

## Statistical Thermodynamics

Assembly: Assembly denotes a no. of 'N' of identical entities such as molecules, atoms, electrons etc.

Macrostate: It is specified by the no. 'N' of particles in each of the energy levels in the system.

Microstate: It is specified by the no. of particles in each of the energy states in the system.

Thermodynamic Probability<sup>(W)</sup>: The no. of microstates leading to a given macrostate is called thermodynamic probability.

\* Ludwig Boltzmann is the father of Statistical Thermodynamics.

$$S = k_b \ln W$$

Boltzmann  
Equation

Q. Assuming that there are 4 students to be assigned into two classrooms, how many possibilities are there to split them? Find the no. of macrostate, microstate and thermodynamic probability.



	Students in Room 1	Students in Room 2
Case 1	4	0
Case 2	3	1
Case 3	2	2
Case 4	1	3
Case 5	0	4

using  $A_1, A_2, A_3$  and  $A_4$  to represent the identity

of this 4 students, there will be many different combination for each case.

	Students in room 1	Total
Case 1	A <sub>1</sub> , A <sub>2</sub> , A <sub>3</sub> , A <sub>4</sub>	1
Case 2	A <sub>1</sub> , A <sub>2</sub> , A <sub>3</sub> A <sub>1</sub> , A <sub>2</sub> , A <sub>4</sub> A <sub>1</sub> , A <sub>3</sub> , A <sub>4</sub> A <sub>2</sub> , A <sub>3</sub> , A <sub>4</sub>	4
Case 3	A <sub>1</sub> , A <sub>2</sub> , A <sub>3</sub> , A <sub>4</sub> A <sub>2</sub> , A <sub>3</sub> , A <sub>4</sub> , A <sub>3</sub> , A <sub>4</sub>	6
Case 4	A <sub>1</sub> , A <sub>2</sub> , A <sub>3</sub> , A <sub>4</sub>	4
Case 5	0	1
		16

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### Assembly of Distinguishable particle

$$\textcircled{1} \quad \sum_{j=1}^n N_j = N$$

\textcircled{2}  $\sum N_j E_j = E$  where  $N_j$  is the no. of particle in the energy level  $j$  with the energy  $E_j$

- Q. Three distinguishable particles labelled as A, B & C are distributed among four energy levels, 0, E, 2E & 3E respectively. The total energy is 3E. Calculate the no. of possible microstate and macrostate.

Ans:  $\sum_{j=1}^3 N_j = 3$

$\sum_{j=1}^3 N_j \cdot E_j = 3E$

No. of Cases	No. of Particles in BY Level 0	Particles in Level 1	Particles in Level 2	Particles in Level 3
Case I	2	0	0	1
Case II	0	3	0	0
Case III	1	1	1	0

So far there are three macrostates in the given system identifying the particles and in every macrostate, the configuration for Case I, Case II, Case III can be presented as

Case III				
No. of Cases	OE	1F	2F	3E
Case I	A B B C A C			C A B
Case II		ABC BCA CBA BAC CAB <u>ACB</u>		
Case III	A-B-C A A B B C C	ABC B C A C A B	ABC C B C A B A	

The Thermodynamic Probability for Case I, W is 3  
 u u u u II, W is 2  
 u u u u III, W is 6

The total microstate of the system is  $10^{10} \times 10^{13} \times 10^8$ .

According to M.B Statistics

$$W = \frac{N!}{n_1! n_2! n_3! \dots}$$

Q. What is no. of ways of distributing 20 identical objects with the arrangement 1, 0, 3, 5, 10, 1.

$$W = \frac{20!}{n_1! n_2! n_3! \dots}$$

$$= \frac{20 \cdot 19 \cdot 18 \cdot 17 \cdot 16 \cdot 15 \cdot 14 \cdot 13 \cdot 12 \cdot 11 \cdot 10!}{1 \cdot 2 \cdot 3 \cdot 4 \cdot 5 \cdot 6 \cdot 7 \cdot 8 \cdot 9 \cdot 10 \cdot 11 \cdot 12 \cdot 13 \cdot 14 \cdot 15 \cdot 16 \cdot 17 \cdot 18 \cdot 19 \cdot 20}$$

$$= 19 \times 3 \times 17 \times 16 \times 14 \times 13 \times 11 \times 6 \times 5$$

$$= 931,170,240$$

$$0! = 1$$

Q. What is the weight of the configuration in which 20 objects are distributed in the arrangement 0, 1, 5, 0, 3, 2, 1, 0, 8.

