SUBJECT - CHEMISTRY

CLASS - B.Sc(Hons) PART-III

PAPER - V

TOPIC - The thermal entropy

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Q Why the thermal entropy of H_2 and CO geses are found less?

Ans. This discrepancy shows that even neas absolute Zero not all molecules are in the same state and that true equilibrium has not been attained e.g for CO, the close similarity in the sizes of the atoms makes different orientations possible in the crystal viz CO and OC. Thus, The crystal does not have one definite structure and therefore it is by no means perfect for entropy to be zero at 0°K the entropy value obtained by statistical method is bound to be higher than values based on 3rd law of thermodynamics. Another case of discrepancy is provided by H_2. Let us Consider the following example —

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$$

ΔS° (Thermal data) = $-153.6\ JK^{-1}mol^{-1}$

$$\Delta S^\circ (\text{Equilibrium}) = \frac{\Delta H^\circ - \Delta F^\circ}{T}$$

$$= 163.3 JK^{-1}mol^{-1}$$

This difference in the values of ΔS° is due to the failure to obtain a true equilibrium between two forms of H_2 i.e ortho and para which differ from their nuclear spin during measurements at low temperatures. In practice, measurements are made on 3:1 mixture of ortho and para.

This mixture at 0°K has a positive entropy. If true equilibrium is established at all times, more para hydrogen would be formed as the temperature is lowered and all the H_2 molecules will be in the para form and entropy will be zero.