KARPAGAM ACADEMY OF HIGHER EDUCATION

CLASS: III BSc PHYSICS COURSE CODE:15PHU602 COURSE NAME: STATISTICAL MECHANICS

#### UNIT: I

BATCH-2015-2018

# UNIT-I

# **SYLLABUS**

#### **Classical Statistics**

Entropy and Thermodynamic Probability. Maxwell-Boltzmann Distribution Law. Ensemble Concept. Partition Function. Thermodynamic Functions of Finite Number of Energy Levels. Negative Temperature. Thermodynamic Functions of an Ideal Gas. Classical Entropy Expression, Gibbs Paradox. Law of Equipartition of Energy – Applications to Specific Heat and its Limitations.

#### **Entropy and Thermodynamic Probability**

Generally, entropy refers to disorder or uncertainty, and the definition of entropy used in information theory is directly analogous to the definition used in statistical thermodynamics. The concept of information entropy was introduced by Claude Shannon in his 1948 paper "A Mathematical Theory of Communication.

## Thermodynamics

Thermodynamics describes the macroscopic prop- erties of matter phenomeno logically with the aid of equations of state which are derived empirically. For thermodynamics it is of no importance, how a certain equation of state comes about. This, of course, is con- sistent with the large universality of thermodynamics, namely that same laws of thermodynamics hold for different materials. However, this doesn't tell us what makes, say, the specific heat of one material different from the other. It is intuitively obvious that specific heat of one material is different from that of the other be- cause microscopically the materials are different. The macroscopic quantities in materials must obviously be resulting from the microscopics properties. For example, the pressure of a gas is due to the collisions of the molecules with a surface, whereas tempera- ture is directly given by the mean kinetic energy of the particles.

## The Maxwell-Boltzmann distribution

We want to apply statistical procedures to the swarm of points in Boltzmann's  $^{\mu}$  space. To do this we first divide that space in 6-dimensional cells of size  $(\Delta x)^3 (\Delta v)^3$ , labelling them

by i = 1, ..., m. There is a characteristic energy  $E_j \equiv E(\vec{r}_j, \vec{v}_j)$  pertaining to each such cell. For instance, in the ideal gas case this energy is simply  $E_j = mv_j^2/2$ , where  $\vec{v}_j$  is the velocity of the particles in cell j.

Now we distribute the N particles over the m cells, such that  $n_j$  particles are allotted to cell no. <sup>j</sup>. In a closed system with total energy E the population numbers  $n_j$  must fulfill the condition  $\sum_j n_j E_j = E$ . The other condition is, of course, the conservation of the number of particles,  $\sum_j n_j = N$ . Apart from these two requirements the allottment of particles to cells is completely random.

We may understand this prescription as the rule of a game of fortune, and with the aid of a computer we may actually play that game!



Instead of playing the game we may calculate its outcome by probability theory. For good statistics we require that N >> 1.

A specific *m*-tuple of population numbers will here be called a **partitioning**. (If you prefer to follow the literature, you may refer to it as a *distribution*.) Each partitioning may be performed in many different ways, since the labels of the particles may be permutated without changing the population numbers in the cells. This means that many specific **allottments** pertain to a single **partitioning**. Assuming that the allotments are

elementary events of equal probability, we simply count the number of possible allottments to calculate the probability of the respective partitioning.

The number of possible permutations of particle labels for a given  $\vec{n} \equiv \{n_j; j = 1, ..., m\}$  is

 $P(\vec{n}) = \frac{N!}{n_1!n_2!\dots n_m!}$ 

(In combinatory this is called *permutations of m elements* - i. e. cell numbers - with repetition).

Since each allotment is equally probable, the most probable **partitioning** is the one allowing for the largest number of **allotments**. In many physically relevant cases the probability of that optimal partitioning very much larger than that of any other, meaning that we can restrict the further discussion to this one partitioning. (See the previous discussion of the multinomial distribution.)