$$W = \frac{20!}{0! 1! 5! 0! 3! 2! 1! 0! 8!}$$

$$= \frac{20 \cdot 19 \cdot 18 \cdot 17 \cdot 16 \cdot 15 \cdot 14 \cdot 13 \cdot 12 \cdot 11 \cdot 10 \cdot 9 \cdot 8!}{1 \cdot 1 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 \cdot 8 \cdot 7 \cdot 6 \cdot 5 \cdot 4 \cdot 3 \cdot 2 \cdot 1 \cdot 8!}$$

$$= 19 \cdot 18 \cdot 17 \cdot 16 \cdot 15 \cdot 14 \cdot 13 \cdot 12 \cdot 11$$

$$= 83,805,321,600$$

Q. Find the no. of configuration in the most probable state according to Boltzmann formula.

Higher thermodynamic probability

$$\ln W = \frac{S}{K_B}$$

$$\Rightarrow W = e^{\frac{S}{K_B}}$$

## Partition Function (2)

$$q = \sum g_i e^{-E_i/kT}$$

$g \rightarrow$  degeneracy of the system.

or

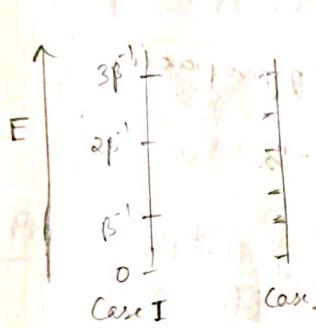
$$q = \sum g_i e^{-\beta E_i}$$

$$\text{where } \beta = \frac{1}{kT}$$

$q$  is a measure of thermally accessible states and represents sum over all terms that describes the probability associated with the variable of interest.

Part 2 9/08/2025

## Partition Function (2) of a SHO oscillating with energy spacing $\beta^{-1}$



$$\text{For a SHO, } q = \sum e^{-\beta E_n}$$

The energy levels of a harmonic oscillator is  $E_n = nh\nu$  for  $n = 0, 1, 2, 3, \dots$

Now, we will employ oscillators where  $\hbar\nu = \beta^{-1}$

$$\therefore E_n = n\beta^{-1}$$

using this value for the energy spacing, we have

$$e^{-\beta E_n} = e^{-\beta \cdot n\beta^{-1}} = e^{-n}$$

$$\text{Now, we know } q = \sum_{n=0}^{\infty} e^{-\beta E_n}$$

$$q = \sum_{n=0}^{\infty} e^{-n} = \frac{1}{1 - e^{-1}}$$

$$= e^{-0} + e^{-1} + e^{-2} + \dots$$

$$= 1 + e^{-1} + e^{-2} + e^{-3} + \dots$$

0.362

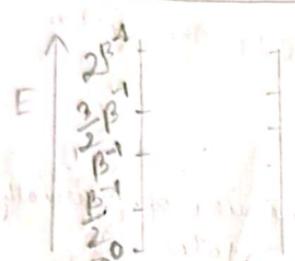
$$\Rightarrow q = \frac{1}{1 - e^{-1}}$$

since

$$= 1.58$$

$$\therefore \frac{1}{1-x} = 1 + x + x^2 + \dots \quad |x| < 1$$

Partition function for a SHO with energy spacing  $\frac{h}{2}\beta^{-1}$



For a SHO,

$$q = \sum e^{-\beta E_n}$$

The energy levels of a harmonic oscillator is  $E_n = nh\nu$  for

Cox 7

Case I    Case II

$$m = 0, 1, 2, 3, \dots$$

Now, we will employ oscillator

where the energy is

$$W = \frac{\beta + 1}{2}$$

$$\therefore E_n = n \frac{B^{-1}}{2}$$

Using this value for the energy spacing,

we have

$$e^{-\beta E_n} = e^{-\beta \cdot n \frac{\beta^{-1}}{2}} = e^{-n \frac{\beta}{2}}$$

