SUBJECT - CHEMISTRY

CLASS - B.Sc(Hons) PART-III

PAPER - V

TOPIC - Using third law of thermodynamics,

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Q Using third law of thermodynamics, prove that -

(a) $\lim_{T\to 0}\left(\frac{\partial V}{\partial T}\right)_T = 0$ and (b) $\lim_{T\to 0}\left(\frac{\partial P}{\partial T}\right)_V = 0$

Ans (a) We know that -

$$F = H - TS \text{ and } dF = -SdT + PdV$$

According to Maxwell's relation we have —

$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

But according to 3rd law of thermodynamics, we have -

$$\left(\frac{\partial S}{\partial P}\right)_{T=0} = 0$$

$$\lim_{T\to 0}\left(\frac{\partial V}{\partial T}\right)_P = 0$$

(b) We know that -

$$A = E - TS \text{ and } dA = -SdT - PdV$$

According to Maxwell's relation, we have -

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

But $\left(\frac{\partial S}{\partial V}\right)_{T=0} = 0$

$$\therefore \lim_{T\to 0}\left(\frac{\partial P}{\partial T}\right)_V = 0$$

Q(a) Explain third law of thermodynamics.

(b) Explain why some crystalline solids deviate from the third law of thermodynamics.

Ans. (a) Third law of thermodynamics: "It states as- At absolute zero of temperature, the entropy of every substance may become zero and it does so become zero in the case of a perfectly crystalline structure".

At absolute zero, each atom in a perfect crystal must be at the lattice point and so it must have the lowest energy. In other words, this state is of perfect order of zero disorder and hence of zero entropy.

(b) The entropy value for gases like CO, NO, N_2O etc obtained from the statistical method is found to be about $4.60 JK^{-1} mol^{-1}$ higher than the values based on the 3rd law of thermodynamics. It shows that entropies of crystalline solids of these gases are not zero at 0K as per the 3rd law.

Actually, two alternative arrangements of molecules occurs in these gases at lattice points like CO & OC. Thus all molecules in the crystal being oriented in one direction two alternative orientations are probable, so the crystal does not have one definite structure. It is by no means perfect for entropy to be zero at 0K. The entropy (S) is related to probability as -

$$S = k \ln W$$

where K = Boltzmann's Constant

In the present case, two alternative orientation are possible, hence $W = 2$ and the entropy of the crystal at 0K should be equal to $R \ln 2 = 5.44 JK^{-1} mol^{-1}$ in place of being zero. This is fairly close to the observed discrepancy of $5.06 JK^{-1} mol^{-1}$