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STATISTICAL MECHANICS

- In physics, statistical mechanics is a mathematical framework that applies **statistical methods** and probability theory to large assemblies of microscopic entities.
- It does not assume or postulate any natural laws, but explains the macroscopic behavior of nature from the behavior of such ensembles.
- Sometimes called statistical physics or **statistical thermodynamics**, its applications include many problems in the fields of physics, biology, chemistry, and neuroscience.
- Its main purpose is to clarify the properties of matter in aggregate, in terms of physical laws governing atomic motion
- **Statistical mechanics** arose out of the development of classical thermodynamics, a field for which it was successful in explaining macroscopic physical properties—such as temperature, pressure, and heat capacity—in terms of microscopic parameters that fluctuate about average values and are characterized by probability distributions.
- The founding of the field of statistical mechanics is generally credited to three physicists:
- **Ludwig Boltzmann**, who developed the fundamental interpretation of entropy in terms of a collection of microstates



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- **James Clerk Maxwell**, who developed models of probability distribution of such states
- **Josiah Willard Gibbs**, who coined the name of the field in 1884
- While classical thermodynamics is primarily concerned with thermodynamic equilibrium, statistical mechanics has been applied in non-equilibrium statistical mechanics to the issues of microscopically modeling the speed of irreversible processes that are driven by imbalances. Examples of such processes include chemical reactions and flows of particles and heat. The fluctuation–dissipation theorem is the basic knowledge obtained from applying non-equilibrium statistical mechanics to study the simplest non-equilibrium situation of a steady state current flow in a system of many particles.

- (i) Classical Statics - Maxwell – Boltzmann statics. – molecules
- (ii) Quantum statistics - Fermi – Dirac statistics
- $\frac{1}{2}$ spin – Elementary particle
- Bose Einstein statics – 0.spin (or) Integral spin
- ↓
- photons

Phase space (T space) :

The combined Position $\Sigma(x, y, z)$ and momentum (P_x, P_y, P_z) space is called as phase space .

A point in the space represents the Position and momentum of the particle at some particular instant .

Constraints :



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The restriction imposed by physical laws on the distribution of molecules among the cells in the Phase space are called the constraints of the system

Total no of molecules N

n_1 molecules in cell 1

n_2 molecules in cell 2

n_r molecules in cell r

The constraints required $\sum_{i=1}^r n_i = N$

Accessible states the permitted number of microstates under the constraints imposed upon the system are called accessible states.

Total energy be E

Suppose n_1 molecules have energy E_1

Suppose n_2 molecules have energy E_2

We have the constraints $\sum_{i=1}^r n_i \varepsilon_i = E$

Ensembles:

An ensemble is defined as a collection of large number of assemblies which are essentially independent of one another but which have been made macroscopically as identical as possible.

Micro canonical ensemble:

It is a collection of essentially independent assemblies having the same energy E volume- V and number N of the system all the system are of the same type.

1. The locus of all the phase points having equal energies in phase space is called an energy surface (or) Ergodic surface

E, V, N	E, V, N	E, V, N
E, V, N	E, V, N	E, V, N
E, V, N	E, V, N	E, V, N

2. Walls are Rigid, impermeable, well insulated walls
3. No exchange of energy (or) particle take place

Canonical ensemble:



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1. It is a collection of essentially independent assemblies having the same temperature $-T$, Volume- V , and number of identical particles N

T,V,N	T,V,N	T,V,N
T,V,N	T,V,N	T,V,N
T,V,N	T,V,N	T,V,N

[System contacted with a heat reservoir]

2. Walls are Rigid, impermeable, diathermic walls
3. Here system can exchange energy but not particles

Grand canonical ensemble:

1. It is a collection of essentially independent assemblies having the same temperature- T , Volume- V , and chemical potential μ

T,V, μ	T,V, μ	T,V, μ
T,V, μ	T,V, μ	T,V, μ
T,V, μ	T,V, μ	T,V, μ

2. Walls are permeable, diathermic walls
3. Exchange of energy as well as of particles takes place with the heat reservoir

Lioville's theorem:

The theorem consists of two parts

i) The principle of conservation of density in phase space:-

This part states the conservation of density in phase space (ie) the rate of change of density of phase point in phase space is zero $\frac{\partial \rho}{\partial t} = 0$

ii) The principle of conservation of extension of phase –space:-



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$$\frac{d}{dt} (\partial \Gamma) = 0$$

↓

Symbol for volume extension

The volume at the disposal of a particular number of phase points is conserved through out the phase space

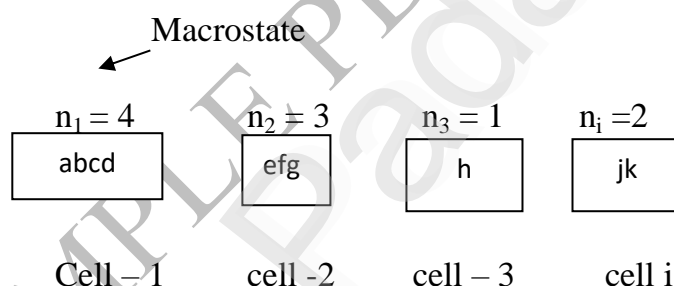
Microstates:

Each arrangement of specified system (or) molecules with their representative points in particular cell is called microstate

(or)

A microstate of an ensemble may be defined by the specification of the individual partition of phase point in each, system (or) molecule of the ensemble.

Macro states: A macrostate of the ensemble may be defined by the specification of phase point in each cell (I,e) by specifying the numbers only and over looking the identities of the system (or) molecule.



❖ There may be different microstates corresponding to the same microstate .

Most probable distribution:

M.P. distribution is a number of particles in each cell is portioned to the size of the cell.

$$g_t = \frac{n_t}{n}$$

n_t – number of particles in cell t



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n – Total number of particles

g_t – The probability of any one particle in cell t

Pivilion of phare space in to cells:

Phase space is divided in to 6 dimentioned cells whose sides are dx, dy, dz , and dp_x, dp_y, dp_z . Such cells are called phase cells.

Number of phase cells in the volume element is

$$= \frac{\delta q_1, \delta q_2, \dots, \delta q_f, \delta p_1, \delta p_2, \delta p_f}{h^f}$$

h = is any arbitrary constant

$h = \delta q_i \delta p_i$

h_f – size of each cell

1) The assemblies in general consist of three types of particles

- ❖ Identical but distinguishable particles
- ❖ Obey Maxwell Boltzmann law
- ❖ Molecules of a gas are the particles of this kind

2) Identical but indistinguishable particles of zero (or) integral spin.

- ❖ Obey Bose Einstein statistics
- ❖ Photons are the particles of this kind
- ❖ Helium at low temp obey Bose Einstein statistics

3) Identical but indistinguishable particles of spin $\frac{1}{2}$

- ❖ Obey Pauli's exclusion principle and Fermi – Dirac statistics
- ❖ Fermions are the particles of this kind ex & electron, Protons, neutrons

Maxwell Boltzmann statistics:

- ❖ Maxwell is used to determine equilibrium state of the system, means, which is most probable



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- ❖ When the gas is in equilibrium the probability is maximum.
- ❖ This law tell us how a fixed amount of energy is distributed among various member of an assembly identical particle.

Consider a system having n distinguishable particles. Let these particles are divided into quantum groups such that n_1, n_2, \dots, n_i particles lie in groups having energies $E_1, E_2, E_3, \dots, E_i$ respectively.

Let g_i be the statistical weight of i^{th} quantum group.

The conditions in Maxwell – Boltzmann statistics are

- 1) Particles are distinguishable (i.e.) there are no symmetry restriction.
- 2) Each eigen state of i^{th} group may contain $0, 1, 2, \dots, n_i$ particles
- 3) The total no of particles in the entire system is always constant.

$$(i.e.) n = n_1 + n_2 + \dots + n_i = \sum n_i = \text{constant}$$

- 4) The sum of energies of all the particles in different quantum groups taken together constitute the total energy of the system

Number of particles =

$$N_i = \frac{g_i}{e^{\beta E_i}}$$

β, B are constant. In terms of temp

$$\beta = \frac{1}{KT} \quad e^{-\beta E_i} = \frac{N_i}{Z}$$

$$N_i = g_i \frac{N}{Z} e^{-\frac{E_i}{KT}}$$

Max well's law of Distribution of velocities :

$$dx = n \left(\frac{m}{2\pi KT} \right)^{3/2} e^{-m(x^2 + y^2 + z^2)/2KT} dx dy dz$$

Which is the form of the Maxwell distribution law for the no of level having components of velocity in the range \dot{x} to $\dot{x} + d\dot{x}$, \dot{y} to $\dot{y} + d\dot{y}$ and \dot{z} to $\dot{z} + d\dot{z}$



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$$dn = \frac{2\pi n}{(\pi KT)^{3/2}} e^{-\epsilon/KT} \epsilon^{1/2} d\epsilon$$

gives the number of molecules with Kinetic energy (translational) lying between ϵ and $\epsilon+d\epsilon$ in any direction. This is known as Maxwell – Boltzmann distribution law of energies.

In M.B statics of perfect g the average K.E per molecules is $3/2 KT$.

