

Chapter IV

Second principle of thermodynamics

Introduction:

The first principle of thermodynamics, which states the conservation of energy, allows for the assessment of the energy balance of systems. If, for instance, an exchange of heat takes place between two systems of different temperature, the first principle demands that the quantity of heat given out by the one system shall be equal to that taken up by the other. Whether the flow of heat, however, takes place from the colder to the hotter system, or vice versa, cannot be answered by the first principle alone. Thus, we appeal to the second principle which is a principle of evolution that allows for predicting the direction in which a process takes place in nature.

A hot substance is brought into contact with a cold substance; after some time, it's observed that both temperatures equalize (T_{eq}). Heat is transferred spontaneously from the hotter substance to the colder substance until equilibrium is reached. A gas contained in one recipient is brought into contact with another empty recipient. It is observed that the gas spontaneously occupies the entire volume offered to it. When a piece of sugar is submerged in a glass of water, it spontaneously dissolves. These transformations are spontaneous (natural). The spontaneous transformation occurs in a well-defined direction; the reverse transformation is never observed (irreversible transformation).

The second principle introduces a new state function called "entropy" denoted by "**S**" which measures the degree of disorder of a system. 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, a highly ordered system has low entropy. It is expressed in units: **cal/K, J/K**. The entropy change of a system is given by:

$$dS = \partial S_e + \partial S_c = \frac{\partial Q}{\partial T} + \partial S_c$$

After integration:

$$\Delta S_{\text{system}} = S_e + S_c = \int_1^2 \frac{\partial Q}{\partial T} + S_c$$

∂Q : quantity of heat exchanged between the system and the surroundings.

T: temperature of the surroundings.

S_e : entropy exchanged between the system and the surroundings.

S_c : entropy created within the system; **$S_c \geq 0$** .

$S_c = 0$; If the transformation is reversible.

$S_c > 0$; If the transformation is irreversible.

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

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

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

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 greater corresponding entropy increase in the rest of the universe.

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

Properties of Entropy:

Thermodynamic function: Entropy is a thermodynamic function, which means it is a property of the system's state and not a property of the process.

State function: Entropy is a state function, meaning it depends only on the system's current state and not on the path taken to reach that state. This property ensures that the second law of thermodynamics is obeyed.

Monotonicity: Entropy is monotonic for adiabatic availability, meaning that it increases in a spontaneous process and decreases in a non-spontaneous process. This property is crucial for understanding the direction of change in a system.

Additivity on composite systems: Entropy is additive on composite systems, meaning that a system's entropy of multiple parts is the sum of the entropies of its individual parts. This property helps analyze the behavior of complex systems.

Extensivity: Entropy is extensive, meaning that it scales with the size or extent of a system. This property implies that the entropy of a large system is much larger than that of a small system.

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.

Change in entropy for Perfect Gas :

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: $dS = dQ/T$

$$\Rightarrow dQ = T dS$$

$$nC_v dT = T dS - P dV$$

$$dS = \frac{nC_v dT}{T} + \frac{P dV}{T}, \quad \frac{P}{T} = \frac{nR}{V}$$

$$dS = n \left[C_v \frac{dT}{T} + R \frac{dV}{V} \right] \dots \dots \dots (1)$$

If C_v is constant:

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

This relationship is generally valid for all transformations:

If T is constant:

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

If V is constant:

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

Entropy as a function of (P,T)

For a perfect gas: $PV = nRT$

$$d(PV) = d(nRT)$$

$$P dV + V dP = nR dT$$

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:

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

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

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

If C_P is constant:

If T is constant:

$$\Delta S = -nR \ln \frac{P_2}{P_1}$$

If P is constant :

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

Entropy as a function of (P,V) :

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

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

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

$$dS = n \left[C_P \frac{dV}{V} + C_v \frac{dP}{P} \right] \dots \dots \dots (3)$$

If P is constant:

$$\Delta S = nC_P \ln \frac{V_2}{V_1}$$

If V is constant:

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

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)

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

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

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

Note:

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 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.