

Quiz : solns

Roll no. 20183011 to 201830120 and 201981101

Questions carry equal marks.

1. Write an expression for the ionization constant at temperature T of an atom $A \rightleftharpoons A^+ + e$ in terms of the relevant microscopic quantities, assuming perfect gas like behaviour for all species. Note that the electron may be treated like a monatomic system.

Ans. Each species involved is monatomic. So, only electronic and translational partition functions are required. For Na (one unpaired 3s electron) and electron, the degeneracy is 2.

$$\therefore K_c(T) = \frac{\frac{q_{Na^+}}{V} \cdot \frac{q_e}{V}}{\left(\frac{q_{Na}}{V}\right)} = \frac{\left(\frac{2\pi m_{Na^+} k_B T}{h^2}\right)^{\frac{3}{2}} \left(\frac{2\pi m_e k_B T}{h^2}\right)^{\frac{3}{2}} \cdot 2}{2 \left(\frac{2\pi m_{Na} k_B T}{h^2}\right)^{\frac{3}{2}}} \approx \left(\frac{2\pi m_e k_B T}{h^2}\right)^{\frac{3}{2}}$$

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_I, U) and (N, V_{II}, U) respectively.

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

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

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

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

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. Using canonical ensemble theory and 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. Why is the ratio of ortho and para hydrogen in ordinary hydrogen at -100K not the same as predicted for an equilibrium mixture by statistical mechanics?

Ans. If left for a long time, the ratio of ortho and para hydrogen in ordinary hydrogen will be the same as predicted for an equilibrium mixture by statistical mechanics. The mixture is prepared by lowering the temperature of hydrogen from room temperature to -100K . For the correct ratio, some of the para form has to change into ortho and this requires a little bit of activation energy. Normally such activation is induced by thermal energy, but at lower temperatures, it becomes inadequate. That is why, the experimental results are different from the statistical predictions.

5. Calculate the molar energy, Helmholtz free energy and entropy of HCl gas at 1 atm, 37°C (given : $\frac{h^2}{2Ik_B} = 15.2\text{K}$; $\frac{h\nu}{k_B} = 4140\text{K}$; $D_0 = 102.2\text{kcal.mol}^{-1}$. 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 $A = U - 310S = \dots$