Mean speed the mean speed \bar{c} is the speed of all particles divided by the total number of particles .

$$\bar{c} = \sqrt{\frac{8KT}{\pi m}} \quad \leftarrow \text{average (or) mean speed}$$

$$\left(\frac{8}{\pi}\right)^{1/2} = 1.59 \quad \bar{c} = \sqrt{\frac{8KT}{\pi m}}$$

$$\bar{c} = 1.59 \frac{kT}{m}$$

Mean square speed

$$\overline{(c)^2} = \frac{3KT}{m}$$

Root mean square speed:

$$\text{c.r.m.s} = \sqrt{\overline{(c)^2}} = \sqrt{\frac{3KT}{m}} = 1.73 \sqrt{\frac{KT}{m}}$$

Most probable speed:



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For the most probable speed the probability of the speed must be maximum.

$$C_{mp} = c \sqrt{\frac{2KT}{m}}$$

R.M.V of the molecule is define by the equ $C^2 = \frac{1}{N} \int_0^{\infty} c^2 dN$

Mean free path

The path covered by a molecule between any two consecutive collision is a straight line and is called mean free path.

Number of collision occur the path appears zig zag.

During N collision the distance travelled in s

According to Baltzman $\lambda = \frac{3}{4\pi d^2 n}$

Mean free path $\lambda = \frac{S}{N}$

According to Maxwell $= \frac{1}{\sqrt{2}\pi d^2 n}$

Bose – Einstein Statistics:

The particles are indistinguishable. So, the interchange of two particles between two energy states will not produce any new state.

The condition of B.E statistics are

- 1) The particles are indistinguishable from each other. So, that there is no distribution between the different ways in which n_i particles can be chosen.
- 2) Each cell (or) subshell of i th quantum state may contain 0,1,2..... N_i identical particles.
- 3) The sum of energies of all the particles in the different – quantum groups taken together constitutes the total energy of the system.



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Number of particles $n_i = e^{\alpha + \beta E_i}$

This represents the most probable distribution of the elements among various energy levels for a system obeying Bose – Einstein statistics Fermi Dirac statistics .

In M-B statistics (or) B.E statistics , there is no restriction on the particles to be present in any energy state But in of Fermi – Dirac, Statistics, applicable to particle like electrons and obeying Pauli exclusion principle (no two electrons in an atom have same energy state) . only one particle can occupy only a single energy state.

Thus in Fermi – Dirac statistics the conditions are

- (1) The particles are indistinguishable from each other. (ie) there is no restriction between different ways in which n_i Particles are cho
- (2) Each sublevel (or) well may contain 0 (or) one particle. Obviously g_i must be greater than (or) equal to n_i
- (3) The sum of energies of all the particles in the different quantum groups taken together constitute the, total energy of the system.

$$n_i = \frac{g_i}{e^{\alpha + \beta E_i} + 1}$$

$$\alpha = -E_f / KT \quad \beta = \frac{1}{KT}$$

$$n_i = \frac{g_i}{e^{-(E_f - E_i) / KT} + 1}$$

Fermi energy:

At absolute zero of temp the maximum K.E that a free electron can have is called Fermi energy.

Comparison of the statistics

S.No	Max well Boltzmann	Fermi – Dirac	Bose – Einstein
1	Particles are distinguishable and only particles are	Particles are indistinguishable and quantum states are	Particles are indistinguishable and quantum states



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	taken in to consideration	taken into consideration	are taken in to consideration
2	There is no restriction on the number of particles in a given state	Only one particle may be in a given quantum state	No restriction on the number of particles in a given quantum states
3	Applicable to ideal gas molecule	Applicable to electron and elementary long particle	Applicable to photons and symmetrical particles
4	Volume in six dimensional space is not known	In Phase space is known h^3	In phase space is known h^3
5	Internal energy of ideal gas molecules at absolute zero is taken as zero	Even at absolute zero, the energy is not zero	The energy at absolute zero is taken as zero
6	-	At high temp Fermi distribution approaches M-B distribution	At high temp B.E distribution approaches M.B distribution
7	$n_i = \frac{g_i}{e^{\alpha + \beta E_i}}$	$n_i = \frac{g_i}{e^{\alpha + \beta E_i} + 1}$	$n_i = \frac{g_i}{e^{\alpha + \beta E_i} - 1}$

Black body Radiation:

The most important application of Bose Einstein statistics to electron magnetic radiation in thermal equilibrium, called “Black body radiation”.

In quantum theory, radiation energy occurs in energy packets (or) photon (or) light quantum of energy $h\nu$ and momentum $\frac{h\nu}{c}$. Photons have zero rest mass and a spin quantum number of 1, they obey Bose – Einstein statistics.

Consider a black body radiation chamber of volume containing radiation in equilibrium with the walls at temp T.

Total energy density is

$$\frac{u}{v} = \frac{8\pi h}{c^3} \left(\frac{KT}{h} \right)^4 \frac{\pi}{15}$$



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$$\frac{u}{v} = bT^4 - \text{Stefan - Boltzmann} + 2 \text{ mann law}$$

$$\text{Where } b = \frac{8\pi K^4 \pi^4}{15c^3 h^3}$$

Wein – constructed black body in the form of cylinder. Lummer and kurlban bolometer is used to measure the intensity of heat .

Electron Gas

- ❖ Electrons in the metal are free to move exactly like the particle of gas
- ❖ Free electron gas in a solid obey Fermi – Dirac statistics.
- ❖ A metal can be considered to be compiled of a system of fixed positive nuclei and a number of mobile electrons returned to as the electron gas.

$$\text{Fermi energy } E_f = \frac{h^2}{2m} \left(\frac{3n}{8\pi v} \right)^{2/3}$$

$$\text{Fermi Temp } T_f = \left(\frac{E_f}{K} \right)$$

$$\text{Zero point energy} = \frac{3}{5} n \varepsilon_f$$

- ❖ All the levels below E_f are completely filled
- ❖ All the above E_f are completely empty
- ❖ At $T = \text{levwl OK}$ all electrons have energies less than (or) equal to Fermi energy

$$\text{❖ Degeneracy factor of electron gas} = \frac{1}{D} = \frac{h^2}{2 \times 9.1 \times 10^{-28} \times KT} \left(\frac{3n}{8\pi v} \right)^{2/3} =$$

$$\frac{10^5}{1.5T}$$

For electron gas, the classical statistics is not valid, and can be applied only at temperatures of the order of 10^5K .

At low temp, it is necessary to use F-D statistics to study electron gas in the metals.

$$\text{Pressure of electron gas } P_o = \frac{2}{5} \frac{n\varepsilon_f}{v}$$



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$$= \frac{nh^2}{20mv} \left(\frac{3n}{\pi v} \right)^{2/3}$$

Which means at 10^5 atoms normal temperature the pressure of the gas is sufficiently high.

Pauli's theory of par magnetism:

In metals free conduction electrons are present. As each atom is endowed with intrinsic magnetic moment μ , it acts like a elementary magnet. Thus all free electrons acting as elementary magnets, can orient themselves in the direction of an applied magnetic field and make metals highly paramagnetic.

Let us consider an assembly of N free fermions of spin $\frac{h}{2}$ each of which is describe by a single particle Hamiltonian.

$$H = \frac{P^2}{2m} - \vec{\mu} \cdot \vec{B} \quad \text{and the single particle, energy levels}$$

$$E_{is} = \frac{P^2}{2m} - \mu S B \quad \text{Where } S = \pm 1$$

Intensity of magnetization $I = \frac{\text{total magnetic moment}}{\text{Volume}}$

$$= \frac{\mu (\overline{N_+} - \overline{N_-})}{V}$$

$\overline{N_+}$ - average no of molecules spin up to

$\overline{N_-}$ - average no of molecules spin down to

μ - magnetic moment

Thermionic emission:

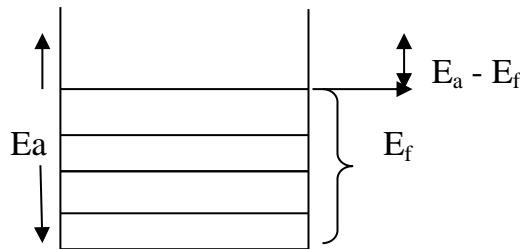
In free electron model of a metal, the zero of the energy is taken at the bottom. At the absolute zero of temp, the electrons will fill $n/2$ lowest energy states up to the energy value ϵ_f



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The minimum amount of energy necessary to remove an electron from the metal is equal to $(E_a - E_f)$ and is defined as the work function ϕ of the metal.

Emission current density as per unit area = $J = AT^2 e^{-e\phi/KT}$

$e\phi$ is called Work function

$$e\phi = E_a - E_f$$

$$A = \frac{4\pi me k^2}{h^3}$$

This equation is called Richardson – Dushman equation of thermionic emission.

As the temp of the filament is doubled, thermionic current increases 4 times.

Gas degeneracy, the deviation from perfect gas behavior exhibited by Bose – Einstein gas is termed as degeneracy.

