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Class  $\Rightarrow$  B.Sc.(Hons.) Part-IISubject  $\Rightarrow$  ChemistryChapter  $\Rightarrow$  ThermodynamicsTopic  $\Rightarrow$  Entropy of mixing  
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## 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

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

$\therefore$  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

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

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

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

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

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$$\Delta S_{\text{mixing}} = n_1 R \ln \frac{P_i^0}{P} + n_2 R \ln \frac{P_2^0}{P_2} \quad \textcircled{3}$$

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,

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

Substituting these values in equation (3) we get

$$\Delta S_{\text{mixing}} = n_1 R \ln \frac{P_i^0}{x_1 P} + n_2 R \ln \frac{P_2^0}{x_2 P} \quad \textcircled{4}$$

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

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

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

Gas 1	Gas 2	
pressure = $P$	pressure = $P$	pressure = $P$
Temp. = $T$	Temp. = $T$	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

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

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

(3)

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

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

which can be generalized to the form

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

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

The following conclusions from the above equation

- (i)  $\Delta S_{\text{mixing}}$  is independent of temperature.
- (ii) As  $x_i < 1$ ,  $\Delta S_{\text{mixing}}$  will always be positive i.e. mixing of gases accompanied by increase in entropy.

$$\rightarrow \Delta S_{\text{mixing}}$$