Thus we want to determine that specific partitioning  $\vec{n}^*$  which renders the expression a maximum, given the additional constraints

$$\sum_{j=1}^{m} n_j - N = 0 \text{ and } \sum_{j=1}^{m} n_j E_j - E = 0$$

Since the logarithm is a monotonically increasing function we may scout for the maximum of  $\ln P$  instead of P - this is mathematically much easier. The proven method for maximizing a function of many variables, allowing for additional constraints, is the **variational method with Lagrange multipliers** (see Problem 2.1). The variational equation

$$\delta \ln P - \delta \left( \alpha \sum_{j} n_{j} + \beta \sum_{j} E_{j} n_{j} \right) = 0$$

with the undetermined multipliers  $\alpha$  and  $\beta$  leads us, using the Stirling approximation for  $\ln P$ , to

 $-\ln n_i^* - \alpha - \beta E_j = 0$ 

Thus the optimal partitioning  $n_j^*$  is given by  $n_j^* = e^{-\alpha - \beta E_j}$ ;  $j = 1, \dots m$ 

Consequently  $f(\vec{r_j}, \vec{v_j}) \propto n_j^* = A \exp\{-\beta E(\vec{r_j}, \vec{v_j})\}$ 

In particular, we find for a dilute gas, which in the absence of external forces will be homogeneous with respect to  $\vec{\underline{r}}$ ,

$$f(\vec{v}_j) = B \exp\{-\beta (mv_j^2/2)\}$$

Using the normalizing condition  $\int f(\vec{v}) d\vec{v} = 1$  $B \int 4\pi v^2 e^{-\beta m v^2/2} dv = 1$ 

$$B = (\beta m / 2\pi)^{3/2}$$
  
we find and therefore  
$$f(\vec{v}) = \left[\frac{\beta m}{2\pi}\right]^{3/2} e^{-\beta m v^2/2}$$

Now we take a closer look at the quantity  $\beta$  which we introduced at first just for mathematical convenience. The mean kinetic energy of a particle is given by

$$\langle E \rangle \equiv \int d\vec{v} (mv^2/2) f(\vec{v}) = \frac{3}{2\beta}$$

But we will learn in Section 2.3 that the average kinetic energy of a molecule is related to the macroscopic observable quantity T (temperature) according to  $\langle E \rangle = 3kT/2$ ; therefore we have  $\beta \equiv 1/kT$ . Thus we may write the distribution density of the velocity in the customary format

$$f(\vec{v}) = \left[\frac{m}{2\pi kT}\right]^{3/2} e^{-mv^2/2kT}$$

This density in velocity space is commonly called **Maxwell-Boltzmann distribution density**. The same name is also used for a slightly different object, namely the distribution density of the **modulus** of the particle velocity (the ``speed") which may easily be derived as

$$f(|\vec{v}|) = 4\pi v^2 f(\vec{v}) = 4\pi \left[\frac{m}{2\pi kT}\right]^{3/2} v^2 e^{-mv^2/2kT}$$

So we have determined the population numbers "<sup>1</sup> of the cells in " space by maximizing the number of possible allottments. It is possible to demonstrate that the partitioning we have found is not just the most probable but **by far** the most probable one. In other words, any noticeable deviation from this distribution of particle velocities is extremely improbable (see above: multinomial distribution.) This makes for the great practical importance of the MB distribution: it is simply **the** distribution of velocities in a many particle system which we may assume to hold, neglecting all other possible but improbable distributions.



