Unit 5: ENTROPY AND THE SECOND LAW OF THERMODYNAMICS

5.1 Entropy of a System

In unit 1 we defined a system as a restricted region of space one has chosen to study. Also, we mentioned that the properties or coordinates used to describe thermodynamic system are the thermodynamic properties or coordinates. One of such properties is entropy. Entropy, S, is the degree of disorderliness of a system. Unlike energy, entropy of a system does not always obey a conservation law.

5.2 Change in Entropy

The change in entropy ΔS of a system during a process that takes the system from initial state i to a final state f is defined as

$$\Delta S = S_f - S_i = \int_i^f \frac{dQ}{T}$$

5.1

Equation 5.1 implies that change in entropy depends on both the energy transfer as heat during the process and the temperature of the system. The S.I unit of entropy and change in entropy is Joule per Kelvin (JK^{-1}).

5.2.1 Reversible Process

For a reversible process that occurs in a closed system, the entropy always remains constant. That is, the change in entropy for a reversible process is zero ($\Delta S = 0$). This statement can be explained using a Carnot cycle

5.2.2 Irreversible Process

An irreversible process can be defined as one which direction cannot be reversed by an infinitesimal change in some property of the system. A good example of irreversible process is illustrated in figure 5.1. Figure 5.1 shows a hot reservoir at temperature T_H in thermal contact through a conductor with a cold reservoir at temperature T_C. Suppose the arrangement is isolated from the surrounding (i.e. no heat flows in or out of the arrangement), heat flows from hot reservoir to cold reservoir and not in reversed direction. This process is an irreversible process. Suppose heat Q flows from the hot reservoir to the cold reservoir, we can then write the equation for the total entropy change ΔS during the process.

The change in entropy for the cold reservoir ΔS_C, using equation 5.1 is

$$\Delta S_C = \frac{Q}{T_C}$$

5.2

ΔS_C is positive because heat Q flows into the cold reservoir and is positive Q. Similarly the change in entropy of the hot reservoir ΔS_H, using equation 5.1 is

$$\Delta S_H = -\frac{Q}{T_H}$$

5.3

ΔS_H is negative because heat Q flows out of the hot reservoir (i.e. − Q).

The total entropy is

$$\Delta S = \Delta S_H + \Delta S_C$$

5.4

which gives

$$\Delta S = -\frac{Q}{T_H} + \frac{Q}{T_C} > 0$$

5.5

The total entropy ΔS is greater than zero because T_H is greater than T_C . We can then say that $\Delta S > 0$ for irreversible process.
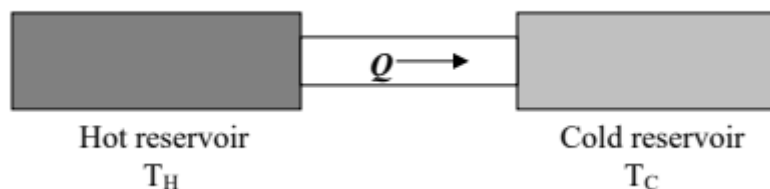

Fig. 5.1: Heat Q Flows from Hot Reservoir to Cold Reservoir

5.2.3 Change in Entropy during Adiabatic and Isothermal Processes

Change in entropy is given by equation 5.1 and it is a function of Q and T.

 Reversible adiabatic process: during adiabatic process, **dQ = 0**, and this implies that during reversible adiabatic process dQr = 0. Then, going by equation 5.1

$$dS = 0 \qquad \textbf{5.6}$$

Reversible isothermal process: An example of reversible isothermal process is phase change and this occurs at constant pressure during which the temperature also remains constant.

$$S_f - S_i = \int_i^f \frac{dQ_r}{T} = \frac{1}{T}\int_i^f dQ_r = \frac{Q}{T}$$

5.7

where Q is the latent heat or latent heat of transformation.