We know,

$$q = \sum_{n=0}^{\infty} e^{-\beta E_n}$$

$$= \sum_{n=0}^{\infty} e^{-\eta z}$$

$$= e^{-0} + e^{-\frac{1}{2}} + e^1 + e^{-\frac{3}{2}} + e^{-2} +$$

$$= 1 + e^{-\frac{1}{2}} + e^1 + e^{-3} + e^{-2} + \dots$$

$$\Rightarrow q = \frac{1}{1-e^{-\frac{1}{k}}}$$

$$= \frac{1}{1 - 0.605}$$

$$= \frac{1}{0.394}$$

= 2.538

$$= 2.54$$

The probability of occupying a given energy level is given by

$$P_n = \frac{e^{-\beta E_n}}{q}$$

$n \rightarrow \text{no. of states}$

Probability of a harmonic oscillator occupying the first three energy levels,  $n=0, 1, 2$  with energy spacing  $\beta^{-1}$

$$n=0$$

$$P_0 = \frac{e^{-\beta E_0}}{1.58}$$

$$= \frac{e^0}{1.58}$$

$$= \frac{1}{1.58}$$

$$= 0.632$$

$$n=1$$

$$P_1 = \frac{e^{-1}}{1.58}$$

$$= \frac{0.367}{1.58}$$

$$n=2$$

$$P_2 = \frac{e^{-2}}{1.58}$$

$$= \frac{0.135}{1.58}$$

$$= 0.232$$

$$= 0.085$$

Probability of a harmonic oscillator occupying the first three energy levels,  $n=0, 1, 2$  with energy spacing  $\frac{\beta}{2}$ .

$$n=0$$

$$P_0 = \frac{e^{-0}}{2.54}$$

$$= \frac{1}{2.54}$$

$$= 0.393$$

$$n=1$$

$$P_1 = \frac{e^{-\frac{1}{2}}}{2.54}$$

$$= \frac{0.606}{2.54}$$

$$= 0.238$$

$$n=2$$

$$P_2 = \frac{e^{-1}}{2.54}$$

$$= \frac{0.367}{2.54}$$

$$= 0.144$$

## Molecular Partition Function

We know, partition function,  $q = \sum g_i e^{-\beta E_i}$

For a polyatomic molecule, there are four energetic degrees of freedom; translational, rotational, vibrational and electronic. Assuming that degrees of freedom are not coupled, the total molecular partition function that includes all of this degrees of freedom can be decomposed into a prod of partition function corresponding

ding to each degrees of freedom. Let  $E_{\text{Total}}$  be represents the energy associated with a given molecular energy level. The energy will depend on the translational, rotational, vibrational and electronic level energies as follows.

$$E_{\text{Total}} = E_{\text{Trans}} + E_{\text{Rotational}} + E_{\text{Vibrational}} + E_{\text{Electronic}}$$

$$q_{\text{Total}} = q_{\text{trans}} \cdot q_{\text{rot}} \cdot q_{\text{vib}} \cdot q_{\text{elec}} \quad \text{①}$$

$$\therefore q_{\text{Total}} = \sum q_{\text{Total}} \cdot e^{-BE_{\text{Total}}}$$

$$= \sum (q_{\text{Trans}} \cdot q_{\text{Rotat.}} \cdot q_{\text{Vib.}} \cdot q_{\text{Elect.}}) \cdot e^{-B(E_{\text{Trans}} + E_{\text{Rot}} + E_{\text{Vib}} + E_{\text{Elec}})}$$

$$= \sum q_{\text{Trans}} e^{-BE_{\text{Trans}}} \cdot q_{\text{Rot}} e^{-BE_{\text{Rot}}} \cdot q_{\text{Vib}} e^{-BE_{\text{Vib}}} \cdot q_{\text{Elect.}} e^{-BE_{\text{Elec}}}$$

$$q_{\text{Total}} = q_{\text{Trans}} \cdot q_{\text{Rot}} \cdot q_{\text{Vib.}} \cdot q_{\text{Elect.}}$$

$$q_T = q_{\text{Trans}} \cdot q_{\text{Rot}} \cdot q_{\text{Vib.}} \cdot q_{\text{Elect.}}$$

i.e. the total partition funct<sup>n</sup> is the prod<sup>t</sup> of partition funct<sup>n</sup> for each molecular energetic degrees of freedom.

