Thermodynamics: Classical to Statistical

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Lecture 24
Problems on statistical thermodynamics - 2

Problem 6. Consider two moles of a monatomic ideal gas at 10 bar pressure, and a temperature of 300 kelvin in an isolated system. While remaining isolated, the gas is, the gas is expanded into a vacuum from a volume of V_1 = 1 lit to V_2 = 10 lit. Calculate ΔS and q_{rev} for the process and we need to use statistical, mechanical concept only.

Ans. So, we are not allowed to use tthermodynamical equation here and this problem is based on Sackur–Tetrode equation that we discussed. So, from Sackur–Tetrode equation we know

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

$$T = 300 \text{ K}, N = 2N_A$$

$$\Delta S = 2N_A k_B \ln\frac{V_2}{V_1} = 2R \ ln\frac{V_2}{V_1} = 9.21 \text{ cal K}^{-1}$$

$$q_{rev} = T\,\Delta S = 2.76 \text{ k cal}$$

Problem 7. The partition function for Einstein's proposed model for atomic crystals can be written as $Q = e^{-\beta\nu_0}\ (\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}})$ where,ν is the frequency with which atoms vibrate about their lattice positions and U_0 (which is independent of temperature) is the sublimation energy at 0 K temperature or the energy needed to separate all atoms from one another at 0 K temperature. Calculate the molar heat capacity of an atomic crystal from this partition function.

Ans. Partition function $Q = e^{-\beta\nu_0} \left(\frac{e^{-\beta h\nu/2}}{1-e^{-\beta h\nu}}\right)^N$

To calculate molar heat capacity we have to consider $N = N_A$

$$\ln Q = -\beta\nu_0 - \frac{N\beta h\nu}{2} - N\ln(1-e^{-\beta h\nu})$$

$$\left(\frac{\partial \ln Q}{\partial\beta}\right)_{N,V} = 0 - \frac{N\beta h\nu}{2} - \frac{N}{1-e^{-\beta h\nu}} \times (-e^{-\beta h\nu}) \times (-h\nu)$$

$$< E > = \frac{N\beta h\nu}{2} + \frac{Nh\nu}{e^{-\beta h\nu}-1}$$

$$< C_V > = \left(\frac{\partial <E>}{\partial T}\right)_V = 0 + \frac{Nh\nu}{(e^{-\beta h\nu}-1)^2} \times (-1) \times e^{-h\nu/k_BT} \times \left(-\frac{h\nu}{k_BT}\right)$$

Molar heat capacity $\overline{c_V} = N_A\, k_B\left(\frac{h\nu}{k_BT}\right)^2 \frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT}-1)^2}$

Problem 8. The average kinetic energy ($= \frac{3K_BT}{2}$) of hydrogen gas, or hydrogen atoms in a stellar gas is 1 eV. What is the ratio of the number of hydrogen atoms in the second excited state to the number in the ground state (n =1). The energy levels of the hydrogen atoms are $\epsilon_n = \frac{-\alpha}{n^2}$, where α = 13.6 eV and the degeneracy of the n-th level is $2n^2$.

Ans. For ground state (n = 1), $\epsilon_1 = -\frac{13.6}{1^2} = -13.6$ eV

Degeneracy $g_1 = 2\times 1^2 = 2$

For 2nd excited state (n = 3), $\epsilon_1 = -\frac{13.6}{3^2} = -\frac{13.6}{9}$ eV

Degeneracy, $g_1 = 2\times 3^2 = 18$

$$\frac{n_3}{n_1} = \frac{g_3}{g_1} \times e^{-\beta(\epsilon_3 - \epsilon_1)}$$

$$\Rightarrow \frac{n_3}{n_1} = \frac{18}{2} \times e^{\frac{(13.6\times 9 - 13.6)\times \frac{1}{k_B T}}{9}} \qquad [\frac{3}{2} k_B T = 1 \text{ eV}]$$

$$\Rightarrow \frac{n_3}{n_1} = 1.2\times 10^{-7}$$

Problem 9. The length of the bond in oxygen molecule is 1.207 Å. Determine the rotational temperature, determine rotational temperature and the rotational partition function for oxygen at 300 K temperature. [It is given molar mass of oxygen, oxygen molecule or oxygen is 32 gram.]

