

$$\sum_i \varepsilon_i \exp(-\beta \varepsilon_i) = \frac{UZ}{N}$$

On combining this result with Eq. (3.46), we can write

$$\left(\frac{\partial Z}{\partial \beta}\right)_V = -\frac{UZ}{N} \quad (3.47)$$

On substituting this result in Eq. (3.45), we get

$$\begin{aligned} \frac{1}{T} &= -\frac{Nk_B}{Z} \frac{UZ}{N} \left(\frac{\partial \beta}{\partial U}\right)_V + \beta k_B + k_B U \left(\frac{\partial \beta}{\partial U}\right)_V \\ &= -k_B U (\partial \beta / \partial U)_V + \beta k_B + k_B U (\partial \beta / \partial U)_V \\ \Rightarrow \quad \beta &= \frac{1}{k_B T} \end{aligned} \quad (3.48)$$

Now that we have evaluated both Lagrange multipliers, we can rewrite Eq. (3.38) for Maxwell-Boltzmann distribution as



$$(\varepsilon_j - \mu) / k_B T.$$

A plot of n_j versus $(\varepsilon_j - \mu) / k_B T$ is shown in Fig. 3.4. As may be noted, the distribution function approaches zero at higher energies. This is in conformity with the behaviour obtained using kinetic theory of gases.

You would recall that we had mentioned that it is possible to express thermodynamic variables in terms of the partition function and understand the thermodynamic behaviour of a system, in terms of Z . Let us learn to do so now.

Before proceeding further, you may like to solve an SAQ.

SAQ 4

Determine the equilibrium population ratio of a doubly-degenerate energy level E_j lying at energy 2 units higher than a lower non-degenerate energy level E_i assuming $k_B T = 1$ unit.

3.5 THERMODYNAMIC VARIABLES

To express different thermodynamic quantities in terms of the partition function, we begin by considering Eq. (3.44). On substituting the value of β in terms of temperature, we can express entropy in terms of the partition function as

$$S = Nk_B \ln Z + \frac{U}{T} \quad (3.50)$$

Now, we express internal energy U in terms of Z . For this we calculate partial derivative of the partition function with respect to temperature at constant volume and write

$$\left(\frac{\partial Z}{\partial T}\right)_V = \left(\frac{\partial Z}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial T}\right)_V = -\frac{1}{k_B T^2} \left(\frac{\partial Z}{\partial \beta}\right)_V$$

$$\text{since } \left(\frac{\partial \beta}{\partial T}\right)_V = -\frac{1}{k_B T^2}.$$

On substituting for $\left(\frac{\partial Z}{\partial \beta}\right)_V$ from Eq. (3.47), we get

$$\left(\frac{\partial Z}{\partial T}\right)_V = -\frac{ZU}{N} \times \left(-\frac{1}{k_B T^2}\right) = \frac{U}{k_B T^2} \frac{Z}{N}$$

Hence, the expression for internal energy of the system in terms of partition function is obtained by inverting this relation:

$$U = Nk_B T^2 \frac{1}{Z} \left(\frac{\partial Z}{\partial T}\right)_V = Nk_B T^2 \frac{\partial}{\partial T} \ln Z \quad (3.51)$$

The Helmholtz free energy F can be expressed in terms of the partition function by inverting Eq. (3.50) for entropy:

$$F = U - TS = -Nk_B T \ln Z \quad (3.52)$$

For an isothermal process, the pressure exerted by a gas is related to the Helmholtz free energy through the relation

$$p = -\left(\frac{\partial F}{\partial V}\right)_T = \frac{Nk_B T}{Z} \left(\frac{\partial Z}{\partial V}\right)_T \quad (3.53)$$

From this discussion we can conclude that once we evaluate Z we can readily determine a thermodynamic function of interest.

Let us now end the unit with a very important topic in statistical mechanics, known as *postulate of equal a priori probabilities*. We have been using this postulate throughout our discussion, however, we have not explicitly defined the postulate. Now, that we are familiar with the basics of statistical mechanics, let us discuss the postulate.

