THE SECOND LAW OF THERMODYNAMICS

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Limitations of the First law. Need for the Second law.

The First law of thermodynamics, though exact, has certain limitations, as discussed below.

1. The First law establishes definite relationship between the heat absorbed and the work performed by a system in a given process. But *it puts no restriction on the direction of flow of heat.* According to the first law, for example, it is not impossible to extract heat from ice by cooling it to a low temperature and then use it for warming water. But it is known from experience that such a transfer of heat from a lower to a higher temperature is not possible without expenditure of energy, *i.e.*, without doing some external work. It is known, on the other hand, that heat flows spontaneously, *i.e.*, of its own accord, from a higher to a lower temperature.

2. According to the First law, the energy of an isolated system remains constant during a specified change of state. But it does not tell whether a specified change or a process including a chemical reaction can occur spontaneously, *i.e.*, whether it is feasible.

3. The First law states that energy of one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work. There is thus need for another law, *viz.*, the Second law of thermodynamics.

The Second law helps us to determine the direction in which energy can be transferred. It also helps us to predict whether a given process or a chemical reaction can occur spontaneously. It introduces a new concept of entropy. It also helps us to know the equilibrium conditions.

It is known from experience that although various forms of energy can be completely transformed into one another, yet heat is a typical form of energy which cannot be completely transformed into work. The Second law helps us to calculate the maximum fraction of heat that can be converted into work in a given process. Entropy can be thought of as arising from the *dispersal* or *degradation* of the total energy of an isolated system.

Spontaneous or Irreversible Processes

Natural processes are spontaneous and irreversible. A few examples are given below.

1. Water flows downhill spontaneously. We cannot reverse the direction of flow without some external aid.

2. If a bar of metal is hot at one end and cold at the other end, heat flows spontaneously from the hot end to the cold end until the temperature of the rod becomes uniform throughout, *i.e.*, until equilibrium is attained. This process, evidently, cannot be reversed. Our experience does not show that a metal bar having uniform temperature can become hot at one end and cold at the other end spontaneously.

3. The diffusion of a solute from a more concentrated solution to a less concentrated solution when these are brought into contact proceeds spontaneously till the concentration becomes uniformly

the same, *i.e.*, till the equilibrium is attained. This process also cannot be reversed because once the concentration becomes uniform, it is not possible to make spontaneously one part of the solution more concentrated than any other part.

4. Heat flows spontaneously from a hot reservoir to a cold reservoir. For the reverse process, *i.e.*, for the transfer of heat from a cold reservoir to a hot reservoir, as in a refrigerator, energy has to be supplied from outside the system.

5. Electricity flows spontaneously from a point at a higher potential to a point at a lower potential. The direction of flow of current can be reversed only by applying an external field in the opposite direction.

6. A gas expands spontaneously from a region of high pressure to a region of low pressure or in vacuum.

Thus, we see that all natural processes proceed spontaneously and are thermodynamically irreversible in character.

Work can be obtained from spontaneous processes. But since these proceed irreversibly, the work obtained is much less than that obtained from thermodynamically reversible processes in which case the work obtained is maximum.

Cyclic Process. When a system, after completing a series of changes, returns to original state, it is said to have completed a cycle. The entire process is known as a **cyclic process.** Since the internal energy of a system depends only upon its state, it follows that in a cyclic process, the net change of internal energy is zero, *i.e.*, $\Delta U=0$. Therefore, according to the First law,

$$\Delta U = 0 = q + w \qquad \text{or} \qquad q = -w$$

If the series of changes in a cycle are conducted at constant temperature, the cycle is said to be an **isothermal cycle.** If the changes are carried out reversibly, the cycle is said to be a **reversible cycle.**

Although the reversible cyclic processes are merely theoretical and imaginary, the concept is highly useful in deriving certain important relationships. The most well known cyclic process is the **Carnot cycle.**

Carnot employed a reversible cycle to demonstrate the maximum convertibility of heat into work. The system consists of one mole of an ideal gas which is subjected to a series of four successive operations, commonly termed as **four strokes,** as given below.

I. Stroke 1. Isothermal Expansion. The gas is allowed to expand reversibly and isothermally at the temperature T_2 so that the volume increases from V_1, represented by the point A, to V_2 represented by the point B (Fig. 1.). Since in the isothermal expansion of an ideal gas $\Delta U=0$, it follows from the First law equation (*viz.*, $\Delta U=q+w$) that $q=-w$, *i.e.*, the heat absorbed is equal to the work done by the system on the surroundings. Let q_2 be the heat absorbed by the system at the temperature T_2 and w_1 be the work done by the system on the surroundings. Then

$$q_2 = -w_1 = RT_2 \ln (V_2/V_1) \qquad \ldots(1)$$

II. Stroke 2. Adiabatic Expansion. The gas is then allowed to expand reversibly and adiabtically from the volume V_2 to V_3, *i.e.*, from the point B to C.