5.3 Entropy as a State Function

Entropy, like pressure, energy, and temperature, is a property of the state of a system and is independent of how that state is reached.

The above statement can be justify from the equation of the first law of thermodynamics

$$\mathbf{dU = dQ - dW}$$

For a reversible isobaric process,

$$\mathbf{dQ = PdV + n\ C_P\ dT} \qquad \mathbf{5.8}$$

Using the equation for the ideal gas, P in equation 5.8 can be replaced with (nRT/V). Then dividing through by T, gives

$$\frac{dQ}{T} = nR\frac{dV}{V} + nC_P\frac{dT}{T}$$

5.9

Suppose each term of equation 5.9 is integrated between an arbitrary initial state i and an arbitrary final state f we get

$$\int_i^f \frac{dQ}{T} = \int_i^f nR\frac{dV}{V} + \int_i^f nC_P\frac{dT}{T}$$

But change in entropy ΔS is already given to be dQ/T in equation 5.1, so

$$\Delta S = S_f - S_i = nR\ln\frac{V_f}{V_i} + nC_P\ln\frac{T_f}{T_i}$$

5.10

Equation 7.9 thus implies that the change in entropy ΔS between the initial state and final state of an ideal gas depends only on properties of the initial and properties of final state (i.e. ΔS does not depend on how the gas changes between the two states).

5.4   The Second Law of Thermodynamics

The change in entropy ΔS for a process occurring in a closed system is zero for reversible process and greater than zero for irreversible process. This is one of the statements of the second law of thermodynamics.

The second law of thermodynamics gives the direction in which the natural process will take place.

Statement of the Second law of thermodynamics

If a process occurs in a closed system, the entropy of the system increases for irreversible processes and remains constant for reversible processes. Entropy of a system never decreases.

Mathematical statement of the Second law of thermodynamics

$$\Delta S \geq 0 \qquad 5.11$$

5.5   Carnot Engine

Carnot engine is the most efficient kind of heat engine and because of this it is sometime referred to as an ideal heat engine. Ideal in the sense that all processes in the cycle are reversible and no wasteful energy transfer occur due to friction and turbulence. This engine is after a French scientist and engineer N.L. Sadi Carnot. The P-V diagram of the Carnot cycle is shown in figure 5.2 and the arrow on the plot indicate the direction of the cycle (i.e. clockwise). During each cycle, the engine (i.e. the working substance) absorbs energy Q_H as heat from a thermal reservior at constant temperature T_H and ejects energy Q_C as heat to a second reservoir at a constant lower temperature T_C .

Description of the Processes

• Process de is an isothermal process during which heat Q_H is transferred at temperature T_H to the working from the hot reservoir. This causes the gas to undergo isothermal expansion from volume V_d to V_e .

• Process ef is an adiabatic expansion i.e no heat is added as the working substance expands from volume V_e to V_f . Temperature decreases during the process from T_H to T_C

• Process fg is an isothermal process during which heat Q_C is transferred at temperature T_C from the working to cold reservoir. This causes the gas to undergo isothermal compression from volume V_f to V_g .

• Processes gd is an adiabatic compression i.e. no heat is transferred as the working substance compresses from volume Vg to Vd Temperatures increases during the process from T_C and T_H .
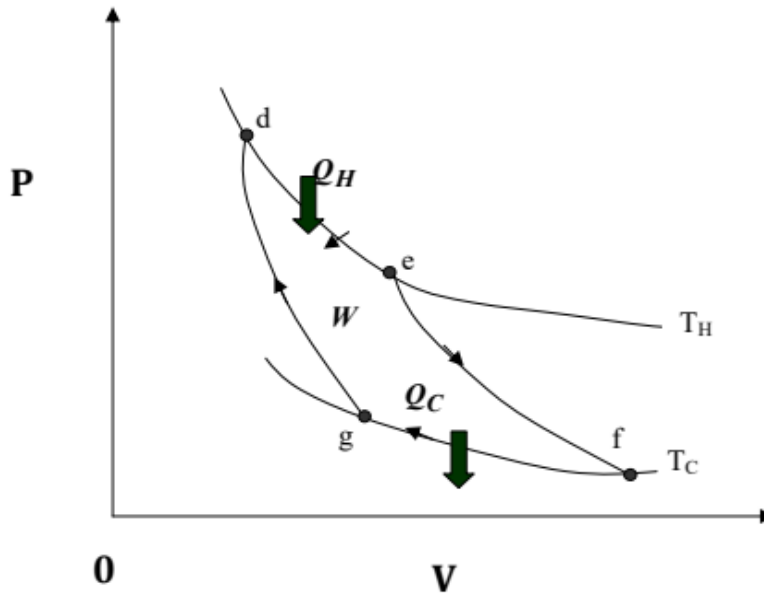