Q. Show that molecular partition function for a polyatomic molecule is the prod<sup>t</sup> of partition function of every energetic degrees of freedom.

→

Q. Using expression for partition funct<sup>n</sup>, when  $T \rightarrow 0$

$$K \cdot T \rightarrow 0 \Rightarrow E_i / kT \rightarrow \infty \Rightarrow e^{-E_i / kT} \rightarrow 0$$

$q = g_i e^{-E_i / kT} \rightarrow q_i \rightarrow 0$

and  $q_{\text{Total}} = q_1 \cdot q_2 \cdot q_3 \cdots \rightarrow q_{\text{Total}} \rightarrow 0$

that's why partition function of polyatomic molecule is zero.

9. For a system the ground state is doubly degenerate. Calculate the partition function when  $T \rightarrow 0$ . (4) M

$$q = \sum g_i e^{-E_i/kT}$$

$$= \sum 2g_i e^{-E_i/kT}$$

$$= \sum 2g_i$$

$$= 2$$

### Classical Particle

- Macroparticles
- Distinguishable
- Maxwell-Boltzmann Statistics (MB)

### Quantum Particle

- Microparticle
- Indistinguishable
- Bose-Einstein & Fermi-Dirac statistics
- Bosons & Fermions

### Bosons

- Quantum particles
- Indistinguishable
- Have integral spin.
- Does not obey Pauli Exclusion Principle

### Fermions

- Quantum particles
- Distinguishable particles
- Have half-integral spin.
- It obeys Pauli Exclusion principle.

### Bosons.

- ① quantum particle
- ② Indistinguishable particle.
- ③ Have integral spins.  
 $-2, -1, 0, +1, +2 \dots$
- ④ Does not obey pauli Exclusion principle.

### Fermions.

- ① quantum particle.
- ② Indistinguishable particle.
- ③ Have half spins.  
 $\frac{1}{2}, \frac{3}{2}, \frac{5}{2} \dots$
- ④ obeys pauli Exclusion principle.

### Spin Multiplicity!

08/09/25

$$2S+1$$

$$S=1$$

$$S=0$$

$$2S+1 = 3P_3$$

$$2 \times \frac{1}{2} + 1 = 2 \text{ doublet}$$

$$2 \times 1 + 1 = 3 \text{ Triplet}$$

$$2 \times 0 + 1 = 1 \text{ Singlet}$$

$$2S+1 = 2 \times \frac{3}{2} + 1$$

$$2S+1 = 4$$

Q. The ground state Spectroscopy term for chlorine is  $2P_{3/2}$ . If Degeneracy is  $\frac{1}{2}$ ,  $\frac{3}{2}$ ,  $\frac{5}{2}$ ,  $\frac{7}{2}$ .

Q. The correct Entropy for 6 identical particle with their occupation numbers, 0, 1, 2, 3, is

$$S = K_b \ln W$$

$$W =$$

$$\frac{6!}{0!1!2!3!4!} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{1 \times 2 \times 3} = \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{0 \times 1 \times 2 \times 3} = 4 \times 10 = 60$$

$$@ K_b \ln 8$$

$$⑥ K_b \ln 12$$

$$⑦ K_b \ln 60$$

$$⑧ K_b \ln 720$$

$$16, 5, 4, 3, 2, 1$$

\* Q. The term symbol for the ground state of a metal ion is  $3P_2$ . Get an expression for the residual Entropy of a crystal of a salt of this metal ion at 0K.

$$\rightarrow 2S+1 = 3P_2$$

$$3P_2$$

$$\rightarrow 2S+1 = 3$$

$$2S+1 = 3$$

$\rightarrow 2J+1 = \text{Thermodynamic probability microstate (W)}$ .

$$W = 2J+1$$

$$= 2S+1 = 3 = 2(2)+1 = 5$$

$$S = K_b \ln W$$

\* Macrostate!

$$\begin{aligned} W &= g_J^n \\ &= 2^4 \\ &= 16 \end{aligned}$$

high probability state.  
high disorder state =  $F_{\text{gb}}^m$

10/10/25

Spin degeneracy is Ground state degeneracy of metal atom  
The spin degeneracy for a metal atom depends on the different possible orientation of the electron spins with in a specific orbital. while ground state Degeneracy refers to the number of distinct quantum states that share the lowest energy level.