3.6 PRINCIPLE OF EQUAL A PRIORI PROBABILITIES

In order to make any progress in theoretical study, it is necessary to introduce some basic statistical postulates. A postulate is an assumption that is

eminently reasonable and does not contradict any law of mechanics. We cannot prove a postulate. However, the validity of a postulate can only be decided by using it for theoretical predictions and checking whether the predictions are confirmed by experiments.

Let us consider an isolated system with a large number of particles ($\sim 10^{23}$). Obviously it will not be possible to obtain the exact solution of 10^{23} coupled equations of motion, neither analytically nor numerically. It is for this reason that in statistical mechanics used the probabilistic distribution functions, which describes the average quantities.

In order to obtain the macroscopic properties of a system using statistical mechanics, the basic assumptions about the system of interest are:

a) the system consists of a large number of particles and this number is fixed

$$\sum_i n_i = N$$

where n_i is the number of particles in a given cell / microstate.

b) the total energy of the system is conserved

$$\sum_i n_i \varepsilon_i = E$$

ε_i is the energy of the particle in the i^{th} cell.

In a given thermodynamic system there exists a set of accessible microstates. A system will not stay in a given microstate forever, it will continually make transition between the various accessible microstates. As such there is nothing intrinsic in the laws of mechanics that gives preference to any accessible microstate over others. Thus, we can infer that the probability of the system occupying any of the accessible microstates will be same for all microstates. In other words, if the systems are initially uniformly distributed over all the accessible microstates, this distribution will remain unchanged in time. From this argument, we can conclude that for ensembles of isolated systems: if the systems are uniformly distributed, the ensemble is time-independent.

The system will make transitions between all the accessible states by virtue of interaction between the particles in the system. As a result the system will ultimately pass through all accessible microstates. Once uniform distribution is obtained, it will correspond to time-independent equilibrium situation.

From the preceding arguments, we can extrapolate that: if an isolated system does not have equal probability in each accessible microstate, it is not in equilibrium. However, the distribution tends to evolve with time and ultimately the equilibrium will be reached where the distribution probability is same for all accessible microstates.

This statement is of special importance as it leads to the following assertion: ***If an isolated system is in equilibrium, all the accessible microstates of the system are equally probable.***

This statement makes an unambiguous assertion that in an equilibrium, all accessible microstates are equally likely to be occupied. This is a fundamental statement and the theory of macroscopic systems in equilibrium is based on it.

This postulate is known as **the postulate of equal a priori probabilities or postulate** of equilibrium statistical mechanics.

It is important to note that the postulate of equal a priori probabilities implies that a system which is not in equilibrium tends to change in the direction of equilibrium condition. Note that the postulate does not provide any information about the time required by the system to attain equilibrium condition. The time required to reach equilibrium condition is known as *relaxation time*. Thus, we may say that the relaxation time could be in microsecond or years, depending on the nature of the interaction between the particles in the system.

Quantitative description of a non-equilibrium system is fairly complicated. However for a system in equilibrium, the problem can be solved by using postulate of equal a priori probabilities.

Another important hypothesis in statistical mechanics is the **Ergodic hypothesis**, which states that a stationary system for which time averages and ensemble averages are equal is said to be ergodic. This important hypothesis will be discussed in the next unit of the course.

Let us now consider an example.

Example 3.4

Consider a system of 4 non-interacting particles fixed at a position, where each particles has spin $1/2$ and a magnetic moment μ_0 . A magnetic field \vec{B} is applied on the system. The spin of the particles can be parallel ('up') or anti-parallel ('down') to \vec{B} . Suppose the energy of parallel spin is $-\mu_0 B$ and the anti-parallel spin is $+\mu_0 B$. If the system is isolated and the total energy $E = -2\mu_0 B$,

- calculate the accessible microstates for the system
- calculate the probability that the system is in any of the accessible microstate.

Solution : a) Since the total energy of the system is $E = -2\mu_0 B$, the distribution should be such that there are 3 spin up (+) and 1 spin down (-) particles. Hence, the total number of microstates is

$$\Omega = \frac{4!}{3! 1!} = 4$$

If σ_j represents the spin, let spin up be represented by (+) and spin down by (-). Hence, for a spin up, $\sigma_j \equiv +$ and the corresponding energy $\varepsilon_j = -\mu_0 B$. Similarly for spin down, $\sigma_j \equiv -$, the corresponding energy ε_j will be $-\mu_0 B$.