The gas degeneracy is obviously a function of $= \frac{1}{D}$

$$\frac{1}{D} = \frac{n}{gsZ_t} \text{ Here } Z_t - \text{translation Partition function}$$

Phonon gas

- ❖ Quantum of acoustical energy is commonly referred as phonon
- ❖ Phonon Vibrates with the frequency of 10^4 to 10^{13} cycles per second
- ❖ Low frequency part is acoustic range



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- ❖ High frequency part is infra red range
- ❖ In solid it travels like a short elastic waves, In solid travels with, the velocity of sound
- ❖ In elastic ether medium travels with the velocity of light.
- ❖ Indistinguishable particle
- ❖ More phonons can be created by increasing the temp of the crystal

Momentum

$$p = \frac{h}{\lambda}$$

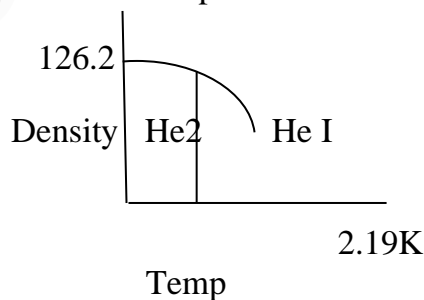
Properties of Liquid Helium (An application of B.E statistic)

Liquefaction of helium

- ❖ Helium was the last gas to be liquefied because of its extremely low critical pressure
 $T_c = -5.25K$
- ❖ Temperature of inversion T_i for Helium is 33K
- ❖ Kamerling Onnes precooled helium to 23K by means of liquid hydrogen boiling under reduced pressure and then liquefied it by subjecting it to J.T expansion.

Properties of liquid helium:

- ❖ Kamerling Onnes found a specific discontinuity in the density of helium at 2.19K
- ❖ The density of liquid helium increases as the temp decreases from 4K to 2.19K



- ❖ The density becomes maximum (146.2 kg/m^3) at 2.19K

Thus liquid helium which is contracting when cooled, suddenly begins to expand below 2.19K

Later Keesom also found another specific discontinuity at 2.19K.

1. He measured the specific heat capacity of helium at different temp.

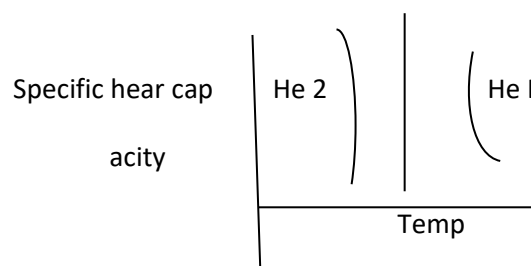


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2. As helium is gradually cooled from 4.2K the specific heat capacity remains constant at first and near 2.19K it increases a little



3. Exactly at 2.19.12 S.P. heat capacity increases suddenly to a new large value. Then it gradually falls as the temperature is reduced from 2.19.12.
4. The graph resembles the Greek letter λ and hence in this temp at which the S.P. heat changes abruptly is called the λ point.
5. The properties of liquid helium above and below λ point are quite different.
6. Liquid helium above 2.19K is called Helium I and it behaves in a normal manner.
7. Liquid helium below 2.19K is called helium II, because of its abnormal properties.

Helium II is called superfluid why?

- ❖ Co-efficient of viscosity of liquid, increases with decrease in temperature.
- ❖ Viscosity of liquid helium decreases with decrease in temp.
- ❖ The viscosity of helium II is almost zero and it can flow rapidly through narrow capillary tube.
- ❖ Hence it is called a super fluid.

Some peculiar properties of Helium II :

❖ Extreme fluidity:

He II has practically zero viscosity and is called super fluid.

❖ High heat conductivity:

He II has an extraordinarily high co-efficient of thermal conductivity. He II is said to be about 800 times more conducting than copper.



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Principle of equi portion of energy:

The law states that the total 12KE of a dynamical system consisting of a large number of particles. In General is equally divided among its all the degrees of freedom.

The average energy associated with each degree of freedom is $\frac{1}{2} KT$.

The Relation between the partition function (z) and thermo dynamic quantities.

Various thermodynamical quantities such as energy E, Helm – holtzs free energy, Entropys 3 and specific heat C_v etc....



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$$\text{Energy } E = RT^2 \frac{\partial}{\partial T} (\log Z)$$

$$= \frac{RT^2}{Z} \left(\frac{\partial z}{\partial T} \right)$$

$$\text{Helum holtz free energy } F = -RT \log z \text{ and } C_v = \left(\frac{\partial E}{\partial T} \right)_v = \frac{\partial}{\partial T} \left[\frac{RT^2}{z} \left(\frac{\partial z}{\partial T} \right) \right]$$

Comparison of Ensembles

S.No	Property	Microcomonical	Canonical	Grand canonical
1	Contact with the environment	Isolated system, (ie) energy and the number of particles of the system are constant E, V, N	System in thermal contact with heat reservoir. (ie) system can exchange energy but not particles	System can exchange both energy and particles $(-2 + nu - E) / KT$ $\frac{(\Omega + nu - E)}{KT}$
2	Probability distribution	$P(E) = \text{constant}$ in range E and $E + dE = 0$. out side this range	$P(E) = Ae^{E/KT}$	$P(n) = e$
3	Fluctuation	None	In energy only	In energy and number of particles
4	Partition function	$\Delta \Gamma$	$Z = \int e^{-BE} d\Gamma$	$Z = \frac{\epsilon}{n} e^{un/-z}$

Some important points:

- ❖ All accessible microstates, corresponding to possible macro states are equally probable.
- ❖ An equilibrium microscopic state is one for which the number of microscopic state is maximum.
- ❖ Stirling's approximation to find $n! \log n! = n \log n - n$
- ❖ The classical partition function z gives the sum of states of the system.
- ❖ The partition function Z is related to the thermo dynamical quantities in the following way.



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$$S = Nk \log z + \frac{3}{2} KT$$

S – entropy

$$NK = R$$

$$S = R \log Z + \frac{E}{T}$$

More points in phase space:

The phase space available to the 3- dimensional harmonic oscillator having energy between E and E + dE, is given by

$$\delta A = 2\pi \sqrt{m/K} \delta E$$

A – Area of the ellipse

A – semi major axis

B - semi minor axis = πab

$$A = 2\pi E \sqrt{m/K}$$

Volume of phase space :

$$\Delta \tau = 4\pi P^2 dp.V$$

P – momentum

V = Volume in ordinary space

Number of phase cells in given energy range of

$$\text{harmonic oscillator} = \frac{\text{Area of phase space}}{\text{Area of phase cell}}$$

$$= \frac{E/v}{h} = \frac{E}{hv}$$

No of phase cells in the given energy range for 3- dimensional free particle.

$$= \frac{4\pi v}{3h^3} (2mE)^{3/2}$$

h^3 = volume of phase cell.

The unit of phase space volume is $\text{Kg}^3 \text{m}^6 \text{s}^{-3}$ (or) $\text{J}^3 \text{S}^3$

Gibbs function:

$$G = F + Pv$$

H- enthalpy

$$G = H - Ts$$

F- Helmholtz free energy

$$G = U - TS + PV$$

s – entropy



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U – Internal energy

Gibbs function – pdv – work

1. Gibbs function has also be called the free energy of a system
2. Gibb's function is also known as thermo dynamical potential
3. Gibb's function is the difference between enthalpy and latent energy
4. Gibb's function is constant in sublimation

Gibbs paradox:

If the particles in the two systems are the same and if for convenience we take

$$V_a = V_b = v \quad n_a = n_b = n.$$

We have to consider 3n particles in a volume 2v.

$$\text{We get } S_{ab} = S_a + S_b + 2nK \log_e 2$$

Which shows that by joining two moles of two different gases by removing a partition between them, the entropy of the joint system increases by an additional factor $2nK \log_e 2$ which

Can not be accounted.

This is called Gibbs paradox:

- ❖ Gibbs paradox can be resolved, by the removal of partition, by considering the two systems as the same.
- ❖ Hence the gas molecules are completely identical and indistinguishable.
- ❖ Gibbs paradox is thus resolved by a concept of quantum mechanics
- ❖ Gibbs paradox in statistical mechanics can be resolved if the Maxwell – Boltzmann constant is divided by N!

Thermodynamics & statistical Mechanics

Polytechnic

Laws of thermodynamics:

1) Zeroth law:



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If two systems are separately in thermal equilibrium with a third, they will also be in thermal equilibrium.

Equation of state:

At low pressure $Pv = nRT$ for all gases (ideal) but real gases don't have this equation.

At high pressure, there is correction in P and V so that

$$(P + \frac{a}{v^2})(V-b) = RT \Rightarrow \text{Vander waal's equation } V - \text{Volume of gas}$$

$$P = \frac{RT}{V-b} - \frac{a}{v^2}$$

Critical constants:

$$P_c = \frac{a}{27b^2}; T_c = \frac{8a}{27}; V_c = 3b$$

When a, b , are critical constants then $\frac{RT_c}{P_c V_c} = \frac{8}{3}$; Boyle's temperature $T_B = \frac{a}{Rb}$
temperature inversion $T_i = 2 T_B = \frac{2a}{Rb}$.

