Date = 21/08/2015

Statistical Thermodynamic

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

Macrostate : It is specify 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 (W) : The no. of microstates leading to a given macrostate is called thermodynamic probability.

* Ludwig Boltzmann is the father of Statistical Thermodynamic.

$$\boxed{S = K_b \ln W}$$ 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_1, A_2, A_3, A_4	1
Case 2	A_1, A_2, A_3 A_1, A_2, A_4 A_1, A_3, A_4 A_2, A_3, A_4	4
Case 3	A_1A_2, A_1A_3, A_1A_4 A_2A_3, A_2A_4, A_3A_4.	6
Case 4	A_1, A_2, A_3, A_4	4
Case 5	0	1
		16

Date - 22/08/2025

Assembly of Distinguisable Particle

① $\sum_{j=1}^{n} N_j = N$

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

Q. Three distinguisable particles levelled 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: $\sum_{j=1}^{3} N = 3$

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

No. of Cases	No. of Particles in ~~E4~~ 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 ~~Ent~~ in every macrostate, the configuration for Case I, Case II, Case III can be presented as

No. of Cases	0E	1E	2E	3E
Case I	A B B C A C			C A B
Case II		ABC ~~BCA~~ ~~CBA~~ ~~BAC~~ ~~CAB~~ ~~ACB~~		
Case III	A ~~B C~~ A A B B C C	A B C B C A C A B	~~ABC~~ C B C A B A	

The Thermodynamic Probability for Case I, W is 3

" " " " " II, W is 1

" " " " " III, W is 6

" " "

The total microstate of the system is 10.

Date = 28/07/2025

According to M.B Statistics

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

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

$$W = \frac{20!}{1!\,0!\,3!\,5!\,10!\,1!}$$

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

***

$\boxed{0! = 1}$

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

$$= 931,170,240$$

H/W

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.

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

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

$$\Rightarrow 19 \cdot 18 \cdot 17 \cdot 16 \cdot 15 \cdot 14 \cdot 13 \cdot 6 \cdot 5 \cdot 11$$

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

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

highest thermodynamic probability

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

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

Partition Function (q)

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

$g \rightarrow$ degeneracy of the system.

or

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

where $\beta = \frac{1}{KT}$

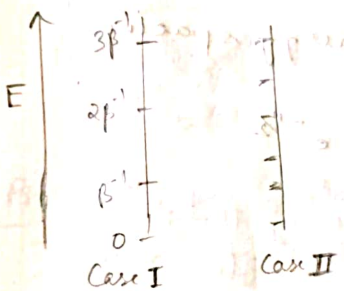
q is a measure of thermally accessible states and represents sum over all terms that describes the probability associated with the variable of interest.

Date - 29/08/2025

Partition Function (q) of a SHO oscillating with energy spacing β^{-1}

For a SHO,

$$q = \sum e^{-\beta E_n} \quad (E_n = nh\nu)$$



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

$n = 0, 1, 2, 3 \ldots\ldots\ldots$

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

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

using this value for the energy spacing, we have

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

$$= e^{-n}$$

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

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

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

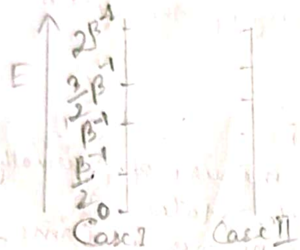
$$= 1 + e^{-1} + e^{-2} + e^{-3} + \ldots\ldots$$

0.362

$$\Rightarrow q = \frac{1}{1 - e^{-1}} \qquad \because \frac{1}{1-x} = 1 + x + x^2 + x^3 \ldots \quad |x| < 1$$

$$= 1.58$$

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



For a SHO,

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

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

$$n = 0, 1, 2, 3 \ldots$$

Now, we will employ oscillator where the energy is

$$h\nu = \frac{\beta^{-1}}{2}$$

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

Using this value for the energy spacing, we have

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

we know,

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

$$= \sum_{n=0}^{\infty} e^{-n/2}$$

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

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

$$\Rightarrow q = \frac{1}{1 - e^{-1/2}}$$

$$= \frac{1}{1 - 0.606}$$

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

$$= 2.538$$

$$= 2.54$$

The Probability of occupying a given energy level is given by $\boxed{P_n = \frac{e^{-\beta \varepsilon_n}}{q}}$ $n \to$ no. of state