σ_1	σ_2	σ_3	σ_4	E
+	+	+	-	$-2\mu_0 B$
$(-\mu_0 B)$	$(-\mu_0 B)$	$(-\mu_0 B)$	$(+\mu_0 B)$	
+	+	-	+	$-2\mu_0 B$
+	-	+	+	$-2\mu_0 B$
-	+	+	+	$-2\mu_0 B$

The system could be found in any of these four accessible microstates.

b) The probability that the system is in any of these microstates is:

$$P_i = \frac{\Omega_i}{\Omega}$$

Hence, the probability for the system to be in the first microstate as given in the table is:

$$P_1 = \frac{1}{4}$$

We can see that the probabilities for all microstates are the same.

Let us now summarize what you have learnt in this unit.

3.7 SUMMARY

- The Lagrangian function is defined as:

$$L(x_1, x_2, \dots, x_n, \lambda_1, \lambda_2, \dots, \lambda_n) = f(x_1, \dots, x_n) - \sum_{j=1}^n \lambda_j g_j(x_1, \dots, x_n)$$

where g_j s are the constraints and λ_j s are the Lagrange's multipliers.

- The critical points are found by solving the system of equations obtained from setting the partial derivatives of $L(x_1, x_2, \dots, x_n, \lambda_1, \lambda_2, \dots, \lambda_n)$ to zero:

$$\frac{\partial L}{\partial x_i} = 0, \quad i = 1, 2, \dots, n$$

$$\frac{\partial L}{\partial \lambda_j} = 0$$

- The normalized probability for a discrete distribution obtained using the Lagrange's multiplier method:

$$P_j = \frac{e^{-\beta \epsilon_j}}{\sum_{j=1}^k e^{-\beta \epsilon_j}}$$

- Using the method of entropy maximization, the Maxwell-Boltzmann distribution of velocities for a classical ideal gas is:

$$\rho(v) = \sqrt{\frac{m}{2\pi k_B T}} e^{-\frac{mv^2}{2k_B T}}$$

The distribution is normally distributed. Therefore, for an equilibrium system, Gaussian distribution is the only distribution that maximized entropy.

- The Boltzmann entropy relation is obtained as:

$$S = k_B \ln \Omega$$

where Ω is the number of accessible microstates.

- The Maxwell-Boltzmann distribution law for discrete energy levels is

$$n_i = \frac{1}{\exp(\alpha + \beta \varepsilon_i)} = \frac{1}{\exp[(\varepsilon_i - \mu) / k_B T]}$$

where ε_i represent the discrete energy levels, α, β are the Lagrange's multipliers and μ is known as chemical potential.

- The partition function for a system of N distinguishable particles distributed in non-degenerate levels is given by

$$Z = \sum_{i=1}^N \exp(-\beta \varepsilon_i)$$

- For a non-degenerate thermodynamic system made up of N identical and non-interacting particles enclosed in volume V , the thermodynamic parameters are related to Z as

$$U = Nk_B T^2 \frac{\partial}{\partial T} (\ln Z)$$

$$S = Nk_B \ln Z + \frac{U}{T}$$

$$F = -Nk_B T \ln Z$$

$$p = \frac{Nk_B T}{Z} \left(\frac{\partial Z}{\partial V} \right)_T$$

- The hypothesis that all microstates are equally probable. This hypothesis is known as the **postulate of equal a priori probabilities**.

