Chapter IV :

Second principle of thermodynamics

I- Introduction :

Thermodynamics is a branch of physics which deals with the energy and work of a system. Thermodynamics deals only with the large scale response of a system which we can observe and measure in experiments. In aerodynamics, the thermodynamics of a gas obviously plays an important role in the analysis of propulsion systems. The first law of thermodynamics defines the relationship between the various forms of kinetic and potential energy present in a system, the work which the system can perform and the transfer of heat. The law states that energy is conserved in all thermodynamic processes.

However, we can imagine thermodynamic processes which would conserve energy but which never occur in nature. For example, if we bring a hot object into contact with a cold object, the hot object cools down and the cold object heats up until an equilibrium is reached. The transfer of heat goes from the hot object to the cold object. We could imagine a system in which the heat would instead be transferred from the cold object to the hot object, and such a system would not violate the first law of thermodynamics. The cold object would get colder and the hot object would get hotter but energy would be conserved. Obviously we don't encounter such a system in nature and to explain this and similar observations, thermodynamicists proposed a second law of thermodynamics. The second law states that there exists a useful state variable called entropy S where :

$$\Delta S = S_f - Si$$

II- Second Law of Thermodynamics :

II.1. Entropy Definition :

Entropy is a scientific concept, as well as a measurable physical property and It is an extensive property of a thermodynamic system. Entropy is a measure of the randomness of the system, or it is the measure of energy or chaos within an isolated system. In equations, entropy is usually denoted by the letter S and has units of joules per kelvin ($J{\cdot}K^{-1}$) or $kg{\cdot}m^2{\cdot}s^{-2}{\cdot}K^{-1}$. A highly ordered system has low entropy.

The change in entropy (**ΔS**) is equal to the heat transfer (**Q**) divided by the temperature (**T**).

$$\Delta S = Q_{rev}/T$$

II.2. text of second law of thermodynamics:

The entropy of the universe increases in a spontaneous process and stays the same in an equilibrium process.

Mathematically, the second law of thermodynamics is represented as :

- **For an non equilibrium process:** $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$
- **For an equilibrium process:** $\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} = 0$

There is no possible process where the entropy of the universe decreases. It's possible for the entropy of a system to decrease, but that results in a greater corresponding entropy increase in the rest of the universe.

$$\Delta S_{total} = \Delta S_{surroundings} + \Delta S_{system} > 0$$

II.3. Properties of Entropy :

- It's a function of thermodynamics.
- It's a state function, after all. It is determined by the condition of the system rather than the path is taken.
- It is represented by the letter S, though it is normally represented by the letter S°.
- It is a scalable property, meaning it grows in proportion to the size or scope of a system.
- It is a broad attribute, implying that it is solely dependent on the mass of a system.
- In the universe it is constantly increasing.
- This can never be zero.
- The entropy of an adiabatic thermodynamic system is constant.
- The change in entropy is inversely proportional to the temperature, meaning that as the temperature rises, the change in entropy decreases, but as the temperature falls, the change in entropy increases.

- Since, the state of a cyclic process does not change, the change in entropy is zero.
- For an irreversible or spontaneous process, the change in total entropy is greater than 0.

III- Change in entropy for Perfect Gas :

III.1. Entropy as a function of (V,T) :

According to the first principle: $dU = \delta Q + \delta w$; with, $\delta W = - PdV$

According to the second principle: $dS = dQ/T$

$$\Longrightarrow dQ = T\,dS$$

$$nCvdT = TdS - PdV$$

$$\mathrm{dS} = \frac{nCvdT}{T} + \frac{PdV}{T}, \qquad \frac{P}{T} = \frac{nR}{V}$$

$$\mathrm{dS} = n\left[Cv\frac{dT}{T} + R\frac{dV}{V}\right] \ldots\ldots\ldots\ldots\ldots.(\mathbf{1})$$

If C_V is constant :

$$\Delta S = n\left[C_v ln\frac{T_2}{T_1} + Rln\frac{V_2}{V_1}\right]$$

This relationship is generally valid for all transformations :

If T is constant :

$$\Delta S = nRln\frac{V_2}{V_1}$$

If V is constant :

$$\Delta S = nC_v ln\frac{T_2}{T_1}$$

III.2. Entropy as a function of (P,T)

For a perfect gas: $PV = n\,RT$

$d(PV) = d\,(nRT)$

$P\,dV + V\,dP = n\,R\,dT$

dividing by PV we find:

$$\frac{dV}{V}+\frac{dP}{P}=\frac{nRdT}{nRT}=\frac{dT}{T}$$

$$\frac{dV}{V}=\frac{dT}{T}-\frac{dP}{P}$$

By replacing relation $\frac{dV}{V}$ in equation (1) we find:

$$\mathrm{dS}=n\left[Cv\frac{dT}{T}+R(\frac{dT}{T}-\frac{dP}{P})\right]$$

$$\mathrm{dS}=n\left[(Cv+R)\frac{dT}{T}-R\frac{dP}{P}\right]$$

$$\mathrm{dS}=n\left[C_P\frac{dT}{T}-R\frac{dP}{P}\right]\ldots\ldots\ldots\ldots\ldots\ldots..(\mathbf{2})$$