\* Translational partition function! - (9 terms)

$$q = \sum e^{-\beta E_i} = \sum e^{-E_i/kT}$$

$$E_{tx} = \frac{n_x^2 h^2}{8ma^2} + \frac{n_y^2 h^2}{8mb^2} + \frac{n_z^2 h^2}{8mc^2}$$

$$\text{or } E_{tx} = \frac{h^2}{8m} \left[ \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right]$$

where, it's op. then quantum number here  $n_x, n_y, n_z$  vary from 1 to  $\alpha$ , substituting these values of translational Energy in the Eq<sup>n</sup> of partition function.

$$(i) \Rightarrow \sum \sum \sum \exp \left[ \frac{h^2}{8m k T} \left( \frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right) \right] \quad (iii)$$

where, the  $\sum \sum \sum$  is taken over all the integral values of  $n_x, n_y, n_z$  from one to  $\alpha$ . The motion of the particle in the 3 direction i.e.  $a_x, a_y, a_z$  being independent, we can replace the  $\sum$  as a product of  $3 \sum$ .

$$(ii) \Rightarrow \sum_{n=1}^{\infty} \exp \left( \frac{-h^2 n_x^2}{8ma^2 k T} \right) \sum_{n=1}^{\infty} \exp \left( \frac{-h^2 n_y^2}{8mb^2 k T} \right) \sum_{n=1}^{\infty} \exp \left( \frac{-h^2 n_z^2}{8mc^2 k T} \right) \quad (iv)$$

It is well known that the spacing between the Energy level of the particles in the 3D box is very small, compare with the thermal Energy  $kT$ . Hence, the  $\Sigma$  in Eqn (iv) can be replaced by Integration and we get

$$(iv) \Rightarrow \int_0^{\alpha} \exp\left[-\frac{n_x^2 h^2}{8\pi a^2 kT}\right] dn_x \int_0^{\alpha} \exp\left[-\frac{n_y^2 h^2}{8\pi b^2 kT}\right] dn_y \int_0^{\alpha} \exp\left[-\frac{n_z^2 h^2}{8\pi c^2 kT}\right] dn_z \quad (v)$$

Again, we know,

$$\int_0^{\alpha} e^{-\alpha x^2} dx = \frac{1}{2} \left(\frac{\pi}{\alpha}\right)^{1/2}$$

$$(v) \Rightarrow \frac{1}{2} \left(\frac{8\pi m a^2 kT}{h^2}\right)^{1/2} \frac{1}{2} \left(\frac{8\pi m b^2 kT}{h^2}\right)^{1/2} \frac{1}{2} \left(\frac{8\pi m c^2 kT}{h^2}\right)^{1/2}$$

$$\Rightarrow \frac{1}{2} \left(\frac{8\pi m a^2 kT}{h^2}\right)^{1/2} \frac{1}{2} \left(\frac{8\pi m b^2 kT}{h^2}\right)^{1/2} \frac{1}{2} \left(\frac{8\pi m c^2 kT}{h^2}\right)^{1/2}$$

$$q_{in} = \left(\frac{2\pi m a^2 kT}{h^2}\right)^{1/2} \left(\frac{2\pi m b^2 kT}{h^2}\right)^{1/2} \left(\frac{2\pi m c^2 kT}{h^2}\right)^{1/2}$$

or,

$$q_{in} = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} abc$$

or,

$$\boxed{q_{in} = \left(\frac{2\pi m kT}{h^2}\right)^{3/2} V}$$

where,  $V \rightarrow$  vol<sup>m</sup> of the box in which molecule moves.