3.8 TERMINAL QUESTIONS

1. Calculate the mean of velocity and the variance of Maxwell-Boltzmann distribution in three-dimensional system.
2. There are 6 distinguishable particles, distributed over non-degenerate energy levels 0, E and $2E$. a) What is the most probable microstate? b) Find the total energy of the distribution. c) Find the entropy for the distribution.
3. Consider two systems having N and N' particles, respectively. Let them be brought in thermal contact. Show that β is same for both the assemblies.
4. For a system in equilibrium with a heat bath at temperature T , the probability of being in a state corresponding to energy E_i is proportional to $\exp(-\beta E_i)$. Calculate the relative root mean-square fluctuation of E .
5. Consider a system of N particles and a phase space consisting of only two levels with energies 0 and ε ($\varepsilon > 0$), respectively. Calculate the partition function and the internal energy.
6. N particles obey Maxwell-Boltzmann distribution. They are distributed among three states with energies $E_1 = 0$, $E_2 = k_B T$ and $E_3 = 3k_B T$. If the equilibrium energy of the system is $2000k_B T$, calculate the total number of particles.

7. The molecules of a gas have two states of internal energy with statistical weights g_1, g_2 and energies 0 and ϵ , respectively. Calculate the number of particles in each state and hence the internal energy of the gas.
8. Obtain the partition function of a harmonic oscillator whose energy levels are given by

$$E_n = \left(n + \frac{1}{2}\right)h\nu \quad \text{where } n = 0, 1, 2, 3, \dots$$

9. The vibration frequency of a homonuclear diatomic molecule is ν . Calculate the temperature at which the population of the first excited state will be half of the ground state given that the vibrational modes of molecules, the energy levels are quantized and given by

$$E_n = \left(n + \frac{1}{2}\right)h\nu \quad \text{for } \nu = 0, 1, 2, 3, \dots$$

3.9 SOLUTIONS AND ANSWERS

Self-Assessment Questions

1. Since $S = k_B \ln \Omega$
- $$S = 1.38 \times 10^{-23} \times \ln(1000) \text{ J/K} = 1.38 \times 10^{-23} \times 2.303 \times \log(1000) \text{ J/K}$$
- $$S = 1.38 \times 10^{-23} \times 2.303 \times 3 \text{ J/K}$$
- $$S = 9.53 \times 10^{-23} \text{ J/K}$$

2. From the given distribution in Example 3.3, we find that $\Omega_4 = 360$.
Therefore, value of entropy:

$$S = k \ln \Omega = k \ln(360)$$

$$S = k \times 2.303 \times \log(360) = 5.886 k$$

which is the maximum value of entropy when compared with various other distributions.

Hence, the most probable distribution is for the microstate corresponding to Ω_4 .

3. Given the total number of particles $N = 2000$. According to Maxwell-Boltzmann distribution law, the number of particles in a state $n_i(\epsilon_i)$ is proportional to $\exp(-\epsilon_i / k_B T)$, where n_i is the number of particles in the i^{th} state. Therefore, we can write

$$n_1 : n_2 : n_3 = \exp(-k_B T / k_B T) : \exp(-2k_B T / k_B T) : \exp\left(-\frac{3k_B T}{k_B T}\right)$$

or we can write

$$n_1 : n_2 : n_3 = e^{-1} : e^{-2} : e^{-3}$$

$$\frac{n_1}{1} \cdot \frac{n_2}{1} \cdot \frac{n_3}{1} = \frac{n_1 + n_2 + n_3}{\frac{1}{e} + \frac{1}{e^2} + \frac{1}{e^3}} = \frac{N}{\frac{1}{e} + \frac{1}{e^2} + \frac{1}{e^3}} = \frac{N}{0.5530}$$

$$n_1 = \frac{N}{0.5530} \times \frac{1}{e} = \frac{N}{1.503} = 0.665 N = 1330$$

$$n_2 = \frac{N}{0.5530} \times \frac{1}{e^2} = \frac{N}{4.085} = 490$$

$$n_3 = \frac{N}{0.5530} \times \frac{1}{e^3} = \frac{N}{11.107} = 180$$

Therefore, the value of equilibrium energy

$$\begin{aligned} U &= n_1 \varepsilon_1 + n_2 \varepsilon_2 + n_3 \varepsilon_3 \\ &= 1330 k_B T + 490 \times 2k_B T + 270 \times 3k_B T \\ &= 1330 k_B T + 980 k_B T + 810 k_B T \\ U &= 3220 k_B T \end{aligned}$$

4. The partition function Z of the system with energy E_i is given by

$$Z = \sum_i g_i \exp\left(\frac{-E_i}{kT}\right)$$

which gives the equilibrium population ratio as

$$\frac{n_i}{n_j} = \frac{g_i}{g_j} \exp\left(\frac{-\Delta E}{kT}\right)$$

where n_i = number of particles in i^{th} state, g_i = degeneracy of the i^{th} state, E_i = energy of the i^{th} state, k is the Boltzmann constant and T is the absolute temperature.

