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CY101-Assignment II

1. N independent particles exist in one of the 3 non-degenerate energy levels of energies $-E, 0, +E$. The system is in contact with a thermal reservoir at temperature T. What is the partition function of the system? Use **canonical ensemble** to show that
   (i) The maximum possible entropy in the limit $T \to \infty$ is $S = Nk \ln 3$
   (ii) The minimum possible energy in the limit $T \to 0$ is $\overline{E} = -NE$

2. Consider a system of distinguishable particles having only two non-degenerate energy levels separated by an energy which is equal to the value of kT at 10K. Calculate at 10K (a) the ratio of populations in the two states (b) the molecular partition function (c) the molar energy (d) the molar heat capacity (e) the molar entropy.
   Ans. (a) 0.4; (b) 1.4; (c) 22 J mol^{-1}; (d) 1.6 J K^{-1} mol^{-1}; (e) 4.8 J K^{-1} mol^{-1}.

3. Calculate the translational partition function of an H_2 molecule confined to a 100 cm^3 vessel at 25°C.
   Ans. $q_{trans} = 2.77 \times 10^{26}$

4. A certain atom has a threefold degenerate ground level, a non-degenerate electronically excited level at $3500cm^{-1}$, and a threefold degenerate level at $4700cm^{-1}$. Calculate the partition function of these electronic states at 1900K.
   Ans. 3.156

5. An electron spin can adopt either of two orientations in a magnetic field, and its energies are $\pm\mu_B\mathcal{B}$, where μ_B is the Bohr magneton
   (a) Deduce an expression for the partition function and mean energy of the electron.
   (b) Calculate the relative populations of the spin states at 4K and $\mathcal{B} = 1.0T$.
   Ans. (b) 0.71

6. Write down the molecular partition function with and without degeneracy factor. How is molecular partition function related to canonical partition function for distinguishable and indistinguishable particles?

7. Calculate the ratio of translational partition functions of H_2 and D_2 molecules at 300 K confined separately to a volume of 2.0 cm^3.
   Ans. 2.828

8. Estimate the rotational partition function for HCl at 25°C for J values up to 10. B for HCl is 10.59 cm^{-1}.
   Ans. 19.9

9. Calculate the fraction of N_2(g) molecules in the v = 0 and v = 1 vibrational states at 300K, given that $h\nu/k_B = 3374K$.
   Ans. Fraction $(v = 0) \approx 1$ and Fraction $(v = 1) \approx 1.305 \times 10^{-5}$

10. What is the electronic partition function for a system with two energy levels which are triply degenerate with energies $E_1 = 0$ and $E_2 = \epsilon$. What is its value at T = 0K.
    Ans. 3