\*Q. calculate the translational partition function for benzene in a vol<sup>m</sup> of 1 m<sup>3</sup> at 25°C.

$$q_{in} = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} \text{ molecule}$$

$$m = \frac{M}{N_A}$$

$$m: \text{Kg.} \quad = \quad \left( \frac{2\pi m k T}{h^2} \right)^{3/2} n \left( m^{-2} \right)^{3/2} = m^{-3}$$

$$KT : J = \text{Kg m}^2 \text{s}^{-2}$$

$$h: JS = \frac{kg}{m^2 s^{-1}}$$

$\therefore$  partition  $f^n$  are dimensionless

Q1) Define partition function?

(2) Obtain an expression for translational partition function?

(3) Show that the molecular partition function is a product of partition of translational, rotational, vibrational and electronic partition f?

Q. calculate the translational partition function  $\bar{f}_T^{\text{trans}}$  for benzene in a volume of  $1\text{m}^3$  at  $25^\circ\text{C}$ .

Ans Given,

$$T = 25^\circ\text{C} \Rightarrow 298.15\text{ K}$$

$$V = 1.0\text{ m}^3$$

Benzene molar mass.

$$M = 78.11\text{ g mol}^{-1} = 0.07811\text{ kg mol}^{-1}$$

$$K = 1.380649 \times 10^{-23}\text{ J K}^{-1}$$

$$h = 6.6 \times 10^{-34}\text{ Js}$$

$$N_A = 6.022 \times 10^{23}\text{ mol}^{-1}$$

$$2\lambda \approx 6.28$$

Mass of 1 benzene molecule,

$$m = \frac{M}{N_A} = \frac{0.07811}{6.022 \times 10^{23}} = 1.29 \times 10^{-25}\text{ kg}$$

$$q_m = \left( \frac{2\pi m k T}{h^2} \right)^{3/2} V$$

$$\begin{aligned} h^2 &= (6.6 \times 10^{-34})^2 \\ &= 4.390 \times 10^{-67} \end{aligned}$$

$$q_m = \left( \frac{6.28 \times 1.29 \times 10^{-25}\text{ kg} \times 1.38 \times 10^{-23}\text{ J K}^{-1} \times 298.15}{6.6 \times 10^{-34}} \right)^{3/2} \text{ m}^3$$

$$q_m = \left( \frac{3.35 \times 10^{-45}}{6.6 \times 10^{-34}} \right)^{3/2} 1.0\text{ m}^3$$

$$q_m \approx 6.68 \times 10^{32}$$

\* The quantity  $\left(\frac{n}{2\pi mkT}\right)^{1/2}$  is called thermal wavelength ( $\lambda$ )  $\lambda_T = \frac{V}{N^3}$

The condition for the applicability of Boltzmann statistic is that the thermal wavelength must be small compared to the mean distance between molecules.

### # Ensemble:-

An ensemble of system is a collection of various microscopic states of the system that correspond to the single macroscopic state of the system whose properties we are investigating. Depending upon the thermodynamic environment of the system we can create various representative ensembles. In commonly encounter ensembles are -

(1) Microcanonical ensemble:- In microcanonical ensemble, no. of moles ( $N$ ), volume ( $V$ ) and energy ( $E$ ) are kept constant. example is an isolated system.

(2) Canonical ensemble:- In this ensemble, the no. of moles ( $N$ ), volume ( $V$ ) and Temperature ( $T$ ) are kept constant. example is an closed isothermal system.

(3) Grand canonical ensemble:- In this grand canonical ensemble, the chemical potential ( $\mu$ ), volume ( $V$ ) and Temp<sup>r</sup> ( $T$ ) are kept constant. example is an open isothermal system.

(4) Isothermal-isobaric ensemble :- Here no. of moles ( $N$ ), pressure ( $P$ ) and Temp $^{\circ}$  ( $T$ ) are kept constant. example is closed system.

Q:- What do you mean by an ensemble. Describe the various type of ensembles.