Given that $g_j = 2, g_i = 1$ and $\Delta E = 2$, the value of $\frac{n_i}{n_j}$ turns out to be

$$\frac{n_i}{n_j} = 2e^{-2} \text{ which is the value of equilibrium population ratio.}$$

Terminal Questions

1. We know, the mean of a continuous velocity distribution is defined as:

$$\langle v \rangle = \int_{-\infty}^{+\infty} v \rho(v) dv$$

Using Eq. (3.20)

$$\rho(v) dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} dv$$

Therefore,

$$\langle v \rangle = \int_{-\infty}^{+\infty} v 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-\frac{mv^2}{2k_B T}} dv = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} \int_{-\infty}^{+\infty} v^3 e^{-\frac{mv^2}{2k_B T}} dv$$

Let $x = \frac{mv^2}{2k_B T} \Rightarrow v = \sqrt{\frac{2k_B T}{m}} \sqrt{x}$, then

$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \frac{1}{2} \int_0^{+\infty} \left(\frac{2k_B T}{m} \right)^2 e^{-x} x dx$$

$$\Rightarrow \langle v \rangle = \left(\frac{8k_B T}{\pi m} \right)^{1/2} \int_0^{+\infty} e^{-x} x dx \quad \because \int_0^{+\infty} e^{-x} x dx = 1$$

$$\Rightarrow \langle v \rangle = \left(\frac{8k_B T}{\pi m} \right)^{1/2} \quad (i)$$

Similarly,

$$\langle v^2 \rangle = \int_{-\infty}^{+\infty} v^2 p(v) dv = \sqrt{\frac{8k_B T}{\pi m}} \sqrt{\frac{2k_B T}{m}} \Gamma(5/2)$$

$$\Rightarrow \langle v^2 \rangle = \frac{3k_B T}{m} \quad (ii)$$

Therefore, Using Eqs. (i) and (ii), we get:

$$\sigma^2 = \langle v^2 \rangle - \langle v \rangle^2 = \frac{3k_B T}{m} - \frac{8k_B T}{\pi m} = \frac{k_B T}{m} \left(3 - \frac{8}{\pi} \right)$$

2. Since the particles are distributed over a non-degenerate energy levels, we know that there is only one state associated with each energy.

If N_1, N_2 and N_3 are the number of particles in energy level 0, E and $2E$ respectively then

$$N_1 + N_2 + N_3 = 6$$

Since the particles are distinguishable and distributed across 3 energy levels, the accessible microstates are given by the relation:

$$\Omega = \frac{6!}{N_1! N_2! N_3!}$$

- a) The most probable distribution is one where the number of microstates is maximum and Ω is found to be maximum when $N_1 = 2, N_2 = 2$ and $N_3 = 2$.

$$\Omega = \frac{6!}{2! 2! 2!} = 90$$

Hence, the most probable microstate is when the identical particles are distributed such that $N_1 = 2, N_2 = 2$ and $N_3 = 2$.

- b) Since the particles are distributed such that $N_1 = 2, N_2 = 2$ and $N_3 = 2$, we know the total energy of the distribution is given as;

$$\sum N_i E_i = E_{Total}$$

$$2 \times 0 + 2 \times E + 2 \times 2E = E_T$$

$$6E = E_T$$

c) The entropy of the distribution is

$$S = k \ln \Omega = k \ln(90)$$

$$S = 1.38 \times 10^{-23} \times 2.303 \times \log(90)$$

$$S = 6.21 \times 10^{-23} \text{ J/K}$$

3. When these systems are put in contact, their states will adjust themselves so that they have equal temperature T . Let the set of occupation numbers and energies for the two systems be $\{n_i\}, \{E_i\}$ and $\{n'_j\}, \{E'_j\}$, respectively.