Since work is done by the system adiabatically, it is not in a position to absorb heat. The temperature of the system, therefore, falls from T_2 to say, T_1. As q is equal to

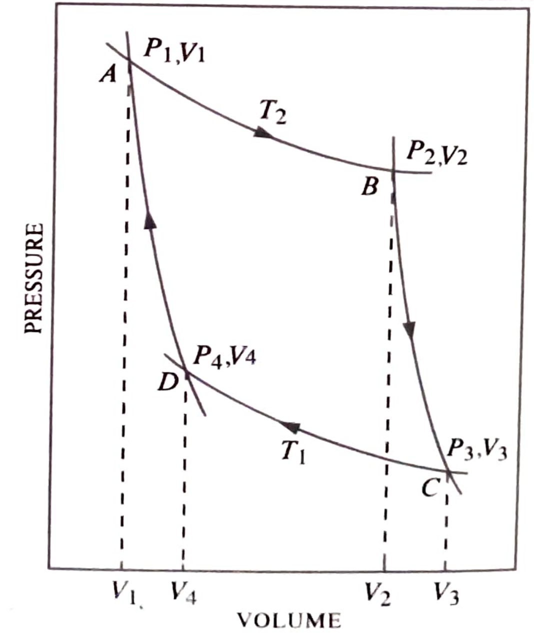

Fig. 1. The four operations in Carnot cycle.

zero in this case, it follows from the First law equation (*viz.*, $\Delta U = q+w$) that $\Delta U = w$. Since the process involves expansion of the gas, therefore, work is done by the system on the surroundings. Hence, by convention, w is negative so that $\Delta U = -w$.

Now, by definition, $C_v = (\partial U/\partial T)_v$ ...(2)

$$\therefore \quad \Delta U = C_v \, \Delta T = C_v(T_1 - T_2) = -w \quad ...(3)$$

(change in temperature, ΔT = final temperature – initial temperature)

$$\text{or} \quad -w = C_v(T_1 - T_2) = -C_v(T_2 - T_1) \quad ...(4)$$

If the work done in this stage is denoted by w_2, then

$$\therefore \quad -w_2 = -C_v(T_2 - T_1) \quad ...(5)$$

III. Stroke 3. Isothermal Compression. After this, the gas is subjected to a reversible and isothermal compression at the lower temperature T_1 so that the volume decreases from V_3 to V_4 (*i.e.*, from the point C to D). In this case, evidently, work is done on the system. Hence, heat will be produced and *given up* to the surroundings. Since compression takes place isothermally and reversibly, $\Delta U = 0$. Therefore, if q_1 is the heat *given out* to the surroundings at the temperature T_1 and w_3 is the work done on the system in this process, then remembering signs of q and w,

$$-q_1 = w_3 = RT_1 \ln (V_4/V_3) \quad ...(6)$$

IV. Stroke 4. Adiabatic Compression. Finally, by an adiabatic and reversible compression, the gas is restored to its original volume V_1 and temperature T_2. Thus, the gas is compressed adiabatically from D to A. In this case, work is done on the system. Hence, w is positive. According to the First law, $\Delta U = q+w$. Since in adiabatic process, $q=0$, hence,

$$\Delta U = w = C_v \Delta T = C_v(T_2 - T_1)$$

Let w_4 be the work done in this stage. Then,

$$w_4 = C_v(T_2 - T_1) \quad ...(7)$$

where $T_2 - T_1$ is the increase in temperature produced by the adiabatic compression.

The net heat absorbed (q) by the ideal gas in the whole cycle is given by

$$\begin{aligned} q &= q_2 + (-q_1) = RT_2 \ln (V_2/V_1) + RT_1 \ln (V_4/V_3) \\ &= RT_2 \ln (V_2/V_1) - RT_1 \ln (V_3/V_4) \quad ...(8) \end{aligned}$$

In the light of adiabatic expansion of an ideal gas discussed in Chapter 12, the following equations can be written :

$$C_v \ln (T_2/T_1) = R \ln (V_3/V_2) \quad \text{(For stage II)}$$

$$C_v \ln (T_2/T_1) = R \ln (V_4/V_1) \quad \text{(For stage IV)}$$

$$\text{or} \quad V_3/V_2 = V_4/V_1 \quad \text{or} \quad V_2/V_1 = V_3/V_4 \quad ...(9)$$

Hence, the **net heat absorbed,** according to Eq. 8, may be put as

$$q = q_2 - q_1 = R(T_2 - T_1) \ln (V_2/V_1) \quad ...(10)$$

Similarly, the **net work done** by the gas is given by

$$\begin{aligned} w &= -w_1 + (-w_2) + w_3 + w_4 \\ &= RT_2 \ln V_2/V_1 - C_v(T_2 - T_1) + RT_1 \ln (V_4/V_3) + C_v(T_2 - T_1) \quad ...(11) \\ &= RT_2 \ln (V_2/V_1) - RT_1 \ln (V_3/V_4) \end{aligned}$$

$$\text{Since} \quad V_2/V_1 = V_3/V_4 \quad ...(12)$$

$$\text{Hence,} \quad w = R(T_2 - T_1) \ln (V_2/V_1)$$

It follows from Eqs. 10 and 12 that $q = w$. Thus, *the essential condition for a cyclic process that the net work done is equal to the net heat absorbed is fully satisfied.*