Fig. 5.2: PV Plot for the Carnot Cycle

Work:

From the first law of thermodynamics **(ΔU = Q − W)**, the total work done during a cycle or cyclic process can be calculated. For a cyclic process **ΔU = 0**, the total heat transfer per cycle **Q = Q$_H$ − Q$_C$** , and the total work done is W . Then, the first law of thermodynamic for the Carnot cycle is

$$W = Q_H - Q_C \qquad 5.12$$

5.5.1 Efficiency of a Carnot Engine

The efficiency of a heat engine is

$$E = \frac{W}{Q_H} = \frac{work\ output}{heat\ in} \qquad \text{(in one cycle)} \qquad 5.13$$

Using equation 5.12, equation 7.13 becomes

$$E = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} \qquad 5.14$$

But the ratio of the rejected heat Q_C to the input heat Q_H for a reversible process can be written as

$$\frac{Q_C}{Q_H} = \frac{T_C}{T_H}$$

5.15

where temperature T_C and T_H are temperatures in Kelvin. Rearranging 5.15 gives

$$\frac{Q_H}{T_H} = \frac{Q_C}{T_C}$$

5.16

Insert equation 5.15 in equation 5.14 to obtain

$$E = 1 - \frac{T_C}{T_H}$$

5.17

Equation 7.17 is the efficiency of a Carnot engine operating between two heat reservoirs in which heat is taking in at temperature T_H and heat is ejecting at temperature T_C. Temperatures T_H and T_C must be in Kelvin. The relation in equation 7.17 gives the maximum possible efficiency for a heat engine operating between two Kelvin temperatures T_H and T_C.

5.5.2 Another Statement of Second Law of Thermodynamics

The efficiency of an ideal heat engine is given by equation 5.17. The implication of this is that no heat engine can have efficiency greater than that of a Carnot engine. It is clear from equations 5.14 and 5.17 that the efficiency of a Carnot engine is less that 100 %. This of course is another statement of the second law of thermodynamics. That is, the efficiency of heat engine is always less than 100 %. This statement is called Kelvin's statement

Kelvin's Statement: No process is possible whose sole result is the complete conversion of heat into work.

5.5.3 Entropy Change of a Reversible Process

A good example of a reversible thermodynamic process is Carnot cycle. In a Carnot engine, there are only two reversible energy transfers as heat (i.e. entropy change at T_H and at T_C). The net entropy change per cycle is

$$\Delta S = \Delta S_H + \Delta S_C = \frac{Q_H}{T_H} - \frac{Q_C}{T_C}$$

5.18

where ΔS_H is the positive entropy because energy Q_H is added to the working substance (i.e. increase in entropy) and ΔS_C is negative entropy because energy Q_C is removed from the working substance as heat (i.e. decrease in entropy). Using equation 5.16, then equation 5.18 becomes

$$\Delta S = \Delta S_H + \Delta S_C = \frac{Q_H}{T_H} - \frac{Q_C}{T_C} = 0$$

5.19

Therefore the entropy for a reversible process ΔS is zero (**i.e. $\Delta S = 0$**)