Then we have

$$W = \frac{M!}{\prod_i n_i!} \frac{N!}{\prod_j n'_j!} \quad (\text{i})$$

and

$$\ln \Omega = N \ln N - \sum_i n_i \ln n_i + N' \ln N' - \sum_j n'_j \ln n'_j \quad (\text{ii})$$

Now we have to maximize $\ln \Omega$ by calculating $\delta(\ln \Omega)$ and equating the resultant to zero:

$$\begin{aligned} \delta \ln \Omega = 0 = & \sum_i \delta n_i (\ln n_i) + \sum_i n_i \frac{1}{n_i} \delta n_i \\ & + \sum_j \delta n'_j (\ln n'_j) + \sum_j n'_j \frac{1}{n'_j} \delta n'_j \end{aligned}$$

That is,

$$\sum_i \delta n_i (\ln n_i) + \sum_i \delta n_i + \sum_j \delta n'_j (\ln n'_j) + \sum_j \delta n'_j = 0 \quad (\text{iii})$$

Since the total number of particles in both the system are constant and total energy of the system is conserved, we have the following three constraints:

$$\left. \begin{aligned} \sum_i n_i = N, \quad \sum_j n'_j = N', \end{aligned} \right\}$$

and

$$\left. \sum_i \sum_j (n_i E_i + n'_j E'_j) = \sum_i n_i E_i + \sum_j n'_j E'_j = U \right\} \quad (\text{iv})$$

From the first two constraints we can substitute

$$\sum_i \delta n_i = 0 \quad \text{and} \quad \sum_j \delta n'_j = 0$$

in Eq. (iii) and we can write

$$\sum_i \delta n_i (\ln n_i) + \sum_j \delta n'_j (\ln n'_j) = 0 \quad (\text{v})$$

Note that the number of particles in the two systems is different but their total energy is conserved. It means that the given systems have three constraints. To remove these we use the method of Lagrange multipliers.

Multiplying Eq. (iii) with Lagrange multipliers α , α' and β , and adding to Eq. (v), we get

$$\sum_i (\ln n_i + \alpha + \beta E_i) \delta n_i + \sum_j (\ln n'_j + \alpha' + \beta E'_j) \delta n'_j = 0$$

Since $\delta n_i, \delta n'_j$ are arbitrary and independent, we obtain

$$n_i = e^{-\alpha - \beta E_i}, \quad n'_j = e^{-\alpha' - \beta E'_j}$$

Thus, β has the same value for two systems which are in thermal equilibrium with each other.

4. The mean value of energy is

$$\langle E \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-\beta E_i}}$$

$$\Rightarrow \langle E \rangle \sum_i e^{-\beta E_i} = \sum_i E_i e^{-\beta E_i}$$

Differentiating with respect to β , we have

$$\frac{\partial \langle E \rangle}{\partial \beta} \sum_i e^{-\beta E_i} + \langle E \rangle \sum_i e^{-\beta E_i} (-E_i) = \sum_i E_i e^{-\beta E_i} (-E_i)$$

Dividing by $\sum_i e^{-\beta E_i}$ we get

$$\frac{\partial \langle E \rangle}{\partial \beta} - \langle E \rangle^2 = - \langle E^2 \rangle$$

or

$$\sigma_E^2 = \langle E^2 \rangle - \langle E \rangle^2 = - \frac{\partial \langle E \rangle}{\partial \beta}$$

Also

$$- \frac{\partial \langle E \rangle}{\partial \beta} = - \frac{\partial E}{\partial T} \frac{\partial T}{\partial \beta} = k_B T^2 \frac{\partial \langle E \rangle}{\partial T} = k_B T^2 C_V$$

$$\text{So } \sigma_E^2 = k_B T^2 C_V$$

This is an interesting result in that variance in energy is related to heat capacity, a thermal property of a substance.

For an ideal monatomic gas $\langle E \rangle = (3/2) N k_B T$ and $C_V = (3/2) N k_B$.

