

# 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,

$$Z_g = \prod_{i=1}^{\infty} \left( \sum_{n_i=0}^{\infty} \lambda^{n_i} e^{-\beta n_i \epsilon_i} \right)$$
$$\bar{n}_i = \frac{\lambda e^{-\beta \epsilon_i}}{1 \pm \lambda e^{-\beta \epsilon_i}}$$

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  $\lambda \rightarrow 0$  (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  $\omega_{1e}$  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,

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

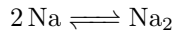
$$z_{rot} = \frac{T}{2\Theta_r}$$

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

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

where  $\Theta_r$  is the characteristic temperature 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,



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,  $K_c(T)$ .