Thermodynamics: Classical to Statistical
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Lecture 25
Problems on statistical thermodynamics - 3

Problem 12. The partition function of a system represented by $Q = \exp(aT^3V)$ where 'a' is a constant. Calculate $<P>$, $<E>^2$ and heat capacity at constant volume (C_V).

Partition function $Q = \exp(aT^3V)$

$$<P> = k_BT\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T}$$

$$\ln Q = aT^3V$$

$$\left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = aT^3$$

$$<P> = k_BT \times aT^3 = k_B aT^4$$

$$<E> = k_BT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{N,V} = k_BT^2 \times 3aT^2V = 3a\, k_BT^4V$$

$$<E>^2 = 9a^2k_B^2\, T^8\, V^2$$

$$C_V = \left(\frac{\partial <E>}{\partial T}\right)_V = 12a\, k_BT^3V$$

Problem 13. Suppose one mole of an argon gas (molecular weight is 40), are first held rigidly in position and then allowed to move freely. What is the change in entropy? You can consider T = 298 K and pressure P = 1 atm.

Ans. Since the molecules or the atoms are rigidly held in their positions and then allowed to move freely, initial entropy is 0. Entropy change, we say

$$\Delta S = S_{final} - S_{initial}, \text{ and } S_{initial} = 0.$$

For calculating S_{final} we need to apply Sackur Tetrode equation.

$$S_{final} = Nk_B \ \ln\left\{\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{Ve^{5/2}}{N}\right\}$$

$$m = \text{mass of argon atom} = \frac{40}{N_A} \times 10^{-3}\text{kg}$$

$$\text{for ideal gas } V = \frac{nRT}{P} = \frac{1\times0.82\times298}{1} \text{ lit}$$

So we get V in some value of lit from there we need to calculate volume in some value of m^3. If we substitute this in Sackur Tetrode equation, we will get S_{final} which is nothing but ΔS that is 155 JK^{-1}.

Problem 14. Consider N_A =Avogadro number, so Avogadro's number of distinguishable and identical particles each of which can be placed into three available energy states having energies 0, ϵ (which is doubly degenerate) and 2ϵ respectively, where $\epsilon = 300\ K_B$. By considering canonical ensemble calculate Helmholtz free energy (A) in joule unit at a temperature of 300 K.

Ans. Molecular partition function $q = \sum_{i=1}^{3} g_i e^{-\beta\epsilon_i}$

$$q = g_1 e^{-\beta\epsilon_1} + g_2 e^{-\beta\epsilon_2} + g_3 e^{-\beta\epsilon_3}$$

$$\Rightarrow q = 1 + 2e^{-\beta\epsilon} + e^{-2\beta\epsilon}$$

$$g_1 = 1, g_2 = 2, g_3 = 1$$

$$\epsilon_1 = 0, \epsilon_2 = \epsilon, \epsilon_3 = 2\epsilon$$

$$\Rightarrow \quad q = (1+ e^{-\beta\epsilon})^2 = (1+ e^{-\frac{\epsilon}{k_B T}})^2$$

$$\Rightarrow \quad q = (1+ e^{-\frac{300\,k_B}{k_B\times 300}})^2 = (1+e^{-1})^2$$

Since particles are distinguishable, canonical partition function of N_A number of particles is

$$Q(N_{A,} V,T) = q^{N_A}$$

$$\Rightarrow \quad Q = (1+e^{-1})^{2N_A}$$

$$\Rightarrow \quad \ln Q = 2\, N_A \ln (1+e^{-1})$$

$$A = - k_B T \ln Q = - k_B T \times 2\, N_A \ln (1+e^{-1})$$

$$\Rightarrow \quad A = 2RT \ln (1+e^{-1}) = -\, 1563 \text{ J mol}^{-1}$$

Problem 15. Consider a system that can be in one of two states having energies 0 and 2ϵ respectively. Considering both the states, are equally likely, calculate the <E> and the variance of energy σ_ϵ^2 in thermal equilibrium at temperature T K.

Ans. Since both the states are equally likely

$p_1 = ½$, $p_2 = ½$ where p_1 and p_2 are theprobability of the states $\in_1$ and $\in_2$ respectively.

$$<\in> = \sum_{i=1}^{2} p_i \ \in_i$$

$$\Rightarrow \quad <\in> = p_1\, \epsilon_1 + p_2\, \epsilon_2 = \frac{1}{2}\times 0 + \frac{1}{2}\times 2 \in$$

$$\Rightarrow \quad <\in> = \epsilon$$

$$\sigma_\epsilon^2 = < \epsilon^2 > \; - < \epsilon >^2$$

$$< \epsilon^2 > = p_1\, \epsilon_1^2 + p_2\, \epsilon_2^2 = \frac{1}{2} \times\ 4 \in^2 = 2\in^2$$

$$< \epsilon >^2 = \in^2$$

$$\sigma_\epsilon^2 = 2\in^2 - \in^2 = \in^2$$

Problem 16. Show that if a partition function is of the form

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

and if q (V, T) = f(T) V, then the ideal gas equation of state results. Here, V is volume and T is absolute temperature and N is number of particles and f(T) is function of temperature only.

Ans. we know $Q = \frac{q^N}{N!} = \frac{[f(T)V]^N}{N!}$

$$\Rightarrow\ \ln Q = N \ln f(T) + N \ln V - \ln N!$$

Differentiating with respect to V

$$\Rightarrow \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = 0 + \frac{N}{V} - 0 = \frac{N}{V}$$

$$<P> = k_B T \left(\frac{\partial \ln Q}{\partial V}\right)_{N,T} = \frac{N k_B T}{V} = \frac{n N_A k_B T}{V}$$

So we get, $<P>V = nRT$

Problem 17. Calculate the equation of state associated with the partition function

$$Q(N, V, T) = \frac{1}{N!}\left(\frac{2\pi m}{\hbar^2 \beta}\right)^{\frac{3N}{2}} (V - Nb)\, e^{\frac{\beta a N^2}{V}}$$

where ‘a’ and ‘b’ are constants, and $\hbar = \frac{h}{2\pi}$, $\beta = \frac{1}{K_B T}$, V is volume, N is number of particles and T is absolute temperature.

Ans. $$Q(N, V, T) = \frac{1}{N!}\left(\frac{2\pi m}{\hbar^2\beta}\right)^{\frac{3N}{2}}(V - Nb)e^{\frac{\beta a N^2}{V}}$$

$$\ln Q = -N\ln N + \frac{3N}{2}\ln(2\pi m) - \frac{3N}{2}\ln \hbar^2 - \frac{3N}{2}\ln\beta + N\ln(V - Nb) + \frac{\beta a N^2}{V}$$

$$< P > = k_B T\,[0 + 0 - 0 - 0 + \frac{N}{V - Nb} - \frac{\beta a N^2}{V^2}$$

$$< P > = \frac{Nk_BT}{V-Nb} - \frac{aN^2}{V^2}$$

$$[< P > + \frac{aN^2}{V^2}](V - Nb) = Nk_BT$$

So this the equation of state of the gas.