Quiz : solns

Roll No. 2018113006 to 2018113010

Questions carry equal marks.

1. What is the Gibbs' principle of equal apriori probabilities? If the principle is correct, then why is a particular distribution overwhelmingly dominant?

Ans. Gibbs' principle of equal apriori probabilities: Corresponding to the macroscopic constraints, there are many possible microscopic distributions of dynamic variables. Each such distribution is equally probable. However, their likelihood varies according to the number of ways (combinatorial) we can obtain them. There is an overwhelming most probable distributon that is obtained in the maximum number of ways possible.

2. Explain briefly how entropy is related to the degeneracy of a state with a certain energy.

Ans. Consider two microcanonical ensembles I and II with systems $(N, V_{\rm I}, U)$ and $(N, V_{\rm II}, U)$ respectively.

#states with energy$\varepsilon \to \varepsilon + d\varepsilon$, $\omega(\varepsilon, d\varepsilon) = V^N$; $\quad \therefore \frac{\Omega_{\rm II}}{\Omega_{\rm I}} = \left(\frac{V_{\rm II}}{V_{\rm I}}\right)^N$

Energy states as well degeneracy (Ω) depend on N, V

But we know that for isothermal expansion, $S_{\rm II} - S_{\rm I} = Nk_B \ln \frac{V_{\rm II}}{V_{\rm I}} = k_B \ln \frac{\Omega_{\rm II}}{\Omega_{\rm I}}$

$\therefore S = k_B \ln \Omega(N, V, U) + S_0$

3. Explain briefly (in words) why the ground rotational state of molecule is not the highest occupied.

Ans. According to the canonical ensemble theory, the population depends on the energy (Boltzmann formula) as well as the degeneracy of a system.

The degeneracy, $2j+1$ increases as the rotational quantum number, j, increases.

the product $(2j+1).e^{-\beta E_j}$ reaches a maximum for a non-zero j.

$\therefore$ the ground rotational state of molecule is not the highest occupied

4. Consider a short polypeptide with four amino acid residues, each labelled h or c for helix or coil respectively. Conformations $hhhh$ and $cchc$ contribute terms q_0 and q_3, to the partition function q. How can we express an approximate value of $\frac{q_3}{q_0}$ and what is the basis for it? Explain briefly.

Ans. $\frac{q_3}{q_0} = e^{-\frac{\gamma}{k_B T}}$, where γ is the difference in energy going from a all coil to three residues in coil format and one in helix format.

The basis lies in that the helix has H-bonds that the coil structure will not have. So, ther eis an energy difference between the two. In a simple model this energy differnce is assumed to be the same irrespective of the prior configuration, i.e., as long as there is a change in the binding of any one residue, γ is assumed to be the same.

5. Calculate the molar energy, Helmholtz free energy and entropy of HCl gas at 1 atm, 37°C (given : $\frac{\hbar^2}{2Ik_B} = 15.2$K; $\frac{h\nu}{k_B} = 4140$K; $D_0 = 102.2$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, $D_e = D_0 + \frac{1}{2}h\nu$; $\quad \therefore \frac{h\nu}{2k_B T} - \frac{D_e}{k_B T} = \frac{D_0}{k_B T}$; $\quad T = 310$K

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

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

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

and $A = U - 310S = cdots$