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As we can see from the figure,  $f(|\vec{v}|)$  is a skewed distribution; its **maximum** is located at

$$\tilde{v} = \sqrt{\frac{2kT}{m}}$$

This most probable speed is not the same as the mean speed,

$$\langle v \rangle \equiv \int_{0}^{\infty} dv \, v f(|\vec{v}|) = \sqrt{\frac{8}{\pi}} \sqrt{\frac{kT}{m}}$$

or the **root mean squared velocity** or *r.m.s. velocity*),

$$\overline{v}_{rms}\equiv \sqrt{\langle v^{\,2}\rangle}=\sqrt{\frac{3kT}{m}}$$

## The ensemble concept

**Ensemble**: Consider a large number of systems each described by the same set of microscopic forces and sharing some common macroscopic property (e.g. the same total energy). Each system is assumed to evolve under the microscopic laws of motion from a different initial condition so that the time evolution of each system will be different from all the others. Such a collection of systems is called an *ensemble*. The ensemble concept then

Prepared by Dr.Mohan Rangam Kadiresan, Asst Prof, Department of Physics, KAHE Page 6/12

states that macroscopic observables can be calculated by performing averages over the systems in the ensemble. For many properties, such as temperature and pressure, which are time-independent, the fact that the systems are evolving in time will not affect their values, and we may perform averages at a particular instant in time. Thus, let A denote a macroscopic property and let a denote a microscopic function that is used to compute A. An example of A would be the temperature, and a would be the kinetic energy (a microscopic function of velocities). Then, A is obtained by calculating the value of a in each system of the ensemble and performing an average over all systems in the ensemble:

$$A = rac{1}{\mathcal{N}} \sum_{\lambda=1}^{\mathcal{N}} a_{\lambda}$$

where  $\mathcal{N}$  is the total number of members in the ensemble and  $a_{\lambda}$  is the value of a in the  $\lambda$  th system.

# **Partition function**

**partition function** describes the statistical properties of a system in thermodynamic equilibrium. Partition functions are functions of the thermodynamic state variables, such as the temperature and volume. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives.

Each partition function is constructed to represent a particular statistical ensemble (which, in turn, corresponds to a particular free energy). The most common statistical ensembles have named partition functions. The **canonical partition function** applies to a canonical ensemble, in which the system is allowed to exchange heat with the environment at fixed temperature, volume, and number of particles. The **grand canonical partition function** applies to a grand canonical ensemble, in which the system can exchange both heat and particles with the environment, at fixed temperature, volume, and chemical potential. Other types of partition functions can be defined for different circumstances; see partition function (mathematics) for generalizations. The partition function has many physical meanings, as discussed in Meaning and significance.

#### **Canonical partition function**

#### Definition

Initially, let us assume that a thermodynamically large system is in thermal contact with the environment, with a temperature T, and both the volume of the system and the numbers of constituent particles are fixed. A collection of this kind of systems comprises an ensemble called a canonical ensemble. The appropriate mathematical expression for the canonical partition function depends on the degrees of freedom of the system, whether the context is classical mechanics or quantum mechanics, and whether the spectrum of states is discrete or continuous.

#### **Negative temperature**

In physics, certain systems can achieve negative temperature; that is, their thermodynamic temperature can be expressed as a negative quantity on the Kelvin or Rankine scales.

In colloquial usage, "negative temperature" may refer to temperatures that are expressed as negative numbers on the more familiar Celsiusor Fahrenheit scales, with values that are colder than the zero points of those scales but still warmer than absolute zero.

A system with a truly negative temperature on the Kelvin scale is *hotter* than any system with a positive temperature. If a negative-temperature system and a positive-temperature system come in contact, heat will flow from the negative- to the positive-temperature system.<sup>[1][2]</sup>

That a system at negative temperature is hotter than any system at positive temperature seems paradoxical if absolute temperature is interpreted as an average kinetic energy of the system. The paradox is resolved by understanding temperature through its more rigorous definition as the trade off between energy and entropy, with the *reciprocal* of the temperature, thermodynamic beta, as the more fundamental quantity. Systems with a positive temperature will increase in entropy as one adds energy to the system.<sup>[3]</sup>

Most familiar systems cannot achieve negative temperatures, because adding energy always increases their entropy. The possibility of decreasing in entropy with increasing energy requires the system to "saturate" in entropy, with the number of high energy states being small. These kinds of systems, bounded by a maximum amount of energy, are generally forbidden classically. Thus, negative temperature is a strictly quantum phenomenon. Some systems, however (see the examples below), have a maximum amount of energy that they can hold, and as they approach that maximum energy their entropy actually begins to decrease.