Work done in various process:

- 1) isothermal process $W = RT \ln \left(\frac{V_2}{V_1} \right)$
- 2) adiabatic Process $W = \dots\dots\dots?$
- 3) Isochoric Process $W = \int P dv = 0$
- 4) Isobaric process $W = P (V_2 - V_1)$

First law of thermodynamics:

The change in heat of a system is $dQ = du + dw$

$$dQ = du + Pdv$$



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Heat capacity:

$$C_v = \left(\frac{2Q}{2T} \right)_v \frac{1}{m} \quad m = \text{mass of the gas}$$

$$dQ = m C_v \Delta T$$

$$C_p = \left(\frac{2Q}{2T} \right)_p \frac{1}{m}; dQ = m C_p \Delta T$$

Heat conduction: $\frac{dQ}{dt} = -KA \frac{dT}{dx}$

- ❖ $C_p - C_v = R$ is called Mayer's relation
- ❖ $TV^{\gamma-1} = \text{Constant}$ adiabatic equation in T & V
- ❖ $PV = \text{Constant}$ isothermal equations
- ❖ $C_p = \left(\frac{\partial H}{\partial T} \right)_p$ Where $H = U + PV$; H – enthalpy
- ❖ $F = U - TS$; $G = F + PV$ F = Helmholtz free function

G – Gibbs free function**Chemical potential:**

It governs the flow of particles between two systems i.e. the particles flow from the system of higher chemical potential to the systems of lower chemical potential.

$$\mu = \left(\frac{\partial F}{\partial n} \right)_{T,V}; \mu = \left(\frac{\partial G}{\partial m} \right)_{T,P}$$

$$dF = (\mu_1 - \mu_2) dn; F \text{ always decreases (or) remains constant}$$

$\mu_1 > \mu_2$ means the system at higher chemical Potential are transferred to the system at lower chemical Potential.

Phase equilibrium:

$$G = \mu_1 n_1 + \mu_2 n_2$$

$$dG = \mu dn_1 + \mu dn_2$$

At equilibrium $dG = 0$; $dn_1 = -dn_2$

ie $\mu_1 = \mu_2$



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Thus one component system having two Phases in equilibrium, the chemical Potential of the two phases must be the same.

Clausius – clapeyron equation (or) I-Latent heat equillies:

$$\frac{dP}{dT} = \frac{L}{T(V_2 - V_1)} \quad L - \text{latent heat}$$

At boiling point: $v_2 > v_1$

$$v_2 - v_1 = +ve ; \frac{dP}{dT} = +ve$$

the boiling point of a liquid must rise or fall according as P increases or decreases

At Melting Point:

$v_2 - v_1 = -ve$ like ice which contract on melting

$= +ve$ like paraffin which expand on melting

$$\frac{dP}{dT} = -ve \quad \text{melting points decrease with increase of pressure}$$

When $v_2 = v_1$:

$v_2 - v_1 = 0$; $\frac{dP}{dT} = \infty$ (or) $\ell = 0$ thus when a liquid passes in to vapour state with little no absorption of heat at a temperature to the critical point . $\ell = 0$.

In fusion th specific volume of liquid and solid are nearly same $v_2 - v_1$ is very small ie $\frac{dP}{dT} = \infty$

Richardson – Dustmen's equation:

$$I = AT^2 e^{-\frac{\delta}{KT}}$$

I – thermo unic current; T – temper unto of to filam -eul

Claudius equation (or) II latent heat equation:

$$C_2 - C_1 = \frac{d\ell}{dT} - \frac{\ell}{T}$$



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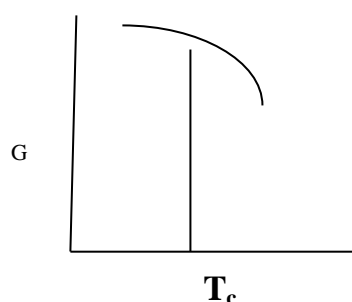
Changes of phase I – Order phase change:

$$\text{Let } dG = -SdT + Vdp = Vdp - SdT$$

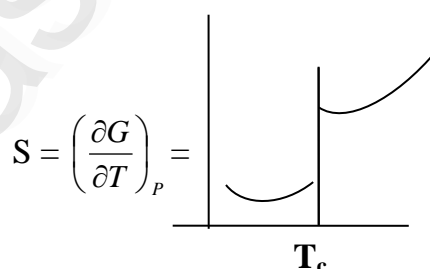
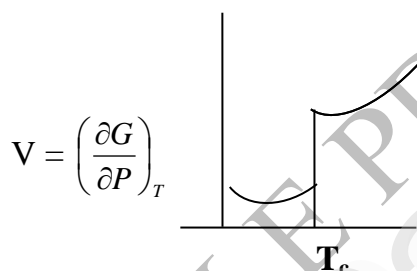
isothermal – isobaric process (T- Constant, P-Constant)

$$dG = 0 ; G = \text{constant}$$

to the value of specific Gibbs potential is same continuous in either phase (liquid → Solid; vapour)

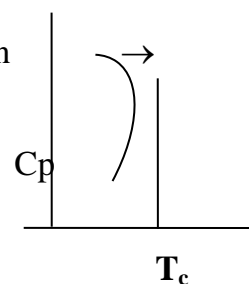


The first derivatives of G ; $\left(\frac{\partial G}{\partial P}\right)_T = V$ & $\left(\frac{\partial G}{\partial T}\right)_P = S$ are a discontinuous change



The heat capacity $C_p = T \left(\frac{\partial S}{\partial T}\right)_P$ also discontinuous and attain

$$\frac{dp}{dT} = \frac{\ell}{T(V_2 - V_1)} = \text{Clausius – Clapeyron equation}$$

**II order phase change:**

At constant P & constant T there is no change (continuous) in first – order derivatives of Gibb's Potential

$$S = \left(\frac{\partial G}{\partial T}\right)_P + V = \left(\frac{\partial G}{\partial P}\right)_T \text{ transition from one phase into the other}$$

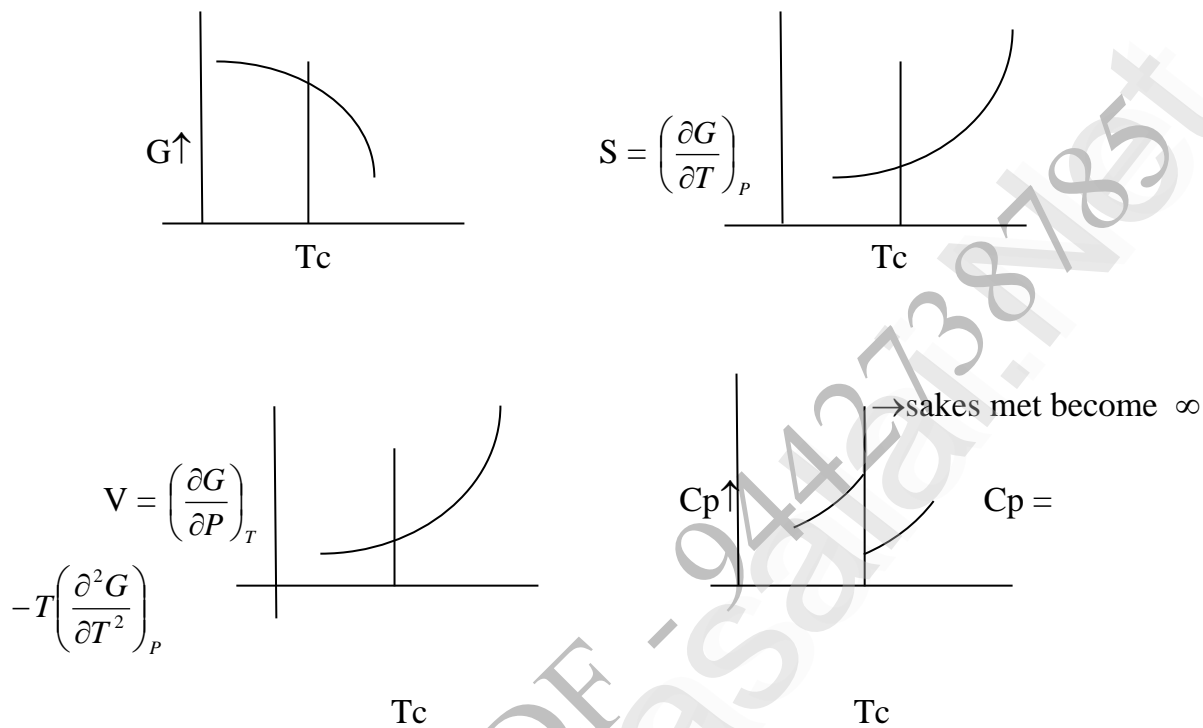


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- ❖ The heat capacity $C_p = \left(\frac{\partial S}{\partial T}\right)_p$ changes discontinuously but does not become infinite
- ❖ The Gibbs Potential change continuously i.e. same in either phase.



The second order phase change is characterized by discontinuous changes in the second order derivatives $\left(\frac{\partial^2 G}{\partial T^2}\right)_p$ of Gibb's potential

Examples of II order phase change :

- ❖ Transition of ferro magnetic material into a Paramagnetic at curie point
- ❖ The transition of super conductor to normal conductor at T_B
- ❖ Order – disorder transitions of certain alloy & chemical compounds at a definite temperature

Planck's radiation law:

The commission of energy takes place in discrete integral multiple of a minute elementary unit of energy called quantam ($E = hv$)

The total energy of variations between the wavelength range λ & $\lambda + d\lambda$ is

$$dE = \frac{8\pi}{\lambda^4} \frac{hc/\lambda}{e^{-1}} d\lambda = \frac{8\pi}{\lambda^5} \frac{hc}{e^{-1}} d\lambda$$



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When $\frac{hc}{\lambda kT} \ll 1$ ie low f ; high λ = when $\frac{w^2}{\pi^2 c^3}$ **KT Rayleigh – Jean's law**

When $\frac{hc}{\lambda kT} \gg 1$ high low $\lambda = \frac{\hbar w^3}{\pi^2 c^3}$ **which is wien's law**

Bose – Einstein condensation:

If the no. of density of particles is increased (or) temperate is reduced, then the behavior of the gas departs more and more from the behaviour of a perfect ideal gas. It is called degeneracy.

