\frac{V_2}{V_1}\right) - T_2 \log_e\left(\frac{V_2}{V_1}\right)\right] = \mu R(T_1 - T_2)\log_e\left(\frac{V_2}{V_1}\right)$$

Hence efficiency, $\eta = \frac{W}{Q_1} = \frac{\mu R(T_1 - T_2)\log_e\left(\frac{V_2}{V_1}\right)}{\mu R T_1 \log_e\left(\frac{V_2}{V_1}\right)}$

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

But by the definition of efficiency, $\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1}$

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

Hence $\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1} \qquad \therefore \quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$$

As $T_2 < T_1$ always, $\eta < 1$. All Carnot engines operating between the same two temperatures have same efficiency. Also efficiency of a Carnot engine operating between any two temperatures is greater than the efficiency of any real engine operating between the same two temperatures. All real engines have less efficiency than Carnot engine, since there is always some loss of energy in all real engines.

Solutions for NCERT Exercises

1. A geyser heats water flowing at the rate of 3.0 litres per minute from 27°C to 77°C. If the geyser operates on a gas burner, what is the rate of consumption of the fuel if its heat of combustion is 4.0×10^4 J/g?

Sol. $W = mC\,\Delta T$

$= (3000 \times 1) \times 4.2 \times (77 - 27)$

$= 63 \times 10^4$ J/min

Heat of combustion $= 4 \times 10^4$ J/g

$\therefore$ Rate of consumption of fuel

$$= \frac{63 \times 10^4 \text{ J/m}}{4 \times 10^4 \text{ J/g}} = 16\text{g/min.}$$

2. What amount of heat must be supplied to 2.0×10^{-2} kg of nitrogen (at room temperature) to raise its temperature by 45°C at constant pressure? (Molecular mass of N_2 = 28; R = 8.3 J mol^{-1} K^{-1}.)

Sol. $1\text{kg} = \frac{1}{28 \times 10^{-3}}$ mole

$$\therefore m = 2 \times 10^{-2}\,\text{kg} = \frac{2 \times 10^{-2}}{28 \times 10^{-3}}\text{ mole} = \frac{20}{28}$$

$$= \frac{5}{7}\text{mole}$$

$C_p = \frac{7R}{2}$, (N_2 is triatomic),

$C_p = \frac{7}{2} \times 8.3$ J/mole/K; $\Delta T = 45°$

$$\therefore Q = mC_p\Delta T = \frac{5}{7} \times \frac{7 \times 8.3}{2} \times 45 = 934\text{J}$$

3. Explain why

a. two bodies at different temperatures T_1 and T_2 if brought in thermal contact do not necessarily settle to the mean temperature

$\frac{T_1 + T_2}{2}$.

b. The coolant in a chemical or a nuclear plant (i.e., the liquid used to prevent the different parts of a plant from getting too hot) should have high specific heat.

c. Air pressure in a car tyre increases during driving.

d. The climate of a harbour town is more temperate than that of a town in a desert at the same latitude.

Sol.

a. They may have different masses and different specific heats.

b. Higher the value of specific heat, more heat will be absorbed by the coolant for the same temperature rise.

c. On driving , heat is produced due to friction between road and tyre. So temperature and hence pressure increases.

d. Due to the presence of large amount of water in air due to the proximity to sea.

4. A cylinder with a movable piston contains 3 moles of hydrogen at standard temperature and pressure. The walls of the cylinder are made of a heat insulator, and the piston is insulated by having a pile of sand on it. By what factor does the pressure of the gas increase if the gas is compressed to half its original volume?

Sol.

$\gamma = 1.4, \quad V_1 = V; \; V_2 = \frac{V}{2}$

PV^{γ} = constant

$$\therefore \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma} = \left[\frac{V}{(V/2)}\right]^{1.4} = (2)^{1.4} = 2.64$$

5. In changing the state of a gas adiabatically from an equilibrium state A to another equilibrium state B, an amount of work equal to 22.3 J is done on the system. If the gas is taken from state A to B via a process in which the net heat absorbed by the system is 9.35 cal, how much is the net work done by the system in the latter case? (Take 1 cal = 4.19 J)

Ans. Work done on the system $W_1 = 22.3$ J

Heat absorbed by the system $W_2 = 9.35 \text{ cal} = 9.35 \times 4.19 = 39.2$ J

$\therefore$ Net work done by the system, $W_2 - W_1 = 39.2 - 22.3 = 16.9$ J

6. Two cylinders A and B of equal capacity are connected to each other via a stopcock. A contains a gas at standard temperature and pressure. B is completely evacuated. The entire system is thermally insulated. The stopcock is suddenly opened. Answer the following:

a. What is the final pressure of the gas in A and B?

b. What is the change in internal energy of the gas?

c. What is the change in the temperature of the gas?

d. Do the intermediate states of the system (before settling to the final equilibrium state) lie on its P-V-T surface?

Sol.

a. 0.5 atm, b. Zero,

c. Zero (for ideal gas)

d. No. Since the process is rapid and cannot be controlled. The intermediate states are non-equilibrium state, and does not satisfy the gas equation. In due course the gas returns to an equilibrium state which lies on P-V-T surface.

7. A steam engine delivers 5.4×10^8 J of work per minute and services 3.6×10^8 J of heat per minute from

its boiler. What is the efficiency of the engine? How much heat is wasted per minute?

Ans. Heat absorbed per minute by the engine from the boiler = 3.6×10^9 J

Work done per minute by the steam engine = 5.4×10^8 J

∴ Efficiency of the engine,

$$\eta = \frac{\text{Work done}}{\text{Heat absorbed}} \times 100\%$$

$$= \frac{5.4 \times 10^8}{3.6 \times 10^9} \times 100\% \quad \eta = 15\%$$

Heat wasted per minute = Heat absorbed – Work output

$= 3.6 \times 10^9 - 5.4 \times 10^8 = 3.06 \times 10^9$

$= 3.1 \times 10^9$ J

8. An electric heater supplies heat to a system at a rate of 100W. If the system performs work at a rate of 75 joules per second, at what rate is the internal energy increasing?

Sol.

$$\Delta Q = \Delta U + \Delta W$$

$$100 = \Delta U + 75$$

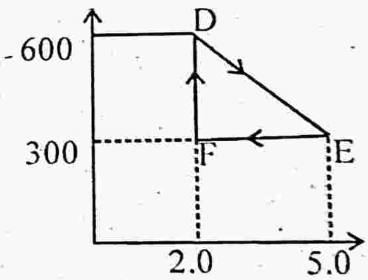
$$\Delta U = 25W = 25 \text{ J/s}$$

9. A thermodynamic system is taken from an original state to an intermediate state by the linear process shown in the figure given. Its volume is then reduced to the original value from E to F by an isobaric process. Calculate the total work done by the gas from D to E to F.

Sol.

Work done = Area of the

$$\Delta DFE = \frac{1}{2} \times DF \times FE$$



$$= \frac{1}{2} \times (600 - 300) \times (5 - 2) = 450 \text{ J}$$

10. A refrigerator is to maintain eatables kept inside at 9°C. If room temperature is 36°C, calculate the coefficient of performance.

Sol.

Coefficient of performance

$$= \frac{T_2}{T_1 - T_2} = \frac{282}{309 - 282} = \frac{282}{27} = 10.4$$