❖ Entropy Concept as a Measure of Unavailable Energy and Criteria for the Spontaneity of Reaction

The entropy change during the course of a process can be used to rationalize the unavailable energy as well as its spontaneity or feasibility. In this section, we will first discuss the entropy concept as a measure of unavailable energy and then we will study the spontaneity of a process in terms of entropy change.

➢ *Entropy Concept as a Measure of Unavailable Energy*

In order to understand the connection between entropy and unavailable energy, consider a heat source at temperature T_2 placed in an atmosphere or surrounding at temperature T_0. The surrounding plays the role of

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heat sink here. Now if Q is the heat transferred from the source to a Carnot heat engine working between T_2 and T_0, then from Carnot's theorem, we have

$$\frac{W_{max,T_2,T_0}}{Q} = \frac{T_2 - T_0}{T_2} \tag{71}$$

$$W_{max,T_2,T_0} = Q\left(1 - \frac{T_0}{T_2}\right) \tag{72}$$

Where W_{max,T_2,T_0} is the maximum work that can be obtained from a heat engine working between T_2 and T_0 temperatures. It is worthy to note that only a part of the heat transferred can be turned into work i.e. available to be used as work.

Now suppose that the same amount of heat is first transferred directly from the source at T_2 to another source at $T_1 < T_2$. In other words, the heat Q is now first transferred from hot source to a cold source without any Carnot bridging. Now the maximum work that can be obtained from a heat engine working between T_1 and T_0 temperatures will be

$$W_{max,T_1,T_0} = Q\left(1 - \frac{T_0}{T_1}\right) \tag{73}$$

Where W_{max,T_1,T_0} is the maximum work that can be obtained after the direct heat transfer, since the heat engine is now working between T_1 and T_0 temperatures. Now before the irreversible heat transfer ($T_2 \rightarrow T_1$), the magnitude of energy that could have been transformed into work is:

$$E_{unavailable} = \left(W_{max,T_2,T_0}\right) - \left(W_{max,T_1,T_0}\right) \tag{74}$$

$$= \left[Q\left(1 - \frac{T_0}{T_2}\right)\right] - \left[Q\left(1 - \frac{T_0}{T_1}\right)\right] \tag{75}$$

$$= Q\left[\left(1 - \frac{T_0}{T_2}\right) - \left(1 - \frac{T_0}{T_1}\right)\right] \tag{76}$$

$$= Q\left(\frac{T_0}{T_1} - \frac{T_0}{T_2}\right) \tag{77}$$

$$= T_0\left(\frac{Q}{T_1} - \frac{Q}{T_2}\right) \tag{78}$$

Since $-Q/T_2$ and Q/T_1 are the entropy loss and gain of sources at T_2 and T_1, respectively; the equation (78) reduces to the following.

$$E_{unavailable} = T_0\left(\Delta S_{source\ at\ T_1} + \Delta S_{source\ at\ T_2}\right) \tag{79}$$

$$= T_0\,\Delta S_{irreversible\ heat\ transfer} \tag{80}$$

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Where $E_{unavailable}$ is lost work or the energy which is no longer available to do any useful work.