Let us consider equation $N = N_0 + \frac{V}{h^3} (2\pi m kT)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{x} dx}{e^x - 1}$ (or)

$$N = N_0 + \frac{V}{h^3} (2\pi m kT)^{3/2} \xi\left(\frac{3}{2}\right)$$

$$N_0 = N - \frac{V}{h^3} (2\pi m kT)^{3/2} \xi\left(\frac{3}{2}\right)$$

Thus as T – decrees, the number of partied in the ground state (N_0) increases.

At absolute Zero ($0^\circ K$) all the partides condense in to the zero energy ground state.

This is called B.E condensation eg above 2.17K helium is called He – I ; below phase 2.17k is known as

He- II ; λ - point is called transition temperature . The normal fluid costs is of He – atoms in the excited state & in super fluid consists of He – atoms in the ground state . He- II has zero viscosity and infinite thermal conductivity

Einstein Model $\epsilon = (n + \frac{1}{2}) \hbar \omega$ discrete values of energy the average energy

of an oscillator = $\frac{\hbar \omega}{e^{\frac{\hbar \omega}{KT}} - 1}$ for N – oscillator – 3 degrees of freedom $\epsilon = \frac{3N\hbar \omega}{e^{\frac{\hbar \omega}{KT}} - 1}$

$$C_v = \frac{\partial E}{\partial T} = 3NK \left(\frac{\hbar \omega}{KT} \right)^2 \left(e^{\frac{\hbar \omega}{KT}} - 1 \right)^{-2}$$

At high temp $e^{\frac{\hbar \omega}{KT}} = 1 + \frac{\hbar \omega}{KT} + \dots$



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$$C_v = 3NK \left(\frac{\hbar \omega}{KT} \right)^2 \frac{\left(1 + \frac{\hbar \omega}{KT} \right)}{\left(\frac{\hbar \omega}{KT} \right)^2} = 3NK \left(1 + \frac{\hbar \omega}{KT} \right)$$

As $T \rightarrow \infty$ $C_v = 3NK = 3R$

At low temperature

$$C_v = 3NK \left(\frac{\hbar \omega}{KT} \right)^2 \frac{e}{\left(e^{\hbar \omega / KT} - 1 \right)^2} = 3NK \left(\frac{\hbar \omega}{KT} \right)^2 \cdot \frac{1}{e^{\hbar \omega / KT}}$$

Debye's Model :

The atoms in a solid cannot be assumed to be independent, but we must take into account their cooperative interactions.

The energy of the system is

$$E = 9NKT \left(\frac{KT}{\hbar \omega} \right)^3 \int_0^{\theta_D / T} \frac{x^3 dx}{e^x - 1}$$

When $\theta_D = \frac{\hbar \omega}{K}$; $x = \frac{\hbar \omega}{KT}$

At high temperature $T \gg \theta_D$

$$\frac{x^3}{e^x - 1} = \frac{x^3}{\left(1 + \frac{x}{1} + \frac{x^2}{2} \right) - 1}$$

$$\therefore E = \frac{9NKT}{x^3} \left(\frac{x^3}{3} \right) = 3NKT$$

$$C_v = \frac{\partial E}{\partial T} = 3NK = 3R$$

At low temperature $T \ll \theta_D$ $\int_0^{\theta_D / T} \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{15}$

$$\therefore E = 9NKT \left(\frac{KT}{\hbar \omega} \right)^3 \cdot \frac{\pi^4}{15} = \frac{9\pi^4 NK^4}{15 \hbar^3 \omega^3} T^4$$

$$C_v = \frac{2E}{2T} = \frac{9NK^4}{60 \hbar^3 \omega^3} T^3$$

$C_v \propto T^3$ = This law known as Debye T^3 law



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Quantum statistics : (B.E &F.D)**B.E**

- ❖ The total number of particle in perfect B.E gas is $n =$

$$\frac{V}{h^3} (2\pi mKT)^{3/2} \left[A + \frac{A^2}{2^{3/2}} + \frac{A^2}{2^{3/2}} + \dots \right]$$

- ❖ The energy of the particle of perfect B.E gas $E = \frac{3}{2} \frac{V}{h^3} (2\pi mKT)^{3/2} KT \left(A + \right.$

$$\left. A + \frac{A^2}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \dots \right)$$

- ❖ $\frac{E}{n} = \left(\frac{3}{2} nKT \right)^{3/2} \left[1 - \frac{A^2}{2^{5/2}} + \frac{A^2}{2^{5/2}} + \dots \right]$

F.D:**Weak degeneracy:**

Total number of particle of perfect F-D gas

- ❖ $n = g_s \frac{V}{h^3} (2\pi mKT)^{3/2} \left[A - \frac{A^2}{2^{3/2}} + \frac{A^2}{3^{3/2}} - \dots \right]$

- ❖ $E = \frac{3}{2} g_s \frac{V}{h^3} (2\pi mKT)^{3/2} KT \left(A - \frac{A^2}{2^{5/2}} + \frac{A^2}{3^{5/2}} - \dots \right)$

- ❖ $\frac{E}{n} = \frac{3}{2} KT \left[1 + \frac{A}{2^{5/2}} - \frac{A}{2^{5/2}} + \dots \right]$

Ideal gas:

- ❖ $n = g_s \frac{V}{h^3} (2\pi mKT)^{3/2} A$

- ❖ $E = \frac{3}{2} g_s \frac{V}{h^3} (2\pi mKT)^{3/2} KTA$

- ❖ $\frac{E}{n} = \frac{3}{2} KT$

Equation 1 & 2 is known as Ehrenfest's equation.

Statistics : (B.E, F. + M.B)

Stirling approximation

$$\log n! = n \log n - n$$



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M.B The number of ways n_i particles arranged is

The total number of microstates

$$\Omega = \frac{N!}{n_i!} \pi g_i^{n_i}$$

The Grand Canonical Distribution:

The most probable distribution of assemblies in grand canonical ensemble is given by

$M_{N_i} = e^{\alpha N + \beta E_{N_i}}$ and the grand canonical partition function

$$Q = \sum_N \sum_i \exp. \left(\frac{\mu N - E_{N_i}}{KT} \right)$$

Thermo dynamical Properties of Grand Canonical Ensemble :

1. $S = K \left[\ln Q + \frac{\bar{E} - \mu \bar{N}}{kT} \right]$
2. $P = kT \frac{\partial}{\partial V} (\ln Q)$
3. $\mu = U - TS + PV$
4. $\bar{E} = kT^2 \frac{\partial}{\partial T} (\ln Q) + \mu kT \frac{\partial}{\partial \mu} (\ln Q)$
5. $PV = kT \ln Q$

Semi – Classical Grand Partition Function:

The grand partition function in terms of chemical potential μ and Partition function Z per system is given by $Q = \exp \left(Z e^{\mu/kT} \right)$

The mean number of systems in the i th assembly $\bar{N} = kT \left(\frac{\partial}{\partial \mu} \left(Z e^{\mu/kT} \right) \right)_{V,T}$

Microcanonical Ensemble

The Microcanonical Ensemble :

The ensemble in which system has same fixed energy and also the same number of particles is called a microcanonical ensemble



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Partition Function:

Partition function indicates how the gas molecules of an assembly are distributed or partitioned among the various energy levels.

$$Z = \sum_i g_i e^{-\epsilon_i/kT}$$

Translational partition function for a gas molecule : $= \frac{V}{h^3} (2\pi mkT)^{3/2}$

Properties Relating Partition Function and Thermodynamical Quantities

1. Entropy : $S = Nk \ln Z + \frac{3}{2} Nk$
2. Free energy : $F = NkT \ln Z$
3. Total energy : $E = NkT^2 \left(\frac{\partial(\ln Z)}{\partial T} \right)_V$
4. Enthalpy : $H = NkT^2 \left(\frac{\partial(\ln Z)}{\partial T} \right)_V + RT$
5. Gibb's potential G : $G = NkT^2 \left(\frac{\partial(\ln Z)}{\partial T} \right)_V + RT - NkT \ln Z - \frac{3}{2} NkT$
6. Pressure : $P = NkT \left(\frac{\partial(\ln Z)}{\partial T} \right)_T$
7. Specific heat at constant volume C_v

$$C_v = Nk \left[2T \frac{\partial(\ln Z)}{\partial T} + T^2 \frac{\partial^2(\ln Z)}{\partial T^2} \right]_V$$

Virial Coefficient:

Consider the real gas, virial expansion is given by $\frac{PV}{NkT} = 1 + \text{correction}$

$$= \sum_{i=1}^{\infty} a_i(T) \left(\frac{\lambda^3}{v} \right)^{i-1}$$

Where $a_1 = 1$ or $\frac{PV}{NkT} = 1 + a_2 \frac{\lambda^3}{v} + a_3 \left(\frac{\lambda^3}{v} \right)^2 + \dots$ and $a_2 = \frac{2\pi}{\lambda^3} \int_0^{\infty} (1 - e^{-\beta u(r)}) r^2 dr$

$\therefore B_2(T) = a_2 \lambda T^3$ is known as second virial coefficient for perfect gas

$$\frac{PV}{NkT} = 1$$

For real gas, $\frac{PV}{NkT} = 1 + \frac{B_2(T)}{V}$

Note – 2nd virial coefficient:

- I. If B_2 is negative, then P is less than the ideal gas



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- II. If B_2 is positive, P is more than the ideal gas where V, N, T are constants. Put $B_2(T) = 0$ for calculating the Boyle's temperature.
- III. Boyle's temperature for a hard sphere is not defined because $B_2(T)$ is independent of T .
The factor $2Nk \ln 2$ arises due to the distinguishability of classical particles and is known as the mixing term.