Hence,

$$\sigma_E^2 = \frac{3}{2} N k_B^2 T^2$$

The relative root mean square fluctuation in energy is

$$\sqrt{\frac{\sigma_E^2}{\langle E \rangle^2}} = \sqrt{\frac{2}{3N}}$$

For one mole of gas, this is 10^{-12} , which is negligible.

5. It is given that $E_2 = \varepsilon$ and $E_1 = 0$.

We have $Z = \sum_i e^{-E_i / k_B T} = 1 + e^{-\theta / T}$ with $\theta = \frac{\varepsilon}{k_B}$. The occupation

numbers are

$$n_1 = \frac{N}{Z} = \frac{N}{1 + e^{-\theta / T}}$$

$$n_2 = \frac{N e^{-\theta / T}}{Z} = \frac{N e^{-\theta / T}}{1 + e^{-\theta / T}}$$

$$\therefore U = n_1 E_1 + n_2 E_2 = \frac{N \varepsilon e^{-\theta / T}}{1 + e^{-\theta / T}}$$

For very low temperature ($T \ll \theta$), we have $n_1 \cong N, n_2 = 0$. At very high

temperatures ($T \gg \theta$), $n_1 \cong \frac{N}{2}, n_2 \cong \frac{N}{2}$. You will note that

$$\frac{n_2}{n_1} = e^{-\theta / T} < 1$$

6. We have $N = N_1 + N_2 + N_3$ and $E = N_1 E_1 + N_2 E_2 + N_3 E_3$

Hence we can write

$$2000 k_B T = N_1(0) + N_2 k_B T + N_3 3 k_B T$$

$$2000 = N_2 + 3N_3 \quad (i)$$

Also,

$$N_1 : N_2 : N_3 :: \exp(-E_1 / k_B T) : \exp(-E_2 / k_B T) : \exp(-E_3 / k_B T)$$

i.e.

$$N_1 : N_2 : N_3 :: 1 : \exp(-1) : \exp(-3)$$

or

$$\frac{N_1}{1} = \frac{N_2}{e^{-1}} = \frac{N_3}{e^{-3}} = \text{Constant (say) } B$$

Hence

$$N_1 = B, N_2 = \frac{B}{e} \text{ and } N_3 = \frac{B}{e^3}$$

$$\text{From (i) we have } 2000 = N_2 + 3N_3 = \frac{B}{e} + \frac{3B}{e^3}$$

Hence

$$B = \frac{2000}{e^{-1} + 3e^{-3}} = \frac{2000}{0.3679 + 0.1493} = \frac{2000}{0.5172} = 3867$$

That is,

$$N_1 = 3867, N_2 = \frac{3867}{e} = 1423 \text{ and } N_3 = \frac{3867}{e^3} = 193$$

And hence the total number of particles $N = 5483$.

7. The partition function in this case can be written as

$$Z = g + g_2 \exp(-\varepsilon / k_B T)$$

Let n_1 and n_2 are the molecules in state 1 and 2 respectively, then

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp(-\varepsilon / k_B T) \quad (\text{i})$$

If N is the total number of particles, it means $N = n_1 + n_2$, then Eq. (i) can be rewritten as

$$\frac{n_2}{n_1} = \frac{g_2}{g_1} \exp(-\varepsilon / k_B T)$$

$$\frac{N}{n_1} - 1 = \frac{g_2}{g_1} \exp(-\varepsilon / k_B T)$$

$$n_1 = \frac{N}{1 + \frac{g_2}{g_1} \exp(-\varepsilon / k_B T)} \quad (\text{ii})$$

$$n_2 = N - n_1 = N - \frac{N}{1 + \frac{g_2}{g_1} \exp(-\varepsilon / k_B T)}$$

$$n_2 = \frac{N \frac{g_2}{g_1} \exp(-\varepsilon / k_B T)}{1 + \frac{g_2}{g_1} \exp(-\varepsilon / k_B T)} \quad (\text{iii})$$

The expression for internal energy of the gas can be written as:

$$U = n_1 \varepsilon_1 + n_2 \varepsilon_2 = n_2 \varepsilon$$

$$U = \frac{N \varepsilon \frac{g_2}{g_1} \exp(-\varepsilon / k_B T)}{1 + \frac{g_2}{g_1} \exp(-\varepsilon / k_B T)}$$

8. The partition function Z of the system with energy E_n is given by

$$Z = \sum_n \exp\left(\frac{-E_n}{k_B T}\right) = \exp\left(\frac{-h\nu}{2k_B T}\right) \sum_n \exp\left(\frac{-nh\nu}{k_B T}\right)$$

where k_B is the Boltzmann constant and T is the absolute temperature.