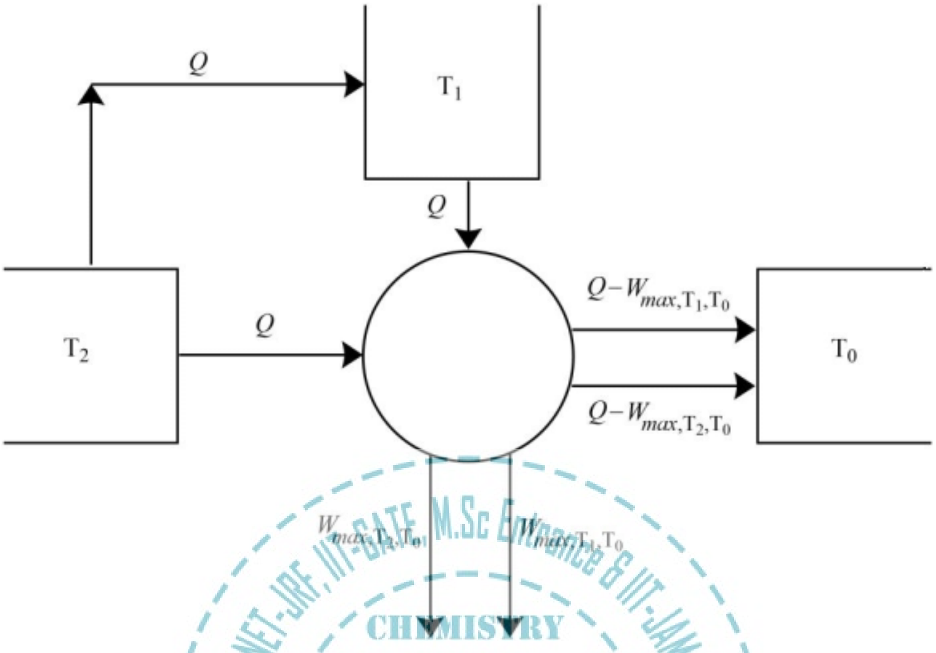

Figure 4. The pictorial representation of the entropy–unavailable-energy.

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The physical significance of equation (80) can also be demonstrated using a live example. Let us consider a Carnot engine working between 800K and 200K is supplied with a heat (Q) of 5000 joules. The efficiency of such an engine will be

$$\eta = \frac{T_2 - T_0}{T_2} = \frac{800 - 200}{800} = 0.75 \tag{81}$$

The maximum work obtained will be

$$W = \eta Q = 0.75 \times 5000\,J = 3750 \tag{82}$$

Now if this 5000 joules of heat is first transferred to the reservoir at 500K, and then it is fed to a Carnot engine working obviously between "500K" and 200K. The efficiency of such an engine will be

$$\eta = \frac{T_1 - T_0}{T_1} = \frac{500 - 200}{500} = 0.6 \tag{83}$$

The maximum work obtained will be

$$W = \eta Q = 0.6 \times 5000\,J = 3000 \tag{84}$$

Comparing the results of equation (82) and (84), we can say that there is 750 J less work from the same heat transfer in the second process.

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➢ *Entropy Concept as the Criteria for the Spontaneity of Reaction*

The second law of thermodynamics states that all the spontaneous processes are thermodynamically irreversible, and accompanied by a net increase in entropy. The entropy change for a reversible process is,

$$\Delta S_{system} + \Delta S_{sorrounding} = 0 \tag{85}$$

And the entropy change for a spontaneous or irreversible process is

$$\Delta S_{system} + \Delta S_{sorrounding} > 0 \tag{86}$$

The results of equation (85) and equation (86) can be combined to give a more generalized form as:

$$\Delta S_{system} + \Delta S_{sorrounding} \geq 0 \tag{87}$$

Where the sign of '=' stands from reversible and '>' stands for irreversible or spontaneous reaction, respectively.

Nevertheless, the criteria from equation (87) is not very much practical as ΔS_{system} and $\Delta S_{sorrounding}$ are not easy to determine. Therefore, some other criteria must be deduced which requires only the knowledge of the change in some simple thermodynamic parameters. In order to do so, write down the equation (87) for infinitesimally small changes as given below.

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$$dS_{system} + dS_{sorrounding} \geq 0 \tag{88}$$

If δq is the heat lost by the surrounding reversibly and isothermally at temperature T, then we can say that

$$dS_{sorrounding} = -\frac{q_{rev}}{T} \tag{89}$$

Also, from the first law of thermodynamics, we have

$$\delta q_{rev} = dU + PdV \tag{90}$$

After putting the value from equation (90) in equation (89), we have

$$dS_{sorrounding} = -\frac{dU + PdV}{T} \tag{91}$$

Now putting the value of $dS_{sorrounding}$ from equation (91) into equation (88), we get

$$dS_{system} - \frac{dU + PdV}{T} \geq 0 \tag{92}$$

$$TdS_{system} - dU - PdV \geq 0 \tag{93}$$

$$TdS \geq dU + PdV \tag{94}$$

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Where $dS_{system} = dS$ i.e. change in the entropy of the system. For a spontaneous or irreversible process TdS must be greater the sum of internal energy change and pressure-volume work.