Semi – Classical Gas:

It consists of indistinguishable particles

$$Z = \frac{V}{h^3} (2\pi mkT)^{3/2} \text{ and } S = Nk \left[\ln \frac{V}{Nh^3} (2\pi mkT)^{3/2} + \frac{5}{2} \right] \text{ is also known as}$$

Sackur – Tetrode equation for the entropy of a semi – classical gas.

$$\text{Free energy : } F = -kT \left[\ln \frac{Z^N}{N!} \right]$$

$$F = -kT \ln(Z)$$

$$\text{Total energy: } E = NkT^2 \frac{\partial}{\partial T} (\ln Z)$$

$$\text{Pressure : } P = NkT \left[\frac{\partial}{\partial V} (\ln Z) \right] \text{ and gas equation is } PV = NkT$$

Separation of Partition Function:

The total partition function can be expressed as the product of the partition function for individual degrees of freedom. $Z = Z_t Z_r Z_v Z_e$

Canonical Ensemble**The Canonical Ensemble :**

In the canonical ensemble the assemblies are having the same volume V , number of system N and are in thermal contact with each other so that they are in equilibrium and have the same temperature T .

The canonical partition function is given by $Z = \sum_i e^{-E_i/kT}$

The Thermodynamical Properties of the canonical ensemble:

$$(i) \text{ Entropy : } S = \frac{E}{T} + k \ln Z \quad (ii) \text{ Free energy : } F = -kT \ln Z$$

$$(iii) \text{ Pressure : } P = \sum_i P_i \left(\frac{\partial E_i}{\partial V} \right)_N \quad (iv) \text{ Chemical Potential : } \mu = \sum_i P_i \left(\frac{\partial E_i}{\partial V} \right)_v$$

Total Partition Function:

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The canonical Partition function of the semiclassical ensemble is given as $Z = \frac{z^N}{N!}$ and classical expression $Z = \frac{1}{h^3 N} \int e^{-E/kT} d\tau$.

Thermo dynamical Properties of a Real Gas:

The real gas particles exert a force of attraction on each other. The total energy of the gas is made up of the kinetic energy of the motion of the gas particles and potential energy of interactions between them.

(i) Total energy:

$$E = \frac{1}{2m} \sum_{i=1}^N (P_{x_i}^2 + P_{y_i}^2 + P_{z_i}^2) + \sum_{i=1}^N \sum_{j>1} U_{ij}$$

(ii) Partition function:

$$Z = \frac{1}{h^3 N!} (2\pi m kT)^{3N/2} Z_r$$

(iii) Fermi energy :

$$Z = -kT \left[\ln \left\{ \frac{(2\pi m kT)^{3N/2}}{h^3 N!} \right\} + \ln Z_r \right]$$

(iv) Pressure :

$$P = \frac{NkT}{V}$$

(v) Gibb's free energy:

$$G = kT \left[-\ln Z + \left(\frac{\partial \ln Z_r}{\partial \ln V} \right)_T \right]$$

(vi) Entropy :

$$S = k \left[\ln Z + \left(\frac{\partial \ln Z}{\partial \ln V} \right)_T \right]$$

(vii) Specific heat :

$$C_v = K \left[2 \left(\frac{\partial \ln Z}{\partial \ln T} \right)_V + T^2 \left(\frac{\partial^2 \ln Z}{\partial T^2} \right) \right]$$



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INCOME TAX STOP, KARAIKUDI -01****The Grand Canonical Ensemble****The Grand Canonical Ensemble:****KARAIKUDI VIDYA SRI SAMPLE MATERIALS****447 PASSED TILL DATE****8015513365****PG TRB / TET PAPER I & II / TNPSC / PSYCHOLOGY**www.vidyasriacdaemy.com**Kindly Send me your Answer Keys to email id - Padasalai.net@gmail.com**

The grand canonical ensemble is a collection of independent assemblies having the same temperature T , volume V and the chemical potential μ .

Partition function is $Z = \frac{V}{h^3} (2\pi mkT)^{3N/2}$ entropy $S = NK \log Z + \frac{3}{2}NK F..$

ideal gas

Helmholtz free energy $F = E - Ts = NKT \log_e Z$

Total energy (E) $\bar{\epsilon} = \frac{E}{N} = \frac{\sum n_i \epsilon_i}{\sum n_i}$

$\bar{\epsilon}$ = average energy of assembly of 'N' independent systems.

$$E = NkT^2 \left[\frac{2 \log z}{2T} \right]$$

Enthalpy (H) $H = E + Pv$

$$H = NkT^2 \left[\frac{2 \log z}{2T} \right] + RT$$

Gibbs potential (G) $G = H - TS = \log Z - \frac{3}{2}NKT.$

B.E:

The total number of possible ways in which n_i particles can be distributed g_i section is

$$\frac{g_i! [(n_i + g_i - 1)!]}{n_i! g_i!}$$

The total number of distinguishable arrangements are given by

$$G = \prod_i \frac{(n_i + g_i)!}{n_i! g_i!}$$

Eg '2' identical particles, which can be any one of '3' single particle state, the number of states (w) of the system as possible in B.E statistics is

$$N_i = 2; g_i = 3$$

$$W = \frac{(N_i + g_i - 1)!}{n_i! (g_i - 1)!} = 6$$

F.D: The number of distinguishable arrangements of n_i particles in g_i cells are

$$\frac{g_i!}{n_i! (g_i - n_i)!}$$



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The total number of regress states of the whole system is $G = \pi_i$

$$\frac{g_i!}{n_i!(g_i - n_i)!}$$

Black body radiation:

- ❖ $\lambda T = \text{Constant}$ wine's displacement law = 0.289 cm –k
- ❖ Stefan's Boltzmann radiate w $E = \sigma T^4$
- ❖ Wien's law $\frac{e_{\lambda}}{e_{\lambda'}} = \left(\frac{T}{T'}\right)^5$
- ❖ Average energy of planeck's oscillator $\bar{E} = \frac{h\nu}{\left(e^{\frac{h\nu}{K_i-1}}\right)}$
- ❖ Stefari's constant $\sigma = \frac{2\pi^5 K^4}{15c^2 h^3}$ u every density
- ❖ Pressure of radiation (diffuse) $P = \frac{1}{3}u$ for perfect reflector $P = \frac{2}{3}u$
- ❖ Plank's distribution law energy density $u(\nu) = \frac{8\pi\gamma^3}{c^3} = \frac{h\gamma}{\left(e^{\frac{h\gamma}{KT}} - 1\right)} d\gamma$
- ❖ $\frac{8\pi hc}{\lambda^5} \frac{1}{e^{\frac{hc}{\lambda KT}} - 1} d\lambda$ $C = \gamma\lambda$ -obeys B.E statesis
- ❖ Small γ (or) laye 'λ'
- ❖ $\mu(\gamma) = \frac{8\pi\gamma^2}{\lambda^5} KTdv$ Raleigh jeens law = $E \lambda d\lambda = \frac{8\pi KT}{\lambda^4} d\lambda$
- ❖ Her laye γ (or) small 'λ' $u(\nu) = \frac{8\pi hc}{\lambda^5} e^{\frac{1}{\frac{hc}{\lambda KT}} - 1}$
- ❖ Wien's law $\therefore d\gamma = \frac{C}{\lambda^2} d\lambda$

Holium – II

- ❖ Never bubbles
- ❖ He I & He – II both same type of entropy and continues across the curve
- ❖ Viscosity increase as temperatune decrease in normal liquid (He –I)
- ❖ He – II has almost Zero viscosity behavior high heat conductivity internal friction is zero

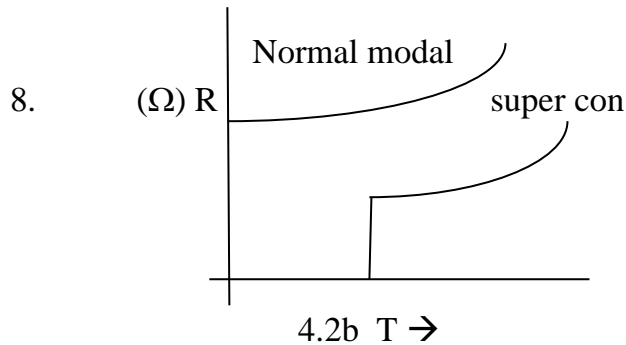


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- ❖ Viscosity of He – II $\approx 10^{-3}$ / He – II = 10^3 He – II viscosity of He – I
- ❖ Heat conductivity He – II = 800 times of 'w'
- ❖ Electrical resistant is almost zero
- ❖ Super fluid bean of zero vistosity
- ❖ He-I heat conductivity in order of 10^{-4} bet He- II very high



M.B	F.D	B.E
$n_i = \frac{g_i}{e^{\beta \epsilon_i}}$	$n_i = \frac{g_i}{e^{-\epsilon_i} + \beta \epsilon_i + 1}$	$n_i = \frac{g_i}{e^{-\epsilon_i} + \beta \epsilon_i - 1}$
Who $\propto = \frac{h^1}{KT}$;	$\beta = \frac{1}{KT}$	

At high 'T' \propto - very low $A = e^{-\epsilon_i} \ll 1$ terms $e^{-\epsilon_i} + \beta \epsilon_i \approx 1$ very lase compane '1'
so the F.D & B.E becomes M.B.