Expanding the value of Z in a series with all values of n , we get a an

infinite geometric series with common ratio $r = \exp\left(\frac{-h\nu}{k_B T}\right)$ as

$$Z = \exp\left(\frac{-h\nu}{2k_B T}\right) \left[1 + \exp\left(\frac{-h\nu}{k_B T}\right) + \exp\left(\frac{-2h\nu}{k_B T}\right) + \exp\left(\frac{-3h\nu}{k_B T}\right) + \dots \right]$$

The sum of the infinite geometric series is given by $\frac{a}{1-r}$ where a is the 1st

term. Hence the partition Z is obtained as $Z = \frac{\exp\left(\frac{-h\nu}{2k_B T}\right)}{1 - \exp\left(\frac{-h\nu}{k_B T}\right)}$.

9. According to Maxwell-Boltzmann distribution, the ratio of the population of two energy states under thermal equilibrium at temperature T is defined by:

$$\frac{N_2}{N_1} = \exp\left(\frac{-\Delta E_n}{k_B T}\right)$$

where N_2 and N_1 are the numbers of molecules in the higher and lower energy states, respectively, ΔE_n is the energy difference between the two states, k is Boltzmann constant and T is the absolute temperature. Since the population of the first excited state ($\nu = 1$) is half that of the ground state ($\nu = 0$), $\frac{N_2}{N_1} = \frac{1}{2}$ and $\Delta E_n = h\nu$, Maxwell-Boltzmann distribution

simplifies to $\frac{1}{2} = \exp\left(\frac{-h\nu}{k_B T}\right)$.

Taking natural logarithm on both sides and solving for T , the temperature at which the population of the first excited state is half that of the ground state is obtained as

$$T = \frac{h\nu}{k_B \ln 2}$$

FURTHER READINGS

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TABLE OF PHYSICAL CONSTANTS

Symbol	Quantity	Value
c	Speed of light in vacuum	$3.00 \times 10^8 \text{ ms}^{-1}$
μ_0	Permeability of free space	$1.26 \times 10^{-6} \text{ NA}^{-2}$
ϵ_0	Permittivity of free space	$8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
$1/4\pi\epsilon_0$		$8.99 \times 10^9 \text{ Nm}^2 \text{ C}^{-2}$
e	Charge of the proton	$1.60 \times 10^{-19} \text{ C}$
$-e$	Charge of the electron	$-1.60 \times 10^{-19} \text{ C}$
h	Planck's constant	$6.63 \times 10^{-34} \text{ Js}$
\hbar	$h / 2\pi$	$1.05 \times 10^{-34} \text{ Js}$
m_e	Electron rest mass	$9.11 \times 10^{-31} \text{ kg}$
$-e / m_e$	Electron charge to mass ratio	$-1.76 \times 10^{11} \text{ Ckg}^{-1}$
m_p	Proton rest mass	$1.67 \times 10^{-27} \text{ kg (1 amu)}$
m_n	Neutron rest mass	$1.68 \times 10^{-27} \text{ kg}$
a_0	Bohr radius	$5.29 \times 10^{-11} \text{ m}$
N_A	Avogadro constant	$6.02 \times 10^{23} \text{ mol}^{-1}$
R	Universal gas constant	$8.31 \text{ Jmol}^{-1} \text{ K}^{-1}$
k_B	Boltzmann constant	$1.38 \times 10^{-23} \text{ J K}^{-1}$
G	Universal gravitational constant	$6.67 \times 10^{-11} \text{ Nm}^2 \text{ kg}^{-2}$