Probability of a Harmonic Oscillator occupying the first three energy levels, $n = 0, 1, 2$ with energy spacing β^{-1}

$n = 0$

$$P_0 = \frac{e^{-\beta \varepsilon_0}}{1.58} = \frac{e^{-0}}{1.58} = \frac{1}{1.58} = 0.632$$

$n = 1$

$$P_1 = \frac{e^{-1}}{1.58} = \frac{0.367}{1.58} = 0.232$$

$n = 2$

$$P_2 = \frac{e^{-2}}{1.58} = \frac{0.135}{1.58} = 0.085$$

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

$n = 0$

$$P_0 = \frac{e^{-0}}{2.54} = \frac{1}{2.54} = 0.393$$

$n = 1$

$$P_1 = \frac{e^{-1/2}}{2.54} = \frac{0.606}{2.54} = 0.238$$

$n = 2$

$$P_2 = \frac{e^{-1}}{2.54} = \frac{0.367}{2.54} = 0.144$$

Molecular Partition Function

we know, partition function, $q = \Sigma g_i e^{-\beta \varepsilon_i}$

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 prodt of partition function corresponding to each degrees of freedom. Let ϵ_{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.

$g_{total} = g_{tr} \cdot g_{Rot} \cdot g_{vib} \cdot g_{elec}$

$$\epsilon_{Total} = \epsilon_{Translational} + \epsilon_{Rotational} + \epsilon_{vibrational} + \epsilon_{electronic} \rightarrow (1)$$

$$\therefore q_{Total} = \sum g_{Total} \cdot e^{-\beta E_{Total}}$$

$$= \sum (g_{Trans} \cdot g_{Rotat.} \cdot g_{vib} \cdot g_{elect}) \cdot e^{-\beta(E_{Trans} + E_{Rot} + E_{vib} + E_{elec})}$$

$$= \sum g_{Trans}\, e^{-\beta E_{trans}} \cdot \sum g_{Rot}\, e^{-\beta E_{Rot}} \cdot \sum g_{vib}\, e^{-\beta E_{vib}} \cdot \sum g_{elec}\, e^{-\beta E_{elec}}$$

$$q_{Total} = q_{tr} \cdot q_{Rot} \cdot q_{vib} \cdot q_{elec}$$

$$q_T = q_{tr} \cdot q_{Rot} \cdot q_{vib} \cdot q_{elect}.$$

ie the total partition funct^n is the prdt of partition funct^n for each molecular energetic degrees of freedom.

Q. Show that molecular partition function for a polyatomic molecule is the prdt of partition function of ~~or~~ every energetic degrees of freedom.

$\rightarrow$

Q. Using expression for partition funct^n, q when $T \rightarrow 0$ K $T \rightarrow \infty$.

$$q = g_i e^{-E_i/K0} \qquad q = g_i e^{-E_i/K\infty}$$

$$= \infty \qquad = g_i$$

8. For a system the ground state is doubly degenerate. Calculate the partition funcⁿ when $T \to \infty$. (4)M

$$q = \sum g_i e^{-\epsilon_i/KT}$$

$$= \sum 2 g_i e^{-\epsilon_i/KT}$$

$$= \sum 2 g_i$$

$$= 2$$

Classical Particle	Quantum Particle
• Macroparticles	• Microparticle
• Distinguisable	• Indistinguisable
• Maxwell Boltzmann Statistics (MB)	• Bose-Einstein & Fermi-Dirac Statistics. Bosons & Fermions.

Bosons	Fermions
• quantum particles	• Quantum particles.
• Indistinguisable	• Indistinguisable particles.
• Have integral spin.	• Have half-integral spin.
• Does not obey Pauli Exclusion Principle	• It obeys Pauli Exclusion principle.

Bosons.	Fermions.
(i) quantum particle	(i) quantum particle.
(ii) Indistinguishable particle.	(ii) Indistinguishable particle.
(iii) Have integral spins. $-2, -1, 0, +1, +2$ ----	(iii) Have Half spins. $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ ---
(iv) Does not obey pauli Exclusion principle.	(iv) obeys pauli Exclusion principle.