- ❖ Fermion \rightarrow electron, proton, Neutron, -positron & holes (F.D)
- ❖ Bosons \rightarrow Photons, Phonons, mesons, ∞ - particle & He – II (B.E)
- ❖ O_2, H_2 are mole obey M-B has any spin value
- ❖ F.D particles only can not be zero energy at absolute zero temperature
- ❖ Boltzmann's statistical definition for entropy is $S = K \log \Omega$
- ❖ Spin degeneracy $G_s = (2S + 1)$ S-spin

❖ Fermi temperature $T_f = \frac{\epsilon_f(0)}{K} = \frac{h_1 F}{K} = \frac{h^3}{2mK} \left(\frac{3n}{4\pi g_s} \right)^{2/3} = \frac{h^2}{2m^{5/2} K} \left(\frac{3\rho}{4\pi g_s} \right)^{2/3}$

❖ when $(g_s = 2s + 1)$

❖ $\epsilon_f(0) = h_1 F = \frac{h^2}{2m} \left(\frac{3n}{4\pi g_s} \right)^{2/3} = \left(\frac{n}{v} = \ell \right)$

❖ Zero Point energy of \bar{e} gas $E_0 = \frac{3}{5} n \epsilon_f(0)$

❖ Zero point energy of \bar{e} gas pressure



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Physics Unit – IV

Previous Year Questions

2001:

1. The value of permittivity of free space in $C^2N^{-1} m^{-2}$ is
 A) $36 \pi \times 10^9$ B) $36 \pi \times 10^{-9}$ C) $10^{-9} / 36\pi$ D) 36π
2. The total normal electric flux over a closed surface surrounding a charge is
 A) directly proportional to the charge
 B) Inversely proportional to the charge
 C) directly proportional to the square of the charge
 D) Inversely proportional to the square of the charge
3. Laplace's equation for free space is
 A) $\nabla_2 V = 0$ B) $\nabla V = 0$ C) $\nabla_2 V \neq 0$ D) $\nabla V \neq 0$
4. Only one phase point can occupy one phase cell according to
 A) classical statistics B) Bose – Einstein statistics
 C) Fermi- Dirac statistics D) All of these
5. The statistical theory which readily leads to Plank's law of radiation is
 A) Maxwell – Boltzmann statistics B) Bose – Einstein statistics
 C) Fermi – Dirac statistics D) None of these
6. The statistical theory which supports the zero point energy of a gas even at absolute zero is
 A) Classical statistics B) B.E.Statistics C) F.D.Statistics D) All of these
7. According to M.B. statistics, the number of particles in the given energy range is given by
 A) $n_i = \frac{Z_i}{Ae^{E_i/KT}}$ B) $n_i = \frac{Z_i}{Ae^{E_i/KT} - 1}$
 C) $n_i = \frac{Z_i}{Ae^{E_i/KT} + 1}$ D) $n_i = \frac{Z_i}{Ae^{E_i/KT} \pm 1}$
8. Phase points are endowed with a distinct unchanging individuality of their own, according to
 A) classical statistics B) B.E. Statistics
 C) F.D. Statistics D) None of these
9. The number of dimensions of phase space is
 A) 3 B) 4 C) 5 D) 6
10. A divergence in the behavior of an actual gas from that of a perfect gas is referred to as



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- A) entropy of the gas
C) thermodynamic probability of the gas
- B) degeneracy of the gas
D) pressure of the gas

2002 – 2003:

41. An equilibrium macroscopic state is one for which the number of microscopic states is
A) zero B) minimum and non-zero C) maximum D) infinite
42. As the energy of a cell increases, the number of particles distributed in the cell
A) decreases B) increases
C) increases and then decreases D) decreases and then increases
43. The unit of phase space volume is
A) $J^3 s^{-3}$ B) $J s$ C) m^3 D) $kg^3 m^6 s^{-3}$
44. Pauli's exclusion principle is imposed on
A) Maxwell – Boltzmann statistics B) Bose – Einstein statistics
C) Fermi-Dirac statistics D) All these three
45. Planck's law governing the blackbody radiation can be deduced using
A) Maxwell- Boltzmann statistics B) Bose-Einstein statistics
C) Fermi-Direc statistics D) All these three
46. The width of the energy band gap is minimum in the case of
A) insulators B) semiconductors
C) metals D) organic materials
47. The value of $(\epsilon_0 \mu_0)^{-1/2}$ in ms^{-1} is
A) 3×10^8 B) 3×10^7 C) 3×10^9 D) 3×10^6
48. The vector $\vec{E} \times \vec{H}$ represents the
A) electric field B) energy per unit area
C) square of energy flux D) intensity of the wave
49. The wave produced by an oscillating electric dipole is a
A) spherical wave B) cylindrical wave
C) elliptical wave D) plane wave
50. If a light source moves with a velocity v towards an observer at rest, the velocity of light (C) as observed by him is
A) $C + v$ B) $C - v$ C) C D) $C \pm v$
51. If a sphere is carried by an observer in motion, it will appear for an observer rest as
A) sphere B) cube C) plane surface D) ellipsoid
52. As the temperature of the filament is doubled, thermonic current



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- A) varies exponentially B) increases 4 times
C) decreases D) decreases 4 times
53. Which of the following statements is wrong?
Gibbs function is
A) also known as thermodynamic potential
B) the difference between enthalpy and latent energy
C) a constant in sublimation
D) a constant in an adiabatic process
54. The electrostatic force between two charges separated by 3m distance is 0.075 N. If the total charge is 20 μC , the individual charges are
A) 5 μC , 15 μC B) 10 μC , 10 μC
C) 2 μC , 18 μC D) 1 μC , 19 μC
55. Gauss's divergence theorem relates
A) line integral and volume integral B) line integral and surface integral
C) volume integral and surface integral D) any two integrals

2003 – 2004:

56. Fermi temperature θ_F is given by
A) $\theta_F = K \times \theta_F$ B) $\theta_F = \frac{E_F}{K}$ C) $\theta_F = \frac{K}{E_F}$ D) $\theta_F = K + \theta_F$
57. Ideal gas molecule is explained by
A) Maxwell – Boltzmann Statistics B) Bose-Einstein Statistics
C) Fermi-Dirac Statistics D) All these three
58. The displacements of all atoms in a linear triatomic molecule are equal and in the same direction if
A) $\omega = \sqrt{\frac{k}{m}}$ B) $\omega = 0$ C) $\omega = \left\{ \frac{k}{m} \left(1 + \frac{2m}{M} \right) \right\}^{\frac{1}{2}}$ D) $\omega = \left\{ \frac{k}{m} \left(1 + \frac{2m}{M} \right) \right\}^{-\frac{1}{2}}$
59. For electron the degeneracy factor is
A) $Q = 0$ B) $Q = 1$ C) $Q = 3$ D) $Q = 2$
60. In canonical ensembles
A) sub-systems exchange particles B) sub-systems exchange energy



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- C) sub-systems exchange energy but not particles
 D) sub-systems exchange both energy and particles
61. Law of addition of velocities applies only when the two velocities are in
 A) Perpendicular direction B) opposite direction
 C) the same direction D) all of these
62. In Galilean transformation
 A) Acceleration is invariant B) Velocity is invariant
 C) time varies D) Acceleration varies
63. The relativistic mass of a particle moving with a velocity $0.9c$ is
 A) $3 m_0$ B) $2 m_0$ C) $2.3 m_0$ D) $1.25 m_0$
64. Minkowski space is
 A) six dimensional space B) four dimensional space
 C) three dimensional space D) three dimensional curvilinear space
65. The macrostate is defined by
 A) Pressure, temperature and volume of the gas
 B) position and velocity component of molecules
 C) pressure and temperature of the gas
 D) pressure and volume of the gas
66. Bose-Einstein Statistics is applied to the system
 A) identical and indistinguishable particle
 B) identical and distinguishable particle
 C) identical, distinguishable and obeying Pauli's exclusion principle
 D) identical, indistinguishable and obeying Pauli's exclusion principle
67. The distribution law according to Maxwell-Boltzmann statistics is
 A) $n_i = \frac{g_i}{f e^{\frac{BE_i}{kT}} - 1}$ B) $n_i = \frac{g_i}{f e^{\frac{BE_i}{kT}} + 1}$
 C) $n_i = \frac{g_i}{e^{\frac{BE_i}{kT}}}$ D) $n_i = \frac{g_i}{f e^{\frac{BE_i}{kT}}}$
68. Micro-canonical ensemble describes
 A) The systems which are perfectly insulated
 B) The system which are in thermal contact with heat reservoir
 C) The systems which are in statistical equilibrium
 D) The systems which are in thermal equilibrium



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INCOME TAX STOP, KARAIKUDI -01****2004 – 2005:**

69. Fermi-Dirac statistics is applicable to

- A) ideal gas molecule
concentration
- B) electrons of high
concentration
- C) photons and symmetrical particles
concentration
- D) electrons of low
concentration

70. In a linear triatomic molecule the motion is translation if

- A) $\omega = 0$ B) $\omega = \frac{\sqrt{k}}{m}$ C) $\omega = \left\{ \frac{k}{m} \left(1 + \frac{2m}{M} \right) \right\}^{\frac{1}{2}}$ D)
- $\omega = \left\{ \frac{k}{m} \left(1 + \frac{2m}{M} \right) \right\}^{-\frac{1}{2}}$

