T. D. C. Part II, Chem. (Hons.)
Paper IV. Physical Chemistry (Gr. A)

Unit I Thermodynamics.

Entropy Change in an Ideal Gas :-

Let one mole of an ideal gas ~~undergo~~ occupying a volume V at a pressure P and temp T. Let the ∂q ~~amount~~ be the amount of heat supplied to the system reversibly, then the increase in entropy is given by.

$$dS = \frac{\partial q_{rev}}{T} \quad \text{or,} \quad TdS = \partial q_{rev} \quad \text{--- (1)}$$

From the first law of thermodynamics

$$\partial q_{rev} = dU + \partial w_{max}$$
$$= dU + PdV \quad \text{--- (2)}$$

From equation (1) and (2)

$$TdS = dU + PdV$$

$$\text{or,} \quad dS = \frac{dU}{T} + \frac{PdV}{T}$$

$$\text{But } C_V = \frac{dU}{dT} \quad \text{or,} \quad dU = C_V dT$$

$$\therefore dS = C_V \frac{dT}{T} + \frac{PdV}{T} \quad \text{--- (3)}$$

For one mole of an ideal gas

$$PV = RT \quad \text{or,} \quad P = \frac{RT}{V}$$

Substituting this value P in equation (3) we get

$$dS = C_V \frac{dT}{T} + R \frac{dV}{V}$$

Integrating above equation by taking C_V is const

$$S = C_V \ln T + R \ln V + S_0$$

Where S_0 = constant of integral and is called standard entropy.

Scanned by TapScanner

The above equation gives entropy of one mole of an ideal gas at any P, V, T.

For the initial state

$$s_i = c_v \ln T_i + R \ln V_i + S_0$$

For the final state,

$$S_f = c_v \ln T_f + R \ln V_f + S_0$$

$$\therefore \Delta S = S_f - S_i = c_v \ln T_f + R \ln V_f + \cancel{S_0} - c_v \ln T_i - R \ln V_i - \cancel{S_0}$$

or,

$$\boxed{\Delta S = c_v \ln \frac{T_f}{T_i} + R \ln \frac{V_f}{V_i}} \quad \text{(i)}$$

An alternative form of equation (i) may be obtained in the following manner;

$$c_p - c_v = R \quad \text{for a ideal gas}$$

So, or, $c_v = c_p - R$

$$S = (c_p - R) \ln T + R \ln \frac{RT}{P} + S_0$$

$$\boxed{PV = RT \quad \therefore V = \frac{RT}{P}}$$

or,

$$S = c_p \ln T - R \ln T + R \ln RT - R \ln P + S_0$$

$$= c_p \ln T - \cancel{R \ln T} + R \ln R + \cancel{R \ln T} - R \ln P + S_0$$

Scanned by TapScanner

$\therefore \quad S = C_p \ln T - R \ln P + (R \ln P + S_0)$

$= C_p \ln T - R \ln P + S_0'$

For initial state

$S_i = C_p \ln T_i - R \ln P_i$

For final state

$S_f = C_p \ln T_f - R \ln P_f$

$\Delta S = S_f - S_i = C_p \ln T_f - R \ln P_f$
$- C_p \ln T_i + R \ln P_i$

or $\boxed{\Delta S = C_p \ln \frac{T_f}{T_i} - R \ln \frac{P_f}{P_i}}$

equation (4) and (5) used for calculating entropy change for ideal or perfect gases.

(I) At constant pressure i.e

$P_i = P_f$

$\Delta S_p = C_p \ln \frac{T_f}{T_i}$

(II) At constant volume i.e

$V_i = V_f$

$\Delta S_v = C_v \ln \frac{T_f}{T_i}$

(13) At constant temp:

$T_i = T_f$

$$\Delta S_T = R \ln \frac{V_f}{V_i}$$

or, $$\Delta S_T = -R \ln \frac{P_f}{P_i}$$