The relationship between w, the net work done by the system and q_2, the quantity of heat absorbed at the higher temperature T_2, in Carnot cycle, can be obtained from the following two equations :

$$w = R(T_2 - T_1) \ln (V_2/V_1) \qquad \text{(Eq. 12)}$$

and

$$q_2 = RT_2 \ln (V_2/V_1) \qquad \text{(Eq. 1)}$$

Hence, dividing Eq. 12 by Eq. 1,

$$w = q_2 \,(T_2 - T_1)/T_2 \qquad (13)$$

Since $(T_2 - T_1)/T_2 < 1$, it follows that $w < q_2$, *i.e.*, work done is less than the heat absorbed. This means that only a part of the heat absorbed by the system at the higher temperature T_2 is transformed into work. The rest of the heat q_1 is given out by the system to the surroundings which is at the lower temperature T_1.

Thus, Kelvin stated the **second law of thermodynamics** as follows :

It is impossible to use a cyclic process to extract heat from a reservoir and to convert it into work without transferring at the same time a certain amount of heat from a hotter to a colder part of the system.

Efficiency of a Heat Engine. *The fraction of the heat absorbed by an engine which it can convert into work gives the* **efficiency** (η) *of the engine.*

From Eq. 13, it is seen that

$$\text{Efficiency, } \eta = w/q_2 = (T_2 - T_1)/T_2 \qquad ...(14)$$

Since $(T_2 - T_1)/T_2$ is invariably less than 1, the efficiency of a heat engine is always less than 1. No heat engine has yet been constructed which has an efficiency equal to unity. Mathematically, however, if $T_1 = 0$, efficiency$=1$.

It follows from Eq. 14 that the efficiency depends upon the difference between T_2 and T_1. Thus, the greater the difference between the temperature of the 'source' and the 'sink', the greater is the efficiency. This explains why superheated steam is used in a steam engine.

The net heat absorbed by the system, q, is equal to $q_2 - q_1$ and according to the First law of thermodynamics, this must be equivalent to the net work done by the system. Thus,

$$w = q_2 - q_1$$

Combining this with Eq. 14, we get

$$(q_2 - q_1)/q_2 = (T_2 - T_1)/T_2 \qquad ...(15)$$

Thus,

$$\text{efficiency, } \eta = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2} \qquad ...(16)$$

Eq. 16 has been arrived at by assuming that the series of changes in the cycle are brought about in a thermodynamically reversible manner so as to obtain maximum possible work. But, in actual practice, it is not possible to carry out the process infinitesimally slowly so that the efficiency is even less than that given by the above equation.

Carnot Theorem. According to Eq. 16, the efficiency of a machine working reversibly depends only on the temperature of the source and the sink. It is independent of the nature of the substance or substances used for operations. The same idea may be expressed by saying that *all periodic machines* *working reversibly between the same two temperatures have the same efficiency.* This statement is commonly known as the **Carnot theorem,** in honour of S. Carnot (1796-1832), the brilliant French physicist, known for important contributions to thermodynamics.

It may be noted that while the First law states that when one form of energy is transformed into another, the amount of energy that disappears is exactly equivalent to the amount of energy that is produced, it is silent about the extent to which such conversion can take place. The Second law of thermodynamics gives information about this point. It tells us that while all other forms of energy can be *completely* converted into heat, the complete conversion of heat into any other form of energy cannot take place without leaving some lasting change in the system. This has led to the following enunciation of the **Second law of thermodynamics :**

It is impossible to convert heat into work without compensation.

Example 1. Calculate the maximum efficiency of an engine operating between 110°C and 25°C.

Solution : Maximum efficiency of an engine working between temperatures T_2 and T_1 is given by

$$\eta = (T_2 - T_1)/T_2 = (383\text{ K} - 298\text{ K})/383\text{ K} = 0{\cdot}222 = \mathbf{22{\cdot}2\%}$$

Example 2. Heat supplied to a Carnot engine is 1897·8 kJ. How much useful work can be done by the engine which works between 0°C and 100°C ?

Solution :

$$T_2 = 100 + 273 = 373\text{ K}\ ; \quad T_1 = 0 + 273 = 273\text{ K}\ ; \quad q_2 = 1897{\cdot}8\text{ kJ}$$

$$w = q_2\,(T_2 - T_1)/T_2 = 1897{\cdot}8\text{ kJ} \times (373\text{ K} - 273\text{ K})/373\text{ K} = 508{\cdot}7\text{ kJ}$$

∴ Work done by the engine = **508·7 kJ**

An important generalisation. Eq. 16 derived from the Carnot cycle may be rearranged as

$$1 - (q_1/q_2) = 1 - (T_1/T_2)$$

or

$$q_1/T_1 = q_2/T_2 \qquad \text{...(17)}$$

Eq. 17 may also be written, in the general form, as

$$q_{rev}/T = \text{constant} \qquad \text{...(18)}$$

where q_{rev} is the quantity of heat exchanged in a process carried out *reversibly* at a temperature T. This is an important generalisation since the quantity q_{rev}/T, as we shall see presently, represents a definite quantity or state function, *viz.*, the entropy change of the system.