#### Thermodynamics functions of ideal gases

## **Internal energy**

we analyzed Bernoulli's model of a gas consisting of essentially non-interacting point-like molecules, and found the pressure  $p = 1/3\frac{1}{2} v^2$  where v is the root-mean-square average molecular speed. Using the ideal gas law the total molecular kinetic energy contained in an amount  $M = \frac{1}{2}V$  of the gas becomes, where n = M = M mol is the number of moles in the gas.

$$\frac{1}{2}Mv^2 = \frac{3}{2}pV = \frac{3}{2}nRT ,$$

The above formula thus expresses that in a mole of a gas there is an internal kinetic energy 1/2RT associated with each translational degree of freedom of the point-like molecules.

The internal energy of n moles of an ideal gas is defined to be,

$$U = 1/2 \ nRT$$
,

# Heat capacity

Suppose that we raise the temperature of the gas by  $\delta T$  without changing its volume. Since no work is performed, and since energy is conserved, the necessary amount of heat is

$$\delta Q = \delta U = C V \ \delta T$$

where, the constant, is naturally called the heat capacity at constant volume.

If instead the pressure of the gas is kept constant while the temperature is raised by  $\delta T$ , we must also take into account that the volume expands by a certain amount  $\delta V$  and thereby performs work on the surroundings. The necessary amount of heat is now larger by this work,  $\delta Q = \delta U + p \delta V$ . Using the ideal gas law (4-26) we have for constant pressure  $p \delta V = \delta (pV) = nR\delta T$ . Consequently, the amount of heat which must be added per unit of increase in temperature at constant pressure is  $C_p = CV + nR$ ,

#### **Classical entropy expression**

When neither the volume nor the pressure are kept constant, the heat that must be added to the system in an infinitesimal process is

$$\delta Q = \delta U + p \delta V = C_V \delta T + nRT \frac{\delta V}{V} \, .$$

It is a mathematical fact that there exists no function, Q(T, V), which has this expression as differential (see problem D.2). It may on the other hand be directly verified (by insertion) that

$$\delta \mathcal{S} = \frac{\delta Q}{T} = C_V \frac{\delta T}{T} + nR \frac{\delta V}{V} ,$$

can be integrated to yield a function,

 $S = CV \log T + nR \log V + \text{const} ,$ 

called the *entropy* of the amount of ideal gas. Being an integral the entropy is only defined up to an arbitrary constant. The entropy of the gas is, like its energy, an abstract quantity which cannot be directly measured. But since both quantities depend on the measurable thermodynamic quantities,  $\rho$ , p, and T, that characterize the state of the gas, we can calculate the value of energy and entropy in any state.

#### **Gibbs paradox**

In statistical mechanics, a semi-classical derivation of the entropy that does not take into account the indistinguishability of particles, yields an expression for the entropy which is not extensive (is not proportional to the amount of substance in question). This leads to a paradox known as the Gibbs paradox, after Josiah Willard Gibbs. The paradox allows for the entropy of closed systems to decrease, violating the second law of thermodynamics. A related paradox is the "mixing paradox". If one takes the perspective that the definition of entropy must be changed so as to ignore particle permutation, the paradox is averted.