Q:- calculate the molar residual entropy of a crystal in which molecule can adopt six orientations of equal energy at  $0K$ .

$$R = N_A \cdot k_B$$

Ans:-  $S = k_B \ln W$

$$= 1.38 \times 10^{-23} \text{ J K}^{-1} \ln 6 \Rightarrow k_B = \frac{R}{N_A}$$

$$= 1.38 \times 10^{-23} \times 1.79$$

$$= 2.47 \times 10^{-23} \text{ J K}^{-1}$$

$$S = k_B \ln W$$

$$= R \ln W = 8.314 \times 10^{-23} \text{ J K}^{-1}$$

## # Rotational Partition Function :-

Rotational energy for diatomic molecules in  $J^{\text{th}}$  rotational level is given by

$$E_J = \frac{J(J+1)\hbar^2}{8\pi^2 I}$$

Where  $J^{\text{th}}$  is the rotational quantum no.

$I$  = moment of Inertia

The degeneracy of  $J^{\text{th}}$  rotational level will be  $2J+1$  and is equal to the rotational statistical weight factor ( $\Omega_J$ )

The rotational partition function for a diatomic molecules will be -

$$\Omega_R = \sum \Omega_J e^{-E_J/kT}$$

$$\Omega_R = \sum (2J+1) e^{-\frac{J(J+1)\hbar^2}{8\pi^2 I kT}}$$

After solving these equation we will get -

$$\Omega_R = \frac{8\pi^2 I kT}{\hbar^2} = \frac{T}{\Theta_R}$$

Where  $\Theta_R$  is the rotational temp.

These eqn is for heteronuclear diatomic molecules like  $\text{NO}$ ,  $\text{HCl}$  etc.

For Homonuclear diatomic molecules the rotational partition function is written as -

$$\Omega_R = \frac{8\pi^2 I kT}{G \hbar^2} \quad \text{or} \quad \Omega_R = \frac{8\pi^2 I kT}{2 \hbar^2}$$

Where  $G$  is called the symmetry no.

$G=2$  for homonuclear diatomic molecule.

For a non-linear polyatomic molecule

$$\Omega_r = \frac{8\pi^2 (ABC)^{1/2} (kT)^{1/2}}{6\pi^3}$$

Where ABC are moment of Inertia about principle axis.

Q:- What is the characteristic rotational temp for H-gas? Calculate the molecular rotational partition function at 3000 K? Given the moment of Inertia is  $4.6 \times 10^{-48} \text{ kg m}^2$ .

$$H = 6.62 \times 10^{-34} \text{ Js}^{-1}$$

$$\text{Boltzmann constant } (k) = 1.38 \times 10^{-23} \text{ J K}^{-1}$$

Ans:- 1st part For rotational temp of H-gas

$$\Omega_r = \frac{8\pi^2 I k T}{6\pi^3}$$

$$= \frac{8 \times (3.14)^2 \times 4.6 \times 10^{-48} \times 1.38 \times 10^{-23} \times 3000}{2 \times 6.62 \times 10^{-34} \times 6.626 \times 10^{-34}}$$

$$= \frac{8 \times 9.86 \times 4.6 \times 10^{-48} \times 4.14 \times 10^{-20}}{8.78 \times 10^{-67}}$$

$$= \frac{1.50 \times 10^{-65}}{8.78 \times 10^{-67}} = \frac{1.50 \times 10^{-65+67}}{8.78}$$

$$= \frac{1.50 \times 10^2}{8.78} = \frac{150}{8.78} = 17.084 \approx 17.1$$

$$\Omega_r = \frac{\hbar^3}{8\pi^2 I k}$$

$$= \frac{(6.626 \times 10^{-34})^3}{8 \times (3.14)^2 \times 4.6 \times 10^{-48} \times 1.38 \times 10^{-23}}$$

$$= \frac{4.390387 \times 10^{-67}}{78.956 \times 6.384 \times 10^{-71}} = \frac{4.3903876 \times 10^{-67}}{5.012 \times 10^{-69}}$$

$$= 87.6 \text{ K} = 87.6 \text{ K} \#$$

## # Vibrational partition function :-

The partition function for vibrational energy of a diatomic molecule is represented as  $\Omega_v = \sum g_v e^{-E_v/kT}$  where,  $g_v$  = the statistical wt. factor for vibration and vibrational energy is given as,  $E_v = (v + \frac{1}{2}) \hbar \nu_0$ . Where,  $v$  is the rotational quantum number with values  $0, 1, 2, \dots, \infty$ .

