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Class  $\Rightarrow$  B.Sc.(Hons.) Part-IISubject  $\Rightarrow$  ChemistryChapter  $\Rightarrow$  ThermodynamicsTopic  $\Rightarrow$  Entropy change for an ideal gas.Name  $\Rightarrow$  DR. Amarendra Kumar

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## Entropy change for an Ideal gas Under different Conditions

Let us consider 1 mole of an ideal gas enclosed in a cylinder fitted with a frictionless piston. If a small amount of heat  $Q_{rev.}$  is supplied to the system reversibly and isothermally at the temperature T, then the entropy change accompanying the process is given by

$$ds = Q_{rev.}$$

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According to the first law of thermodynamics, for an infinitesimal process

$$dq = dE + \delta w \quad ②$$

If the process is carried out reversibly, eqn. ② may be written as

$$Q_{rev.} = dE + \delta w \quad ③$$

Also, if the work is restricted to the work of expansion

$$\delta w = Pdv \quad ④$$

Where dv is the small increase in volume and P is the pressure of the system

Putting the value of  $\delta w$  from eqn. ④ in eqn. ③

We get  $S_{\text{rev}} = dE + PdV$  — (5)

Substituting this value in eqn. (1) we have  
 $ds = \frac{dE + PdV}{T}$

or,  $Tds = dE + PdV$  — (6)

for 1 mole of an ideal gas, we know that

$$C_V = \frac{dE}{dT}$$

∴  $dE = C_V dT$  — (7)

Where  $C_V$  = Molar heat capacity at constant volume

$$PV = RT$$

∴  $P = \frac{RT}{V}$  — (8)

Where  $V$  = volume of the system at temperature

$$T$$

$P$  = Pressure

$R$  = Gas Constant

Substituting the values of  $dE$  and  $P$  from eqn. (7) and (8) in equation (6), we get

$$Tds = C_V dT + \frac{RT}{V} dv$$

or  $ds = \frac{C_V}{T} dT + \frac{R}{V} dv$  — (9)

If the volume changes from  $V_1$  to  $V_2$  when the temperature changes from  $T_1$  to  $T_2$ , then the entropy change accompanying the complete process is given by the equation.

$$\int_{S_1}^{S_2} ds = \int_{T_1}^{T_2} \frac{C_V}{T} dT + \int_{V_1}^{V_2} \frac{R}{V} dv$$
 — (10)

Assuming that  $C_V$  remains constant in the temperature ranges  $T_1$  to  $T_2$ , eqn. (10) may be put as

(3)

$$\int_{S_1}^{S_2} ds = cv \int_{T_1}^{T_2} dT + R \int_{V_1}^{V_2} dv$$

$$\Delta S = cv \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}$$

(11)

This is an expression for the calculation of entropy change of 1 mole of an ideal gas accompanying a process when temperature changes from  $T_1$  to  $T_2$  and the volume changes from  $V_1$  to  $V_2$ .

$$P_1 V_1 = RT_1 \quad \text{for the initial state} \quad (12)$$

$$P_2 V_2 = RT_2 \quad \text{for the final state} \quad (13)$$

Dividing eq. (13) by eq. (12), we have

$$\frac{P_2 V_2}{P_1 V_1} = \frac{T_2}{T_1}$$

$$\text{or, } \frac{V_2}{V_1} = \frac{T_2 P_1}{T_1 P_2} \quad (14)$$

Substituting this value in eq. (11), we get

$$\Delta S = cv \ln \frac{T_2}{T_1} + R \ln \frac{T_2 P_1}{T_1 P_2} \quad (15)$$

Also, we know that

$$C_p - C_v = R$$

$$\text{or, } C_v = C_p - R$$

Putting this value in equation (15), we get

$$\Delta S = (C_p - R) \ln \frac{T_2}{T_1} + R \ln \frac{T_2 P_1}{T_1 P_2}$$

$$\text{or, } \Delta S = C_p \ln \frac{T_2}{T_1} - R \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\therefore \Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \quad (16)$$

(16)

This equation gives the entropy change of 1 mole of an ideal gas accompanying a process when temp. changes from  $T_1$  to  $T_2$  and pressure changes from  $P_1$  to  $P_2$

(1) If temp. is kept constant (Isothermal process)

$$T_1 = T_2$$

Eqn. (11) and (16) are reduced to

$$\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}$$

(2) If pressure is kept constant (Isobaric process)

$$P_1 = P_2$$

Equation (16) is reduced to

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

(3) If volume is kept constant (Isochoric process)

$$V_1 = V_2$$

Equation (11) converts to

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