Ans. For O_2 molecule, the sysmmetry number = 2 as it is a homogneous diatomic molecule.

Rotational temperature $\theta_{rot} = \frac{h^2}{8\pi^2 I k_B}$

$$I = \frac{m_1 m_2}{m_1 + m_2} r^2 = 1/2\ mr^2 \text{ as } m_1 = m_2 = m$$

Substituting all the values we get

$$I = 1.937 \times 10^{-46} \text{ kg m}^2$$

$$\theta_{rot} = \frac{(6.627\times 10^{-34})^2}{8\times 3.14^2\times 1.38\times 10^{-23}\times 1.937\times 10^{-46}} \text{ K}$$

$$= 2.08 \text{ K}$$

Now rotational partition function, $q_{rot} = \frac{T}{\theta_{rot}} = \frac{300}{2\times 2.08} = 72$

Problem 10. Consider the molecule, N_2 ($\theta_{vib} = 3397$ K). A spectroscopic measurement of the populations of n = 0 states shows $p_0 = 0.75$, where p_n is the fraction of molecules in energy level n. What is the temperature of the gas?

Ans. Hint: We know the expression for p_n from vibrational partition function. So once we get p_n, the value ywe substitute, then the value of p_n is 0.75. So, we have some expression here. Once we substitute this, we calculate the value of temperature.

It is given the energy of a 3 dimensional harmonic oscillator is h nu times n1 plus n2 plus n3 plus 3 by 2. Now when value of epsilon is 7 h nu by 2, the degeneracy is suppose g is 7 h nu by 2 we consider.

Problem 11. A 3 dimensional harmonic oscillator has energy levels,

$$\epsilon_{n_{1.}\ n_{2,\ldots\ldots}} = h\nu\,(n_1 + n_2 + n_3 + \frac{3}{2})$$

where n_1, n_2, n_3 can be 0, 1, 2, 3 etc. Calculate the ratio of the population of energy levels having energies $\frac{7h\nu}{2}$ and $\frac{9h\nu}{2}$ at T K temperature. Prove that when $h\nu = 1.2$ times k_BT, the population of $\frac{9h\nu}{2}$ level will be half of that $\frac{7h\nu}{2}$ level.

Ans. Given $\epsilon_{n_{1.}\ n_{2,\ldots\ldots}} = h\nu\,(n_1 + n_2 + n_3 + \frac{3}{2})$

For $\epsilon = \frac{7h\nu}{2}$, degeneracy = $g_{7h\nu/2} = 6$

The population of energy level having energy $\frac{7h\nu}{2}$ is $n_{7h\nu/2}$

For $\epsilon = \frac{9h\nu}{2}$, degeneracy = $g_{9h\nu/2} = 10$

The population of energy level having energy $\frac{9h\nu}{2}$ is $n_{9h\nu/2}$

Now $$\frac{n_{7h\nu/2}}{n_{9h\nu/2}} = \frac{g_{7h\nu/2}}{g_{9h\nu/2}}\, e^{-\beta(\frac{7h\nu}{2}-\frac{9h\nu}{2})}$$

$$\Rightarrow \frac{n_{7h\nu/2}}{n_{9h\nu/2}} = \frac{6}{10}\, e^{\beta h\nu} = \frac{3}{5}\, e^{\frac{h\nu}{k_B T}}$$

When $h\nu = 1.2\ k_B T$

$$\frac{n_{7h\nu/2}}{n_{9h\nu/2}} = \frac{3}{5}\, e^{1.2} = 2$$

So the population of energy level having energy $\frac{9h\nu}{2}$ is half of that of having energy $\frac{7h\nu}{2}$.