Subject ⇒
Chapter ⇒ Thermodynamics
Topic ⇒ Entropy of mixing of an ideal gases.

Name ⇒ Dr. Amarendra Kumar
Deptt. of chemistry
Jain College, Ara.

Entropy of mixing of Ideal gases.

Suppose at constant temperature, n_1 moles of an ideal gas 1 at the initial pressure P_1^0 are mixed with n_2 moles of another ideal gas 2 at initial pressure P_2^0. After mixing let their partial pressures in the mixture be P_1 and P_2 respectively. We know that at temperature, the entropy change of an ideal gas when its pressure changes from initial pressure P_i to final pressure P_f is given by

$$\Delta S = R \ln \frac{P_i}{P_f} \ mol^{-1}$$

∴ Entropy change of the first gas when the pressure of n_1 moles of the gas changes from P_1^0 to P_1 is given by

$$\Delta S_1 = n_1 R \ln \frac{P_1^0}{P_1} \quad \text{———} \quad (1)$$

Similarly, entropy change of the second gas when pressure of n_2 moles of the gas changes from P_2^0 to P_2 is given by

$$\Delta S_2 = n_2 R \ln \frac{P_2^0}{P_2} \quad \text{———} \quad (2)$$

The total entropy change on mixing the two gases will be the sum of the above two changes.

$$\Delta S_{mixing} = n_1 R \ln \frac{P_1^0}{P_1} + n_2 R \ln \frac{P_2^0}{P_2} \quad \text{——— (3)}$$

Let P be the total pressure of the mixture. Then $P = P_1 + P_2$. Further let x_1 and x_2 be the mole fraction of gases 1 and 2 in the mixture. By Dalton's law of partial pressures,

$$P_1 = x_1 P \quad \text{and} \quad P_2 = x_2 P$$

Substituting these values in equation (3) we get,

$$\Delta S_{mixing} = n_1 R \ln \frac{P_1^0}{x_1 P} + n_2 R \ln \frac{P_2^0}{x_2 P} \quad \text{——— (4)}$$

Taking the simplest case in which each gas is taken at the same initial pressure. Under these conditions, after mixing, volume of the mixture will be the sum of their initial volumes, i.e. $V = V_1 + V_2$ and final pressure of the mixture will be nearly the same as initial pressure of each gas, i.e. $P_1^0 = P_2^0 = P$

Equation (4) then is simplified to

$$\Delta S_{mixing} = -n_1 R \ln x_1 - n_2 R \ln x_2$$

or, $$\Delta S_{mixing} = -R(n_1 \ln x_1 + n_2 \ln x_2) \quad \text{——— (5)}$$

Gas 1		Gas 2		
Pressure = P		Pressure = P		Pressure = P
Temp. = T	+	Temp. = T	$\xrightarrow{\text{on mixing}}$	Temp. = T
Volume = V_1		Volume = V_2		Volume = $V_1 + V_2$
no. of moles = n_1		no. of moles = n_2		no. of moles = $n_1 + n_2$

For a mixture of a number of gases, eqn. (5) can be written in the general form

$$\Delta S_{mixing} = -R \sum n_i \ln x_i \quad \text{——— (6)}$$

Entropy change for one mole of the mixing is obtained by dividing eqn. (5) by $(n_1 + n_2)$

$$\Delta S_{mixing} = -R\left(\frac{n_1}{n_1+n_2}\ln x_1 + \frac{n_2}{n_1+n_2}\ln x_2\right)$$

or $\Delta S_{mixing} = -R(x_1 \ln x_1 + x_2 \ln x_2)$

which can be generalized to the form

$$\boxed{\Delta S_{mixing} = -R \sum x_i \ln x_i}$$

This eqn. is known as entropy of mixing of ideal gases.

The following conclusions from the above equation

(i) ΔS_{mixing} is independent of temperature.

(ii) As $x_i < 1$, ΔS_{mixing} will always be positive i.e. mixing of gases accompanied by increase in entropy.

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