Spin Multiplicity! 08/09/25

$2S+1$

$S = \frac{1}{2}$. $2 \times \frac{1}{2} + 1 = 2$ doublet

$S = 1$ $2 \times 1 + 1 = 3$ Triplet

$S = 0$ $2 \cdot 0 + 1 = 1$ Singlet

${}^{2S+1}P_J$

$2S+1 = 2$

$2S+1 = 2 \times \frac{3}{2} + 1 = 4$

Q. The ground state Spectroscopy term for chlorine is ${}^2P_{3/2}$. If Degeneracy is 4
(a) 4 (c) 3/2
(b) 2 (d) 7/2

Q. The correct Entropy for 6 identical particle with their occupication Number 0, 1, 2, 3 is
(a) $K_b \ln 8$ (b) $K_b \ln 12$
(c) $K_b \ln 60$ (d) $K_b \ln 720$

$\boxed{S = K_b \ln W}$ $W = \frac{6!}{0!\,1!\,2!\,3!}$ $= \frac{6 \times 5 \times 4 \times 3 \times 2 \times 1}{0 \times 1 \times 2 \times 3} = 4 \times 10 =$ $[6, 5, 4, 3, 2, 1]$

$= \frac{6 \times 5 \times 4 \times 3}{1 \times 2 \times 3}$

$= 60$

*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.

${}^3P_2$

${}^{2S+1}P_2$

$\boxed{2S+1 = 3}$

→ ${}^{2S+1}P_J$

→ $2S+1$ = Spin degeneracy = Spin Multiplicity.

→ $2J+1$ = Thermodynamic probability microstate (W).

$W = 2J+1$

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

$\boxed{S = K_b \ln W}$

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high probability state.
* high disorder state = $F_q b^m$

Macrostate:
* $W = g_j^{n_j}$
$= 2^4$
$= 16$

10/10/25

Spin degeneracy & Ground state degeneracy of metal atom

The spin degeneracy for a metal atom refers to the different possible orientation of the electron spins within a specific orbital. While ground state Degeneracy refers to the number of distinct quantum state that share the lowest Energy level.

Translational partition function:- (q_{trans})

$$q = \sum e^{-\beta E_i} = \sum e^{-E_i/KT} \longrightarrow (i)$$

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

or $$E_{tr} = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right] \longrightarrow (ii)$$

where, its of their quantum Number here n_x, n_y, n_z vary from 1 to α, Subtituting these value of translational Energy in the Eq^n of partition function.

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

where, the $\sum\sum\sum$ is taken over all the integral values of n_x, n_y, n_z from one to α.
The motion of the particle in the 3 Direction i,e ~~x, y, z~~ being independent, we can replace the $\sum$ as a product of $3\sum$.

$$(iii) \Rightarrow \sum_{n=1} \exp\left(\frac{-h^2 n_x^2}{8ma^2KT}\right) \sum_{n=1} \exp\left(\frac{-n_y^2 h^2}{8mb^2KT}\right) \sum_{n=1} \exp\left(\frac{-n_z^2 h^2}{8mc^2KT}\right) \longrightarrow (iv)$$

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It is well known that the spacing between the Energy level of the particle in the 3D box is very small, compare with the thermal Energy KT. Hence, the Σ in Eq^n (iv) can be replaced by integration and we get

$$(iv) \Rightarrow \int_0^\alpha \exp\left[-\frac{n_x^2 h^2}{8ma^2KT}\right]dn_x \int_0^\alpha \exp\left[-\frac{n_y^2 h^2}{8mb^2KT}\right]dn_y \int_0^\alpha \exp\left[-\frac{n_z^2 h^2}{8mc^2KT}\right]dn_z \longrightarrow (v)$$

