SUBJECT - CHEMISTRY

CLASS - B.Sc(Hons) PART-III

PAPER - V

TOPIC - 3rd law of Thermodynamics fails for H_2O and N_2O?

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Q Why the 3rd law of Thermodynamics fails for H_2O and N_2O?

Ans The entropies of H_2O and N_2O determined with the help of 3rd law using thermal (heat capacity) data are less than those obtained by statistical method using spectroscopic data. This shows the failure of 3rd law. The data suggests that these solids are not perfectly ordered even at 0K. Hence some disorder is present even at 0K and thus have some finite values of entropy at 0K, called 'residual entropy'. The residual entropy of water is $3.4\ JK^{-1}\ mol^{-1}$ This is due to the hydrogen bonding in the ice crystal in which two H-atoms attached by normal short σ-bonds while the two others by long hydrogen bonds. There is a randomness in which two of the four bonds are short and mean approximate analysis of the problem leads to the prediction of a residual entropy of about $R \ln 1.5 = 337\ JK^{-1}$ in good agreement with the experimental value.

In N_2O, There is possibility of two alternative arrangements of the molecules in the crystals as given below-

NNO NNO NNO	NNO ONN NNO
NNO NNO NNO	NNO NNO ONN
Perfect crystals	Actual crystal

If both arrangements are energetically equivalent the two will be equally likely and hence a residual entropy of $R \ln 2 = 5.76\ JK^{-1}mol^{-1}$ However the experimental value is less than this showing that the above two arrangements are not energetically equivalent.