Problem Set

November 15, 2023

1. Derive an expression for the fluctuation in the pressure in a canonical ensemble.

2. Show that for a two-component system, the grand canonical partition function,

$$Z_g(\mu_1, \mu_2, T, V) = \sum_{N_1} \sum_{N_2} Q(N_1, N_2, V, T) \lambda_1^{N_1} \lambda_2^{N_2}$$

where $\lambda_i = e^{\mu_i/kT}$. From this, derive the entropy and average pressure.

3. The grand canonical partition function and the average number of particles in each level for Fermi-Dirac and Bose-Einstein statistics are given by,

$$Z_g = \prod_{i=1}^{\infty} \Big(\sum_{n_i=0}^{\infty} \lambda^{n_i} e^{-\beta n_i \epsilon_i} \Big)$$

$$\overline{n_i} = \frac{\lambda e^{-\beta \epsilon_i}}{1 \pm \lambda e^{-\beta \epsilon_i}}$$

respectively, where the upper sign refers to Fermi-Dirac and lower sign refers to Bose-Einstein statistics.

   (a) Show that the grand canonical potential, pV for both the statistics can be written as,

$$pV = \pm kT \sum_i ln[1 \pm \lambda e^{-\beta \epsilon_i}]$$

   (b) Using the above, show that in the limit $\lambda \to 0$ (classical limit), we can write the canonical partition function as

$$Q(N, V, T) = \frac{q^N}{N!}$$

   where

$$q = \sum_i e^{-\beta \epsilon_i}$$

   is the molecular partition function.

4. The isothermal-isobaric ensemble is an ensemble of systems in which the containing walls of each system are heat conducting and flexible, so that each system of the ensemble is described by N, T and p.

   (a) Show that the partition function in the isothermal-isobaric ensemble $\Delta(N, p, T)$ is given by,

$$\Delta(N, p, T) = \sum_E \sum_V \Omega(N, V, E) e^{-E/kT} e^{-pV/kT}$$

   (b) Derive expressions for entropy, average volume and the chemical potential in terms of $\Delta(N, p, T)$.

   (c) Derive an equation for the fluctuation in volume in the isothermal-isobaric ensemble.

5. (a) The translational and electronic partition functions for a monoatomic ideal gas is given by,

$$z_{trans} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$z_{elec} = \omega_{1e}$$

where ω_{1e} is the degeneracy of the atom in its ground state. Derive the total partition function for the system.

(b) The translational, rotational, vibrational and electronic partition functions of an ideal diatomic gas is given by,

$$z_{trans} = \left(\frac{2\pi mkT}{h^2}\right)^{3/2} V$$

$$z_{rot} = \frac{T}{2\Theta_r}$$

$$z_{vib} = \frac{e^{-\beta h\nu/2}}{(1 - e^{-\beta h\nu})}$$

$$z_{elec} = \omega_{1e} e^{D_0/kT}$$

where Θ_r is the characteristic temperation of rotation, $\Theta_v \equiv \frac{h\nu}{k}$ is the vibrational temperature, $D_0 = D_e - \frac{1}{2}h\nu$ and D_e is the depth of ground state electronic potential. Derive the total partition function for the system.

(c) Consider the reaction,
$2\,Na \rightleftharpoons Na_2$
If $\Theta_v = 229$ K, $\Theta_r = 0.221$ K, $D_0 = 17.3$ Kcal/mol and the ground electronic state of a sodium atoms is $^2S_{1/2}$, find the equilibrium constant of the reaction, $K_c(T)$.