However, the above relation is reduced to the following if the internal energy and volume of the system are kept constant i.e. $dU = 0$ and $dV = 0$.

$$(TdS)_{U,V} \geq 0 \tag{95}$$

or

$$(dS)_{U,V} \geq 0 \tag{96}$$

Here it is worthy to recall that the sign '=' is for reversible reactions whereas '>' condition is applicable to spontaneity or irreversibility of a reaction.

Besides, the spontaneity of equation (94) can also be written in the form of internal energy change,

$$dU \leq TdS - PdV \tag{97}$$

the above relation is reduced to the following if the internal energy and volume of the system are kept constant i.e. $dS = 0$ and $dV = 0$.

$$(dU)_{S,V} \leq 0 \tag{98}$$

Again it should be noted that the sign '=' is for reversible reactions whereas '<' condition is applicable to spontaneity or irreversibility of a reaction.

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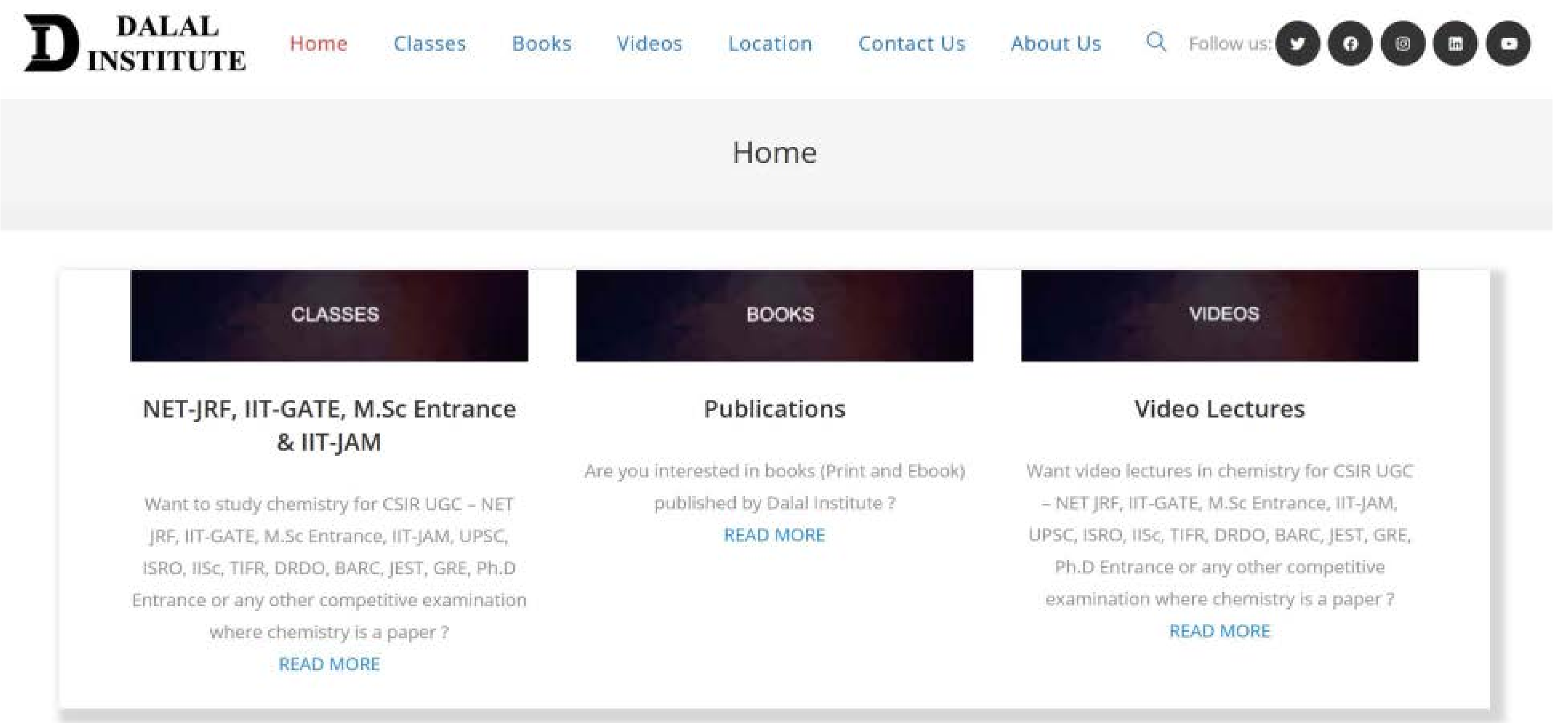

