Thermodynamics: Classical to Statistical

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Lecture 23

Problems on statistical thermodynamics - 1

Problem 1. Consider a model magnet of N dipoles each of which may exist in either of two states or orientations. For the case, N = 2, when only two dipoles are present, identify explicitly and count the different microstates associated with each possible energy macrostate (identified by each possible value of the system energy, E). Consider the formula for the energy of the system,

$$E(n) = -2mH + (2mH) \times n \quad \text{,where n is the number of dipoles in the excited state.}$$

Ans.

Macrostate	Microstate	E(n)
↑↑	↑↑	n =1, E(n)= -2mH + 2mH× 2 + 2mH
↑↓	↑↓ or ↓↑	n = 1, E(n) = 0
↓↓	↓↓	n = 0, E(n) = -2mH

We have 2 dipoles. dipoles can be of upspin and downspin. So, we can write the macrostate like, when both dipoles are in the upspin orientation, we have only one microstate means both the dipoles are in the upspin state and what is the energy value? Here here n equals to 2 we consider upspin state as excited state. So, n is 2 and E(n)= -2mH + 2mH× 2 + 2mH So this is one macrostate.

Second possibility is one dipole is upspin and other is downspin. So, the number of possible orientations are the first dipole is in upspin state and the second dipole is in downspin state or first dipole in downspin state and the second dipole is in upspin state. So, here in the first case the number of microstate is 1 and in second case the number of microstate is 2 and value of E(n) = 0 because if we substitute the value of n equals to 1 in the energy expression, we get energy value 0

and the third possibility here is both the dipoles are in downspin state. So, we have one microstate corresponding to this macrostate and the energy value here is minus 2 mH because n here we consider is 0. So, how many macrostate possible for n equals to 2? In this case we have three macrostates possible. For macrostate 1 means when both the dipoles are in upspin state we get only 1 microstate and the energy value corresponding energy value E(n) = -2mH.

This problem is based on the concept of macrostate and microstate.

Problem 2. Given that the first excited electronic state of oxygen molecule is 15.7×10^{-20} J above the ground level. Calculate the ratio of molecules in the first excited state and ground state at 3000 K temperature. The degeneracies are $g_0 = 3$ and $g_1 = 2$ respectively.

[$k_B = 1.38 \times 10^{-23}$ J K^{-1}].

Ans. From Boltzmann distribution we know,

$$\frac{n_i}{N} = \frac{g_i}{q} e^{-\beta\epsilon_i}$$

$$\frac{n_i}{n_0} = \frac{g_1 e^{-\beta\epsilon_1}}{g_0 e^{-\beta\epsilon_0}} = \frac{g_1}{g_0} e^{-\beta(\epsilon_1 - \epsilon_0)}$$

$$\frac{n_i}{n_0} = \frac{2}{3} e^{-\frac{15.7 \times 10^{-20}}{300 \times 1.38 \times 10^{-23}}}$$

$$\frac{n_i}{n_0} = 0.015$$

Problem 3. How much heat must be added to a system at 300 K temperature for the number of accessible states to increase by a factor of 10^{10} ?

If we consider the process is reversible one, we need to calculate q_{rev}. So, in order to calculate q_{rev} we need to calculate ΔS for this process means we are adding heat to a system so there is change in entropy of the system here that we need to calculate from the number of microstates or accessible states.

$$\text{We know } S = k_B \ln W$$

$$\Delta S = k_B \ln \frac{W_2}{W_1} \quad \left[\frac{W_2}{W_1} = 10^{10} \right]$$

$$\Delta S = 10\, k_B \ln 10 \text{ J K}^{-1}$$

$$q_{rev} = T\,\Delta S = 300 \text{ K} \times 10\, k_B \ln 10 \text{ J K}^{-1}$$

$$q_{rev} = 3000 \times 1.38 \times 10^{-23} \text{J}$$

Problem 4. Consider a system of 'N' number of non-interacting distinguishable particles where each particle can be in two energy levels only. The lowest one called the ground state is non degenerate and its energy is considered to be zero. The other one, at energy epsilon is doubly degenerate. Considering canonical ensemble calculate internal energy, entropy and specific heat at constant volume, C_V of the system.

Ans. Given ϵ_1 = ground state energy = ϵ and g_2 = 12, degeneracy of ground state.

ϵ_2 = excited state energy = 0 and g_1 = 1, degeneracy of excited state.

all particles are non-interacting and distinguishable.

Molecular partition function $q = \sum_{i=1}^{2} g_i\, e^{-\beta\epsilon_i}$

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

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

we have n number of such particles. So, the canonical partition function of n particles which are distinguishable,

$$Q\ (N, V, T) = q^N$$

Internal energy of the system $U = \langle E \rangle = \left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V}$

$$Q = q^N = (1 + 2\ e^{-\beta\epsilon})^N$$

$$\ln Q = N \ln (1 + 2\ e^{-\beta\epsilon})$$

$$\left(\frac{\partial \ln Q}{\partial \beta}\right)_{N,V} = -\frac{2N\epsilon}{2 + e^{\beta\epsilon}}$$

$$\langle E \rangle = -\frac{2N\epsilon}{2 + e^{\beta\epsilon}}$$

$$\text{So, } C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{2N\epsilon^2}{k_B T^2} \times \frac{e^{\epsilon/k_B T}}{(2 + e^{\epsilon/k_B T})^2}$$

$$S = k_B \ln Q + \frac{\langle E \rangle}{T} = N k_B \ln\left(1 + 2e^{-\beta\epsilon}\right) + \frac{2N\epsilon}{T(2 + e^{\beta\epsilon})}$$

Problem 5. Consider a two state system with a ground state energy $\epsilon_0 = 0$ and an excited state energy of $\epsilon_1 = 1.6 \times 10^{-21}$J. Write an expression for the molecular partition function and evaluate it at temperature of 1000 K. What value does the molecular partition function take

as T $\rightarrow$ 0 K and T $\rightarrow \infty$?

So, we need to calculate a molecular partition function and only two states are available and nothing is mentioned about the degeneracy. So, we can consider the states are non-degenerate.

Molecular partition function $q = \sum_{i=0,1} e^{-\beta\epsilon_i}$

$$q = e^{-\beta\epsilon_0} + e^{-\beta\epsilon_1}$$

$$q = 1 + e^{-\frac{1.6\times10^{-21}}{1000\times1.38\times10^{-23}}}$$

$$q = 1.89$$

$$q = 1 + e^{\frac{-\epsilon_1}{k_B T}}$$

when T $\rightarrow 0$, $q \approx 1$ and T $\rightarrow \infty$, $q \approx 1 + 1 \approx 2$