$\nu_0$  is the fundamental frequency of vibration. Since  $g_v$  is unity for each energy level we may express as  $\Omega_v = \sum e^{-E_v/kT}$

or  $\Omega_v = \sum e^{-(v + \frac{1}{2}) \hbar \nu_0 / kT}$

After solving this equation we get,

$$\Omega_v = \frac{1}{1 - e^{-\hbar \nu_0 / kT}}$$

In general, vibrational partition function,

$$\Omega_v = \frac{1}{G \Omega_v} \quad \Omega_v = \frac{\hbar \nu_0}{k}$$

## # Elect

The electronic partition function can be expressed as

$$\Omega_{el} = \sum g_{el} e^{-E_{el}/kT}$$

Where  $E_{el}$  = electronic energy of the molecule

$$g_{el}$$
 = electronic statistical wt. factor

In general,  $\Omega_{el} = 2J + 1$  where  $J$  is the total angular momentum.

$$\therefore \Omega_{el} = \sum (2j+1) e^{-E_{el}/kT}$$

The value of electronic partition function may exceed unity because of degeneracy. for example oxygen has two unpaired  $e^-$  in the ground state and it is triply(3)degenerate. Hence electronic partition function can be represented as -

$$\Omega_{el} = \sum 3 e^{-E_0/kT} = 3$$

For atoms and molecule with one unpaired electron in the ground state will be doubly degenerate ( $\Omega_{el} = 2$ )

$$\Omega_{el} = \sum 2 e^{-E_0/kT} = 2$$

Q The ground state term symbol of the electronic partition function of cl atom is  $2p_{3/2}$ . calculate the electronic partition function if it is assumed that energies of first and excited state are very large.

Ans:-  $\Omega_{el} = \sum (2j+1) e^{-E_0/kT}$

$$= 2 \cdot \frac{3}{2} + 1$$
$$= 4$$

B If energy of the first excited state of cl is 0.11 calculate the contribution to the partition function at 1000 K. The term symbol for cl atom in the excited state  $2p_1, 2p_{1/2}$ .

Ans:-

$$\begin{aligned} g_{el} &= \sum (2j+1) e^{-\epsilon_{el}/kT} \\ &\Rightarrow \sum (2 \cdot \frac{1}{2} + 1) e^{-\epsilon_{el}/kT} \\ g_{el} &= \sum g_{el} e^{-\epsilon_{el}/kT} \\ &= g_0 e^{-\epsilon_0/kT} + g_1 e^{-\epsilon_1/kT} \\ &= 4 + 2 \cdot e^{-0.11 \times 1.6 \times 10^{-19} / 1.98 \times 10^{-23} \times 1000k} \\ &= 4 + 2 \cdot e^{-0.128 \times 10^{-19} / 1.380 \times 10^{-20}} \\ &= 4 + 2 \cdot e^{-14.34} \\ &= 4 + 2 \times 0.24 \\ &= 4 + 0.48 = 4.48 \text{ k.s}^{-1} \end{aligned}$$

Q:- ② For Hydrogen gas at 3000K, calculate the vibrational temp<sup>r</sup> and the vibrational partition func<sup>n</sup>. Given, the fundamental vibrational frequency of Hydrogen molecule is  $4405.3 \text{ cm}^{-1}$ .

## Non-Equilibrium Thermodynamics

OR  
Irreversible thermodynamics.

Flux  $\rightarrow$  current

Force  $\rightarrow$  P.D

phenomenological equations:-

The irreversible thermodynamics or irreversible processes involve the transport of one or more of the quantities such as heat, mass, momentum and electric charges. In all these cases, the quantity called flux is transported as result of a driving force which is derived from the gradient of some physical property of the system. Thus driving force for a heat flux is the temp<sup>r</sup> gradient, for a mass flux is the conc<sup>n</sup> gradient and for an electric current it is the potential difference. In all this cases the magnitude of the flux ( $J$ ) is directly proportional to the driving force ( $x$ ). Thus,

$$J \propto x$$

$$\text{or } J = Lx$$

Where  $L$  is a constant and is called transport coefficient.