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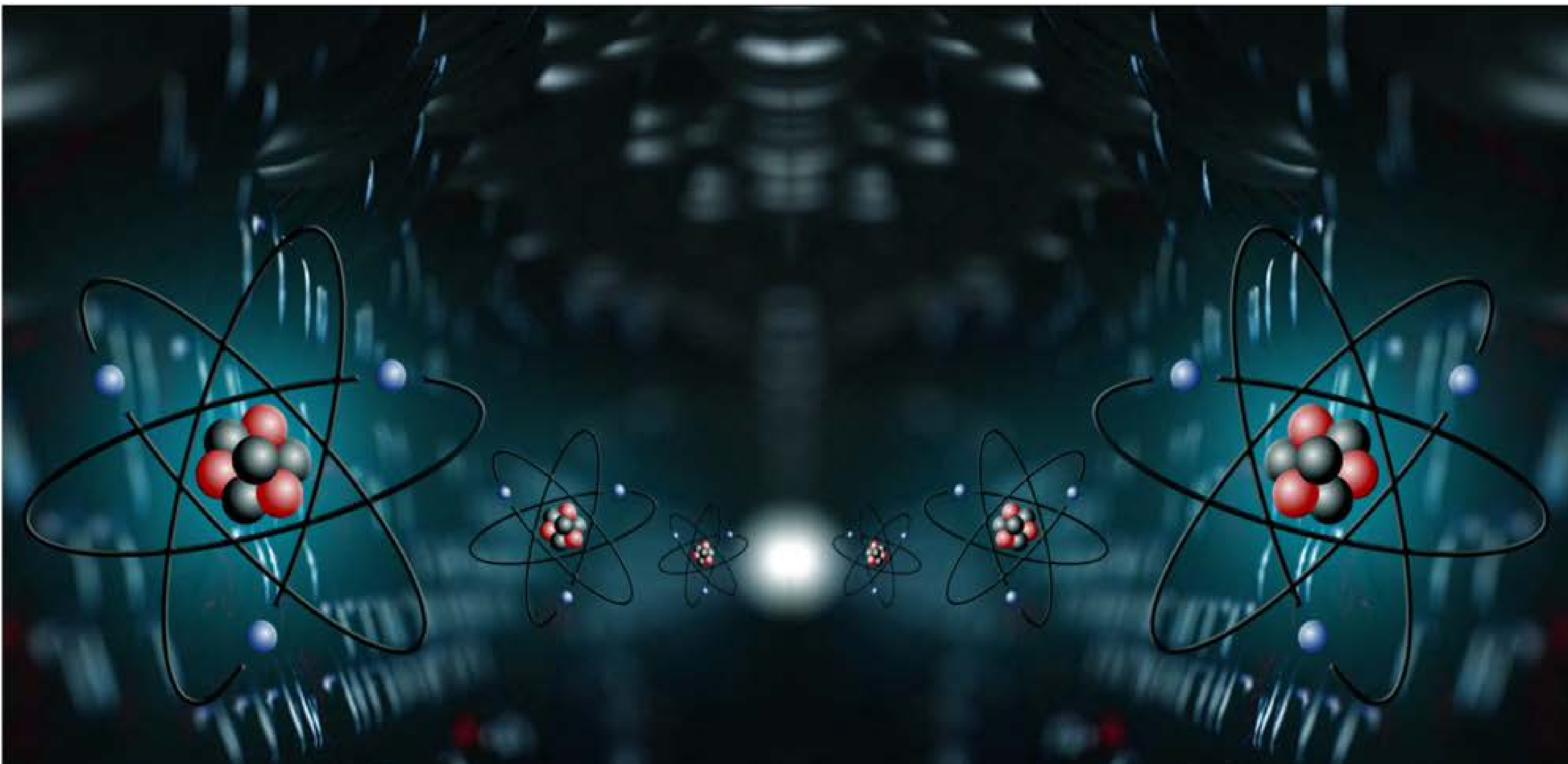

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