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Deg II. Chem. Hons, Paper - III

Topic :- Thermodynamics continued

Entropy change in an irreversible process

In an irreversible process there is an increase in the entropy. Let us assume an irreversible conduction of heat  $\delta Q$  from a body A at higher temperature  $T_1$  to another body at lower temperature  $T_2$ . Hence, the change in the entropy of this irreversible process is given by

$$(\Delta S)_{irr} = \frac{\delta Q}{T_2} - \frac{\delta Q}{T_1}$$
$$= \delta Q \left[ \frac{1}{T_2} - \frac{1}{T_1} \right] \quad \text{--- (1)}$$

When  $\frac{\delta Q}{T_1}$  denotes the decrease in entropy of body A and  $\frac{\delta Q}{T_2}$  is the increase in entropy of B.

As conduction of heat always takes place from a higher to lower temperature it therefore follows that  $T_1 > T_2$

infer

$$\frac{1}{T_2} > \frac{1}{T_1} \quad \text{or} \quad \frac{\delta Q}{T_2} > \frac{\delta Q}{T_1}$$

$$\therefore \frac{\delta Q}{T_2} - \frac{\delta Q}{T_1} > 0$$

Applying the condition to equation (1) we get  $(\Delta S)_{irr} > 0$  --- (2)

This condition implies that entropy increases in an irreversible process like conduction, radiation etc

On combining the two cases we get

$$\Delta S_{\text{system}} + \Delta S_{\text{surr}} \geq 0 \quad \text{--- (3)}$$

In equation (3) "equal to" sign refers to a reversible process whereas the "or greater than" sign refers to an irreversible process.

This equation is useful to predict whether a given process can take place spontaneously or not

$$\Delta S_{\text{rev}} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \dots = 0$$

Entropy increase during isothermal mixing of ideal gases

We know that

$$\Delta S = S_2 - S_1 = C_p \log \frac{T_2}{T_1} - R \log \frac{P_2}{P_1} \quad \text{--- (1)}$$

Therefore, the increase in entropy of one mole of ideal gas with pressure at constant temperature

is obtained by putting  $T_1 = T_2$  in equation (1)  $\Delta S = -R \log \frac{P_2}{P_1}$

$$\text{or } \Delta S = S_2 - S_1 = R \log \frac{P_1}{P_2} \quad \text{--- (2)}$$

for  $n$  moles gas equation (2) becomes

$$S_2 - S_1 = nR \log \frac{P_1}{P_2}$$

$$S_2 = S_1 + nR \log \frac{P_1}{P_2}$$

$$\text{or } S_2 = (S_1 + nR \log P_1) - nR \log P_2$$

In general  $S = n(s^\circ - R \log P)$  — (3)  
 where  $s^\circ$  = molar entropy of one mole gas in standard state,  $s^\circ$  is a function of the nature of the gas, temperature and Pressure of the standard state.

Now Consider two gases A and B  
 They are kept in different Partitions  
 at the same temperature and Pressure  
 These two gases do not react chemically  
 The total entropy of the system as  
 given by —

$$S_A = n_A (s_A^\circ - R \log P) \text{ — (4)}$$

$$S_B = n_B (s_B^\circ - R \log P) \text{ — (5)}$$