

## Quiz (Roll No 2018113001 to 2018113004) : solns

1. Are these statement true or false : (a) According to the Boltzmann distribution, it is always less likely that a molecule is in an excited energy level compared to the ground state (b) The mean square end-to-end distance in a flexible polymer chain in solution always increases linearly with the number of residues in the chain.

**Ans.** (a) False. The populations depend on the energy of the state as well as the degeneracy. (b) False. The mean square end-to-end distance increases linearly with the square root of the number of residues in the chain

2. Write an expression for the entropy change when 20 previously alphabtized books are randomized in their order.

**Ans.** Initial entropy is Zero since there is only one way to arrange the books alphabetically. When randomized, there will be 20! ways of rearranging the books.  $\therefore \Delta S = k_B \ln(20!)$

3. The lower the force constant of a molecule, the higher is the population of excited vibrational states. Use a statistical result to explain this.

**Ans.** Assuming harmonic oscillator model,

population of an excited vibrational state, labelled by vibrational quantum number  $v$  is,  $P_v = \frac{e^{-\beta h\nu}}{q_v} =$

At high temperatures,  $q_v = \frac{1}{1-e^{-\beta h\nu}}$

Thus  $P_v \propto e^{-\beta h\nu} (1 - e^{-\beta h\nu}) = e^{-a\sqrt{k}} - e^{-2a\sqrt{k}}$ , where  $a = \frac{\beta h}{2\pi\mu}$

$\therefore$  unless the force constant is extremely small, generally, the lower the force constant of a molecule, the higher is the population of excited vibrational states.

4. The molar entropy calculated from the spectroscopic properties of CH<sub>3</sub>D is greater than that measured calorimetrically [by integration of  $S = \int_0^\infty \frac{dq_{rev}}{T} + \Delta S(\text{phase changes})$  by 2.8cal K<sup>-1</sup>. How would you explain this phenomenon?

**Ans.** CH<sub>3</sub>D in the frozen state has more than one way of arranging the molecules. Let  $\Omega$  be the number of ways of arranging the molecules at 0K. This means that there is a residual entropy equal to 2.8cal K<sup>-1</sup>

Then  $R \ln \Omega = 2.8$ , then  $\Omega = e^{\frac{2.8}{R}} = e^{1.4} = 4$

D can occupy one of the four tetrahedral positions.

5. Calculate the molar energy, Helmholtz free energy and entropy of HCl gas at 1 atm, 37°C (given :  $\frac{\hbar^2}{2Ik_B} = 15.2\text{K}$ ;  $\frac{h\nu}{k_B} = 4140\text{K}$ ;  $D_0 = 102.2\text{kcal.mol}^{-1}$ . Assume ideal behaviour.

**Ans.**  $\frac{U}{k_B T} = \frac{5}{2} + \frac{h\nu}{2k_B T} + \frac{\frac{h\nu}{k_B T}}{e^{\frac{h\nu}{k_B T}} - 1} - \frac{D_e}{k_B T}$  (HCl has all electrons paired up, so the electronic degeneracy is 1)

Also,  $D_e = D_0 + \frac{1}{2}h\nu$ ;  $\therefore \frac{h\nu}{2k_B T} - \frac{D_e}{k_B T} = \frac{D_0}{k_B T}$ ;  $T = 310\text{K}$

$$\therefore \frac{U(\text{kcal mol}^{-1})}{RT} = \frac{5}{2} + \frac{\frac{4140}{310}}{e^{\frac{4140}{310}} - 1} - \frac{102.2}{0.002 \times 310} = \dots$$

$$\frac{S}{Nk_B} = \ln \left[ \frac{2\pi M_{\text{HCl}} k_B T}{h^2} \right]^{\frac{3}{2}} \frac{V e^{\frac{5}{2}}}{N} + \ln \frac{2Ik_B T e}{h^2} + \frac{\frac{h\nu}{k_B T}}{e^{\frac{h\nu}{k_B T}} - 1} - \ln \left( 1 - e^{-\frac{h\nu}{k_B T}} \right)$$

$$= \ln \left[ \frac{2\pi \cdot 35.5 \times 1.661 \times 10^{-27} \times 1.381 \times 10^{-23} \times 310}{(6.626 \times 10^{-34})^2} \right]^{\frac{3}{2}} \cdot \frac{22.4 \times 10^{-3} \times 310}{273} \cdot \frac{e^{\frac{5}{2}}}{6.023 \times 10^{23}} + \ln \frac{310 \times e}{15.2} + \frac{\frac{4140}{310}}{e^{\frac{4140}{310}} - 1} - \ln \left( 1 - e^{-\frac{4140}{310}} \right) = \dots$$

and  $A = U - 310S = \dots$