The Gibbs paradox involves the contrast between mixing two quantities of (ideal) gases of a different kind and that of mixing two quantities of the same gas. ! In the case of different gases, mixing is accompanied by an entropy increase  $\Delta S = 2R \log 2$ ; in the case of same gases there is no entropy change:  $\Delta S = 0$ . ! This paradox is a useful probe for inter-theory relations: Thermodynamics vs Statistical Mechanics Thermodynamics vs. Quantum Mechanics Statistical Mechanics vs. Quantum Mechanics

consider a classical ideal gas of N 'entirely similar' particles, i.e., its Hamiltonian H(!q1,!p1; ..., ;!qN,!pN) is permutation invariant. ! Should the phase points x = (!q1,!p1; ...,!qN, !pN) and  $x! = \Pi x$  be identified or not? (with  $\Pi$  any permutation of  $\{1, ..., N\}$ ). ! Gibbs distinguishes two points of view, but does not choose sides:

# Law of equipartition of energy: Statement

According to the law of equipartition of energy, for any dynamic system in thermal equilibrium, the total energy for the system is equally divided among the degree of freedom.

The kinetic energy of a single molecule along the x axis, the y axis and the z axis is given as

$$\frac{1}{2}mv_{x}^{2}$$
, along the x-axis  
$$\frac{1}{2}mv_{y}^{2}$$
, along the y-axis  
$$\frac{1}{2}mv_{z}^{2}$$
, along the z-axis

When the gas is at thermal equilibrium, the average kinetic energy is denoted as

$$\left(\frac{1}{2}mv_{x}^{2}\right)$$
, along the x-axis  
 $\left(\frac{1}{2}mv_{y}^{2}\right)$ , along the y-axis  
 $\left(\frac{1}{2}mv_{z}^{2}\right)$ , along the z-axis

According to the kinetic theory of gases, the average kinetic energy of molecule is given by,

 $\frac{1}{2}mv_{rms}^{2} = \frac{3}{2}K_{b}T$ 

where  $V_{rms}$  is the root mean square velocity of the molecules,  $K_b$  is the Boltzmann constant and T is the temperature of the gas.

The mono-atomic gas has three degree of freedom, so the average kinetic energy per degree of freedom is given by  $KE_x = \frac{1}{2}K_bT$ 

If a molecule is free to move in space, it needs three coordinates to specify its location, thus, it possesses three transnational degrees of freedom. Similarly, if it is constrained to move in a plane, it possesses two transnational degrees of freedom and if it is a straight line, it possesses one transnational degree of freedom. In case of a tri-atomic molecule, the degree of freedom is 6. And the kinetic energy of the per molecule of the gas is given as,

$$6 \times N \times \frac{1}{2}K_bT = 3 \times \frac{R}{N}NK_bT = 3RT$$



Molecules of a mono-atomic gas like argon and helium has only one transnational degree of freedom. The kinetic energy per molecule of the gas is given by

$$3 \times N \times \frac{1}{2} K_b T = 3 \times \frac{R}{N} N K_b T = \frac{3}{2} R T$$

The diatomic gases such as  $O_2$  and  $N_2$  which have three transnational degrees of freedom can rotate only about their centre of mass. Since, they have only two independent axis of rotation, as the third rotation is negligible, due to its 2-D structure. Thus, only two rotational degrees of freedom are considered. The molecule thus has two rotational degrees of freedom, each of which contributes a term to the total energy consisting of transnational energy t and rotational energy.

# **POSSIBLE QUESTIONS**

- 1) Explain Maxwell's Boltzmann's Distribution Law.
- 2) Explain Ensembles Concept.
- 3) Explain Partition Functions
- 4) Explain Thermodynamic functions of an ideal gas.
- 5) Explain Gibb's Paradox
- 6) Explain Law of Equipartition of Energy
- 7) Explain Classical Entropy expression using Boltzmann's Relation.