If C_P is constant :

If T is constant :

$$\Delta\mathrm{S}=-nRln\frac{P_2}{P_1}$$

If P is constant :

$$\Delta\mathrm{S}=nC_Pln\frac{T_2}{T_1}$$

III.3. Entropy as a function of (P,V) :

By replacing relation $\frac{dT}{T}=\frac{dV}{V}+\frac{dP}{P}$ in equation (1) we find:

$$\mathrm{dS}=n\left[Cv(\frac{dV}{V}+\frac{dP}{P})+R\frac{dV}{V}\right]$$

$$\mathrm{dS}=n\left[(Cv+R)\frac{dV}{V}+Cv\frac{dP}{P}\right]$$

$$\mathrm{dS}=n\left[Cp\frac{dV}{V}+Cv\frac{dP}{P}\right]\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(\mathbf{3})$$

If P is constant :

$$\Delta\mathrm{S}=nC_Pln\frac{V_2}{V_1}$$

If V is constant :

$$\Delta S = nC_V ln\frac{P_2}{P_1}$$

IV- Entropy Changes during a change of state

- ## Entropy of Fusion

It is the increase in entropy when a solid melt into liquid. The entropy increases as the freedom of movement of molecules increases with phase change.

The entropy of fusion is equal to the enthalpy of fusion divided by the melting point (fusion temperature)

$$\Delta S_{fus} = \Delta H_{fus} / T_f$$

A natural process such as a phase transition (for example, fusion) will occur when the associated change in the Gibbs free energy is negative. Most of the time, ΔS_{fus} is positive.

Exception :

Helium-3 has a negative entropy of fusion at temperatures below 0.3 K. Helium-4 also has a very slightly negative entropy of fusion below 0.8 K.

- ## Entropy of Vaporisation :

The entropy of vaporisation is a state when there is an increase in entropy as liquid changes into a vapour. This is due to an increase in molecular movement which creates a randomness of motion.

The entropy of vaporisation is equal to the enthalpy of vaporisation divided by boiling point. It can be represented as,

$$\Delta S_{vap}=\Delta H_{vap} / T_b$$

Conclusion :

We can conclude that the **entropy of different states of matter increases as you move from solid to liquid to gas**. The increase in entropy is due to the **increasing disorder** between the molecules in the different states:

- **Solids** have the lowest entropy because their particles are held in an ordered arrangement.
- **Liquids** typically have a higher entropy because their particles can move about more randomly.

- **Gases** have the highest entropy out of all three by a significant margin because their particles are free to move about however they like, in a totally disordered way..

All the **physical changes of states** are characterized by positive (an *increase* in entropy) or negative (a *decrease* in entropy) entropy changes. You can see the entropy changes of physical processes in the table below:

Physical process	**Entropy change**
Melting (solid to liquid)	Positive
Boiling (solid to gas)	Positive
Freezing (liquid to solid)	Negative
Sublimation (solid to gas)	Positive
Condensing (gas to liquid)	Negative

In general: reactions that feature **melting**, **boiling**, or **sublimation** typically have a **positive entropy change**, whilst reactions that feature **freezing** or **condensing** have a **negative entropy change**.

V- Standard entropy :

Let's now start thinking about standard entropy as a concept before moving on to entropy changes. We can define standard entropy as such:

Standard entropy is the entropy of a pure substance under standard conditions of pressure and temperature. Usually, we define the standard molar entropy, which is the entropy of one mole of substance under standard conditions.

VI- Entropy change in a chemical reaction (ΔS_R)

Consider the following chemical reaction:

$$aA + bB \rightarrow cC + dD$$

You should now be able to look at a chemical reaction and predict the entropy change that takes place within the system. In this next section, we will explore one formula, which you can use to calculate this entropy change quantitatively.

The change in entropy of the chemical reaction is equal to the total absolute entropy of all the products, minus the total absolute entropy of all the reactants.

the formula given by the following equation:

$$\Delta S°_R = \sum n_p \, S_{porducts} - \sum n_R \, S_{reactants}$$

The entropy variation of a chemical reaction at a new temperature is given by KIRCHHOFF's relation:

$$\Delta S_{T_2} = \Delta S_{T_1} + \int_{T_1}^{T_2} \Delta n C_P \frac{dT}{T}$$

$$\Delta n C_P = \sum n_p \, C_{P_{porducts}} - \sum n_R \, C_{P_{reactants}}$$

VII- Standard Entropy of Formation of a Compound :

It is the entropy change that takes place when one mole of a compound in the standard state is formed from the elements in the standard state.