Again,

we know,

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

$$(v) \Rightarrow \frac{1}{2}\left(\frac{8\pi ma^2KT}{h^2}\right)^{1/2} \frac{1}{2}\left(\frac{8\pi mb^2KT}{h^2}\right)^{1/2} \frac{1}{2}\left(\frac{8\pi mc^2KT}{h^2}\right)^{1/2}$$

$$\Rightarrow \frac{1}{2}\left(\frac{8\pi ma^2KT}{h^2}\right)^{1/2} \frac{1}{2}\left(\frac{8\pi mb^2KT}{h^2}\right)^{1/2} \frac{1}{2}\left(\frac{8\pi mc^2KT}{h^2}\right)^{1/2}$$

$$q_{tr} = \left(\frac{2\pi ma^2KT}{h^2}\right)^{1/2}\left(\frac{2\pi mb^2KT}{h^2}\right)^{1/2}\left(\frac{2\pi mc^2KT}{h^2}\right)^{1/2}$$

or,

$$q_{tr} = \left(\frac{2\pi mKT}{h^2}\right)^{3/2} abc$$

or,

$$\boxed{q_{tr} = \left(\frac{2\pi mKT}{h^2}\right)^{3/2} V}$$

where, $V \rightarrow$ vol^m of the box in which the molecule moves.

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*Q. calculate the translational partition for benzene in a volm of 1 m^3 at 25°C.

Ans

$$q_{tr} = \left(\frac{2\pi m K T}{h^2}\right)^{3/2} V$$

mass of 1 benzene molecule,

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

$$= \frac{0.07811 \text{ Kg/mol}}{6.02214076 \times 10^{23} \text{ mol}^{-1}}$$

$$= 1.29 \times 10^{-25} \text{ Kg}.$$

$$= \left(\frac{2\pi\, 78 \times 1.3 \times 10^{-23} \text{ K}}{6.6 \times 10^{-34} \text{ JS}}\right)^{3/2} 1 m^3$$

$$= \left(\frac{2\pi \times 78.11 \text{ gmol}^{-1} \times 1.38 \times 10^{-23} \text{ JK}^{-1} \times 25°C}{6.6 \times 10^{-34} \text{ JS}}\right)$$

m : Kg.

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

h : JS = Kg $m^2 s^{-1}$

$$\left(\frac{2\pi m K T}{h^2}\right)^{3/2} \sim (m^{-2})^{3/2} = m^{-3}$$

∴ partition f^n are dimensionless

Q1) Define partition function?

Q2) obtain an expression for translational partition function?

Q3) Show that the molecular partition function is a product of partition of translational, rotational, vibrational and electronic partition f^n.

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Q. calculate the translational partition f^n for benzene in a vol^m of $1m^3$ at $25°C$.

Ans Given,

$T = 25°C = 298.15\,K$

$V = 1.0\,m^3$

Benzene molar mass.

$M = 78.11\,g\,mol^{-1} = 0.07811\,Kg\,mol^{-1}$

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

$h = 6.6 \times 10^{-34}\,JS$

$N_A = 6.022 \times 10^{23}\,mol^{-1}$ $\qquad 2\pi \approx 6.28$

Mass of 1 benenene molecule,

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

$$\left[h^2 = (6.6 \times 10^{-34})^2 = 4.390 \times 10^{-67}\right]$$

$$q_{tr} = \left(\frac{2\pi m K T}{h^2}\right)^{3/2} V$$

$$q_{tr} = \left(\frac{6.28 \times 1.29 \times 10^{-25}\,Kg \times 1.38 \times 10^{-23}\,JK^{-1} \times 298.15}{6.6 \times 10^{-34}}\right)^{3/2} 1.0\,m^3$$

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

$$q_{tr} \approx 6.68 \times 10^{32}$$
4

8) *) The quantity $\left(\frac{h^2}{2\pi m k T}\right)^{1/2}$ is called thermal wave-length (Λ) $q_{tr} = \frac{V}{\Lambda^3}$

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) Cannonical 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 cannonical :- In this grand cannonical ensemble, the chemical potential (μ), Volume (V) and Tempr (T) are kept constant. example is an open isothermal system.

(4) Isothermal isobaric ensemble :- Here no. of moles (N), pressure (P) and Tempr (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.

$$\boxed{R = N_A \cdot k_B}$$

Ans:- $S = k_B \ln W$

$= 1.38 \times 10^{-23}\ JK^{-1} \ln 6 \quad \Rightarrow k_B = \frac{R}{N_A}$

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

$= 2.4702 \times 10^{-23}\ JK^{-1}$

$S = k_B \ln W$

$= R \ln W = 8.314 \times 10$