Problem 2 continued …..

(b) Use the expression derived in part **(a)** to estimate the relative magnitude of the fluctuations in the number of particles in an ideal gas system containing 10,000 atoms.

$$\frac{\sigma_N}{\bar{N}} = \frac{1}{\sqrt{N}} = \frac{1}{\sqrt{10{,}000}} = \frac{1}{100} = 10^{-2}$$

(Ans:)

(c) Use the expression derived in part **(a)** to estimate the relative magnitude of the fluctuations in the number of particles in a macroscopic sample of an ideal gas.

$$\frac{\sigma_N}{\bar{N}} = \frac{1}{\sqrt{N}} = \frac{1}{\sqrt{6.023\times10^{23}}}$$

Ans:

For ideal gas, Avogedro NO, $N_A = 6.02\times10^{23}$

8 points

3. Consider a macroscopic sample of a material. In the first approach, the entropy of this system is determined using the canonical ensemble. In the second approach, the entropy of the same system is determined using the isothermal isobaric ensemble.

can $\rightarrow N, V, T$
iso $\rightarrow N, P, T$

State (with reasoning) whether the following statement is True or False:
Since different properties of the system are held constant in the two ensembles, the system entropy determined using the approaches would be different.

For canonical ensemble,

$$A = -KT\ln Q(N,V,T)$$

$$dA = -SdT - PdV + \mu dN$$

$$\therefore S = -\frac{\partial A}{\partial T} = -\frac{\partial}{\partial T}(-KT\ln Q)$$

$$= K\ln Q + KT\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V}$$

For isothermal-isobaric,

$$G = -KT\ln\Delta(N,P,T)$$

$$dG = VdP - SdT + \mu dN$$

$$S = -\left(\frac{\partial G}{\partial T}\right) = -\frac{\partial}{\partial T}(-KT\ln\Delta) = K\ln\Delta + KT\left(\frac{\partial(\ln\Delta)}{\partial T}\right)_{N,P}$$