

Or,
$$\frac{\Delta S}{\Delta V} = \frac{\alpha}{\beta}$$

$$\Delta V = \frac{\Delta S \cdot \beta}{\alpha} = \frac{2 \text{ JK}^{-1} \text{ mol}^{-1} \times 9 \times 10^{-4} \text{ MPa}^{-1}}{1 \times 10^{-3} \text{ K}^{-1}} = 1.8 \text{ cm}^3 \text{ mol}^{-1}$$

Problem-21: The total change in entropy 'ds' for an irreversible process is given by:

- (a) $ds = d_e s - d_i s$ (b) $ds = d_e s + d_i s$
 (c) $ds = 0$ (d) $ds = -d_e s - d_i s$

Where $d_e s$ = entropy exchanged with surroundings

$d_i s$ = entropy generated by irreversible process in the system.

Soln. $dS_{total} = dS_{system} + dS_{sur}$

$$\Rightarrow dS_{total} = d_i S + d_e S$$

Correct option is (b)

Entropy as a function of temperature and pressure :

Since, we know that dependence of entropy on temperature and pressure as

$$S = f(T, P)$$

On differentiating, we get

$$dS = \left(\frac{\partial S}{\partial T} \right)_P dT + \left(\frac{\partial S}{\partial P} \right)_T dP \quad \dots (i)$$

In order to write the equation,

$$dS = \frac{1}{T} dU + \frac{P}{T} dV \quad \dots (ii)$$

From equation (i), we consider the following relation.

$$U = H - PV$$

$$\Rightarrow dU = dH - PdV - VdP$$

Taking $H = f(T, P)$, we get

$$dU = \left\{ \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \right\} - PdV - VdP \quad \dots (iii)$$

Substituting equation (iii) in equation (ii), we get

$$dS = \frac{1}{T} \left\{ \left(\frac{\partial H}{\partial T} \right)_P dT + \left(\frac{\partial H}{\partial P} \right)_T dP \right\} - \frac{P}{T} dV - \frac{V}{T} dP + \frac{P}{T} dV$$

Or,
$$dS = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P dT + \frac{1}{T} \left\{ \left(\frac{\partial H}{\partial P} \right)_T - V \right\} dP$$

Comparing this with equation (i), we get

$$\left(\frac{\partial S}{\partial T} \right)_P = \frac{1}{T} \left(\frac{\partial H}{\partial T} \right)_P = \frac{nC_{p,m}}{T}$$

And
$$\left(\frac{\partial S}{\partial P}\right)_T = \frac{1}{T} \left[\left(\frac{\partial H}{\partial P}\right)_T - V \right]$$

Problem-22 : Calculate ΔS for 2 mol of nitrogen heated at constant pressure from 300 K to 400 K. The temperature variation of C_p of nitrogen is given as

$$C_p / JK^{-1}mol^{-1} = 20 + 4\left(\frac{T}{K}\right) - 2 \times 10^{-3} \left(\frac{T}{K}\right)^2$$

Soln. Since, we know that,

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}$$

Substituting the given expression of C_p , we get

$$\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{20}{T}\right) + 4 - 2 \times 10^{-3} T$$

$$dS = \left(\frac{20}{T} + 4 - 2 \times 10^{-3} T dT\right)$$

On integrating this we have,

$$\begin{aligned} &= \int_{300K}^{400K} \left(\frac{20}{T} + 4 - 2 \times 10^{-3} T dT\right) \\ &= [20 \ln T]_{300K}^{400K} + [4T]_{300K}^{400K} - [2 \times 10^{-3} T^2]_{300}^{400} \\ &= 20 \times 2.303 \times \log\left(\frac{400}{300}\right) + 4(400 - 300) - 2 \times 10^{-3} [(400)^2 - (300)^2] \\ &= 46.06 \times 0.124 + 4 \times 100 - 2 \times 10^{-3} (400 - 300)(400 + 300) \\ &= 5.70 + 400 - 2 \times 100 \times 700 \times 10^{-3} \\ &= 405.70 - 140 = 265.70 JK^{-1} \end{aligned}$$

Entropy change for ideal gas in different cases:

Using Maxwell's equation,

$$dU = TdS - PdV$$

$$dS = \frac{dU}{T} + \frac{PdV}{T}$$

Or,
$$dS = nC_{v,m} \frac{dT}{T} + \frac{PdV}{T} \quad \left[\because P = \frac{nRT}{V} \right]$$

Or,
$$dS = nC_{v,m} \frac{dT}{T} + nR \frac{dV}{V}$$

Integrating it with limits,

$$\int_{S_1}^{S_2} dS = \int_{T_1}^{T_2} nC_{v,m} \frac{dT}{T} + nR \int_{V_1}^{V_2} \frac{dV}{V}$$

Or,
$$S_2 - S_1 = nC_{v,m} \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}$$