71. Grand canonical ensemble is one which allows

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- A) The subsystem to exchange energy
 B) The subsystem to exchange number of particles
 C) exchange of both
 D) The subsystem to exchange neither energy nor number of particles
72. The microstate is defined by
 A) pressure and volume of the gas
 B) pressure and temperature of the gas
 C) pressure, temperature and volume of the gas
 D) position and velocity component of the molecules
73. Fermi-Dirac statistics is applied to systems of
 A) identical and indistinguishable particles
 B) identical and distinguishable particles
 C) identical and indistinguishable particles obeying Pauli's exclusion principle
 D) identical and distinguishable particles obeying Pauli's exclusion principle
74. The distribution law according to Bose- Einstein statistics is
 A) $n_i = \frac{g_i}{fe^{BE}_i}$ B) $n_i = \frac{g_i}{fe^{BE}_i - 1}$
 C) $n_i = \frac{g_i}{e^{BE}_i}$ D) $n_i = \frac{g_i}{fe^{BE}_i + 1}$

2005 – 2006:

75. Fermi-Dirac statistics is applied to systems of
 a) identical and indistinguishable particles
 B) identical and distinguishable particles
 C) identical and indistinguishable particles obeying Pauli's exclusion Principle
 D) identical and distinguishable Particles obeying Pauli's exclusion Principle
76. Grand canonical ensemble is one which allows
 A) the subsystem to exchange energy
 B) the subsystem to exchange number of particles
 C) exchange of both
 D) the subsystem to exchange neither energy nor number of particles.

2011 – 2012:

77. According to which statistics the energy at absolute zero cannot be zero?
 A) Fermi-Dirac B) Maxwell-Boltzmann
 C) Bose-Einstein D) Both Maxwell-Boltzmann and Bose-Einstein



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78. Boson have spin value
A) zero or one B) zero C) one D) $\frac{1}{2}$
79. The most probable velocity of the molecules in a gas is
A) $\sqrt{\frac{3KT}{m}}$ B) $\sqrt{\frac{8KT}{m}}$ C) $\sqrt{\frac{6KT}{m}}$ D) $\sqrt{\frac{2KT}{m}}$
80. Which of the following is correct?
A) $\bar{V} < V_{rms} < V_p$ B) $V_{rms} < V_p < \bar{V}$
C) $V_p < \bar{V} < V_{rms}$ D) $V_{rms} < V_p < \bar{V}$
Where \bar{V} - mean velocity
 V_{rms} - root mean square velocity
 V_p - most probable velocity of the molecules of a gas
81. Richardson – Dushman equation for thermionic emission is
A) $J = T^4 e^{-\phi/KT}$ B) $J = AT^2 e^{-\phi/KT}$
C) $J = AT^3 e^{-\phi/KT}$ D) $J = AT^4 e^{-\phi/KT}$
82. Liouville's Theorem is
A) $\left(\frac{\partial p}{\partial t}\right) + \sum_j \left(\frac{\partial p}{\partial q_j} \dot{q}_j + \frac{\partial p}{\partial p_j} \dot{p}_j\right) = 0$ B) $\left(\frac{\partial^2 p}{\partial t^2}\right) + \sum_j \left(\frac{\partial p}{\partial q_j} \dot{q}_j + \frac{\partial p}{\partial p_j} \dot{p}_j\right) = 0$
C) $\left(\frac{\partial p}{\partial t}\right) + \sum_j \left(\frac{\partial p}{\partial q_j} \dot{p}_j + \frac{\partial p}{\partial p_j} \dot{p}_j\right) = 0$ D) $\left(\frac{\partial^2 p}{\partial t^2}\right) + \sum_j \left(\frac{\partial p}{\partial q_j} \dot{p}_j + \frac{\partial p}{\partial p_j} \dot{q}_j\right) = 0$
83. A micro-canonical ensemble represents
A) an isolated system in equilibrium
B) a system in contact with a heat reservoir
C) a system that can exchange both energy and momentum
D) a system that undergoes pressure change

2012 – 2013:

84. Stirling approximation gives $\log n! = \dots\dots\dots$
A) $n \log n$ B) $n \log n - n$ C) $n \log n + n$ D) $n! - n \log n$
85. The Probable distribution of the Fermi-Dirac gas is
A) $n_i = \frac{gi}{e^\alpha + \beta \epsilon_i}$ B) $n_i = \frac{e^\alpha + \beta \epsilon_i}{gi}$
C) $n_i = \frac{gi}{e^\alpha + \beta \epsilon_i - 1}$ D) $n_i = \frac{gi}{e^\alpha + \beta \epsilon_i + 1}$
86. Total energy of perfect Bose-Einstein gas is



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$$\begin{aligned}
 \text{A) } E &= \frac{3}{2}nkL \left[1 - \frac{A}{2^{5/2}} - \frac{A^2}{3^{5/2}} - \dots \right] & \text{B) } E &= \\
 \frac{1}{2}nkL \left[1 - \frac{A}{2^{5/2}} - \frac{A^2}{3^{5/2}} - \dots \right] & & & \\
 \text{C) } E &= \frac{3}{2}nkL \left[1 + \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \dots \right] & \text{D) } E &= \\
 \frac{1}{2}nkL \left[1 + \frac{A}{2^{5/2}} + \frac{A^2}{3^{5/2}} + \dots \right] & & &
 \end{aligned}$$

87. The independent systems having is called micro canonical ensembles

- A) same energy E, Volume V and temperature
- B) same temperature T, volume V and the number of particles N
- C) same temperature T, volume V and the chemical potential u
- D) same energy E, volume V and the number of particles N

88. Maxwell Boltzmann's Statistics states that the average kinetic energy per molecule associated with each degree of freedom is

- A) KT
- B) $\frac{1}{2}KT$
- C) $\frac{3}{2}KT$
- D) KT

89. According to Dulong-Petit's law, the high temperature limit of specific heat capacity becomes

- A) $C_v = 3NK_B$
- B) $C_v \propto T^3$
- C) $C_v \propto \frac{1}{T^3}$
- D) C_v

$$\propto \exp\left(-\frac{\hbar W}{K_B T}\right)$$

90. The mean square speed of gas molecules in equilibrium is proportional to

- A) T
- B) T^2
- C) T^3
- D) $T^{\frac{1}{2}}$

91. Which of the following statement is wrong for Helium – II?

- A) The viscosity is almost zero
- B) Thermal conductivity is very low
- C) Density is same as Helium -1
- D) Flow through capillaries is independent of pressure difference



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92. The average energy of Plank's Oscillator $\bar{\varepsilon} = \dots\dots\dots$

A) $\bar{\varepsilon} = \frac{hv}{e^{hv/KT}}$

B) $\bar{\varepsilon} = \frac{e^{hv/KT}}{hv}$

C) $\bar{\varepsilon} = \frac{hv}{e^{hv/KT} + 1}$

D) $\bar{\varepsilon} = \frac{hv}{e^{hv/KT} - 1}$

2014 – 2015:

93. Consider a gas of only two particles A, B obeying B-E statistics and each particle be in one of the three possible quantum states 1, 2, 3. How many possible states exist for the whole gas?

A) 9

B) 6

C) 3

D) 2

94. The total energy of the system of 'n' electrons at T = 0 K, using Fermi-Dirac law of distribution of energy is

A) zero

B) $\frac{3}{5}n\mu_f$

C) 1

D) $3/2$

95. A particle of mass 'm' obeys Maxwellian velocity distribution. The average speed of the particle is

A) $\frac{1}{2}KT$

B) $\sqrt{\frac{2KT}{m\pi}}$

C) $\frac{3KT}{m}$

D) $\sqrt{\frac{8KT}{m\pi}}$

96. In a grand canonical ensemble, the system are capable, of exchanging

A) Only energy

B) Only particles

C) Both energy and particles

D) None of the above

97. The co-efficient of viscosity of liquid helium II is

A) Low

B) Abnormally low

C) High

D) Abnormally

high

98. The particles which obey Fermi-Dirac statistics are known as

A) Bosons

B) Photons

C) Fermions

D) Phonons

99. In thermionic emission, the thermionic current varies with the temperature of the filament as

A) T

B) T^2

C) T^{-1}

D) $\frac{1}{T^2}$

100. The energy emitted by a black body at a temperature of 600K is

A) 7350 watt/m²

B) 0.0204 watt/m²

C) 3600 watt/m²

D) 36000 watt/m²

101. In a monoatomic gas, the molecular phase-space has dimension of

A) 2

B) 3

C) 4

D) 6



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102. According to Debye's T^3 law, the specific heat at constant volume C_V at high temperature is

A) Proportional to T^3

B) Proportional to T^2

C) Proportional to T

D) Independent of temperature

Answer Keys:

1		21		41		61		81	
2		22		42		62		82	
3		23		43		63		83	
4		24		44		64		84	
5		25		45		65		85	
6		26		46		66		86	
7		27		47		67		87	
8		28		48		68		88	
9		29		49		69		89	
10		30		50		70		90	
11		31		51		71		91	
12		32		52		72		92	
13		33		53		73		93	
14		34		54		74		94	
15		35		55		75		95	
16		36		56		76		96	
17		37		57		77		97	
18		38		58		78		98	
19		39		59		79		99	
20		40		60		80		100	

101.

102.

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