

B.Sc - I, Paper - I, Group - A

Q. Define entropy and explain its physical significance.
Derive an expression for the entropy of a perfect gas in terms of pressure, volume and specific heat.

Soln: - Entropy: - If a substance takes in an amount of heat Q in a reversible process at a constant temperature T , then $\frac{Q}{T}$ is called the ^{or increase} "increase in entropy" of the substance.

Similarly, if the substance gives up an amount of heat Q at constant temp. T , then $\frac{Q}{T}$ is called the "decrease in entropy" of the substance. The change in entropy is denoted by ΔS . Thus

$$\Delta S = \frac{Q}{T}$$

If the temperature of the substance does not remain constant during the process, we may consider the heat to be taken in or given up in successive small elements dQ such that the temperature remains "sensibly constant for each element".

The change in entropy will then be $\Delta S = \int \frac{dQ}{T}$

Physical significance: - Like energy U and temperature T , the entropy S of a system is a physical property that can be measured in the laboratory. It provides an alternative statement of the second law of thermodynamics according to which "only those processes are possible for a system in which the entropy of the system plus surroundings increase." Thus we can decide whether or not an event will occur spontaneously. An event would occur provided it will cause the ~~total~~ entropy of the universe (system + surroundings) to increase. Events causing decrease in entropy of the universe is impossible.

For example: - Heat can flow from higher to lower temperature but the reverse is not possible. Free expansion of a gas is possible, free compression is not. Therefore, on account of the processes occurring in nature, the entropy of the universe is continuously increasing. Entropy does not obey conservation law (energy does).

Entropy of a perfect gas:- let us consider one mole of a perfect gas at pressure P , Kelvin temperature T and volume V . When an infinitesimal amount of heat dQ is added to it, the increase in entropy is

$$dQ = T ds = \frac{dQ}{T}$$

If dU be the increase in the internal energy of the gas and dW the external work done, then by the first law of thermodynamics

$$dQ = dU + dW$$

If C_v be the molar specific heat of the gas at constant volume, dT the rise in temperature and dV the change in volume, then

$$dU = C_v dT \quad \text{and} \quad dW = P dV = RT \frac{dV}{V} \quad [\because PV = RT]$$

$$\therefore dQ = C_v dT + RT \frac{dV}{V}$$

$$\text{and so, } ds = \frac{dQ}{T} = C_v \frac{dT}{T} + R \frac{dV}{V} \quad \text{--- (i)}$$

The entropy of the gas, measured from an arbitrary zero, i.e. then given by

$$s = \int \frac{dQ}{T} = C_v \int \frac{dT}{T} + R \int \frac{dV}{V} \quad \text{--- (ii)}$$

For an ideal gas $PV = RT$, we have $dT = \frac{P dV + V dP}{R}$ and from Mayer's relation, $C_p - C_v = R$. Thus from eqn (ii)

$$\begin{aligned} s &= C_v \int \frac{P dV + V dP}{PV} + (C_p - C_v) \int \frac{dV}{V} \\ &= C_v \int \frac{dV}{V} + C_v \int \frac{dP}{P} + (C_p - C_v) \int \frac{dV}{V} \\ &= C_v \int \frac{dP}{P} + C_p \int \frac{dV}{V} \end{aligned}$$

$$\text{or, } s = C_v \log_e P + C_p \log_e V + \text{Constant} \quad \text{--- (iii)}$$

This is the entropy change in terms of pressure, volume, and molar specific heats.

This is the required expression.

If a gas passes from an initial state P_i, V_i, T_i to a final state P_f, V_f, T_f then, from eqn (iii), the change in entropy

$$\text{of the gas is } \Delta s = C_v \int_{P_i}^{P_f} \frac{dP}{P} + C_p \int_{V_i}^{V_f} \frac{dV}{V} \quad \text{or, } \Delta s = C_v \log_e \frac{P_f}{P_i} + C_p \log_e \frac{V_f}{V_i}$$