#### DEPARTMENT OF PHYSICS III BSc PHYSICS (15PHU602) STATISTICAL MECHANICS

#### Unit-I

Questions	opt1	opt2	opt3	opt4	Answer
The term "thermodynamics" comes from Greek. words "therme" and					
"dynamis" which means	Heat power	Heat transfer	Heat energy	Heat motion	Heat power
The term "thermodynamics" was first used in 1849 in the publication					
of a	Rudolph Clausius	William Rankine	Lord Kelvin	Thomas Savery	Lord Kelvin
The macroscopic approach to the study of thermodynamics does not					
require a knowledge of the behavior of individual particles is called	Dynamic		Statistical	Classical	Classical
	thermodynamics	Static thermodynamics	thermodynamics	thermodynamics	thermodynamics
	First law of	Second law of	Third law of	Zeroth law of	First law of
What law asserts that energy is a thermodynamic property?	Thermodynamics	Thermodynamics	Thermodynamics	Thermodynamics	Thermodynamics
	First law of	Second law of	Third law of	Zeroth law of	Second law of
What law asserts that energy has quality as well as quantity?	Thermodynamics	Thermodynamics	Thermodynamics	Thermodynamics	Thermodynamics
The first law of thermodynamics is based on which of the following				The entropy-temperature	
principles?	mass of energy	Conservation of energy		relationship	Conservation of energy
	microscopic systems	macroscopic systems	homogeneous systems	heterogeneous systems	macroscopic systems
Thermodynamics is applicable to	only	only	only	only.	only
	it ignores the internal		it is concerned only with		
	structure of atoms and	it involves the matter in	the initial and final states	it is not applicable to	it is not applicable to
Which is not true about thermodynamics ?	molecules	bulk	of the system	macroscopic systems.	macroscopic systems.
A system that can transfer neither matter nor energy to and from its				1 2	1 5
surroundings is called	closed system	an isolated system	an open system	a homogeneous system	an isolated system
Which of the following is incorrect, for an ideal gas?	PV= nRT	V = nRT/P	P=nRT/V	P = RT	PV= nRT
The heat capacity at constant pressure is related to heat capacity at					
constant volume by the relation	Cp-R =Cv	Cv-R =Cp	Cp-Cv=R	R-Cp = Cv	Cp-Cv=R
A system is in equilibrium if the temperature is the same		-		•	-
throughout the entire system.	Static	Thermal	Mechanical	Phase	Thermal
A system is in equilibrium if there is no change in pressure at					
any point of the system with time.	Pressure	Thermal	Mechanical	Phase	Mechanical
If a system involves two phases, it is in equilibrium when the					
mass of each phase reaches an equilibrium level and stays there.	Chemical	Thermal	Mechanical	phase	phase
A system is in equilibrium of its chemical composition does				-	-
not change with time, i.e., no chemical reaction occurs.	Chemical	Thermal	Mechanical	Phase	Chemical
A system is said to be in thermodynamic equilibrium if it maintains			Thermal, mechanical and	Thermal, phase,	Thermal, phase,
equilibrium.	Mechanical and phase	Thermal and chemical	chemical	mechanical and chemical	mechanical and chemical
What is a process with identical end states called?	Cycle	Path	Phase	Either path or phase	Cycle
What is a process during which the temperature remains constant?	Isobaric process	Isothermal process	Isochoric process	Isometric process	Isothermal process
What is a process during which the pressure remains constant?	Isobaric process	Isothermal process	Isochoric process	Isometric process	Isobaric process
What is a process during which the specific volume remains			Isochoric or isometric		Isochoric or isometric
constant?	Isobaric process	Isothermal process	process	Isovolumetric process	process

What states that if two bodies are in thermal equilibrium with a third	Zeroth law of	First law of	Second law of	Third law of	Zeroth law of
body, they are also in equilibrium with each other?	thermodynamics	thermodynamics	thermodynamics	thermodynamics	thermodynamics
What is the study of energy and its transformations?	Thermostatics	Thermophysics	Thermochemistry	Thermodynamics	Thermodynamics
What is considered as the heat content of a system?	Enthalpy	Entropy	Internal heat	Molar heat	Enthalpy
What refers to the amount of heat needed to raise the temperature of					
an object by one degree Celsius or 1K?	Heat capacity	Specific heat	Latent heat	Molar heat	Heat capacity
What is the heat capacity of one mole of substance?	Molecular heat	Specific heat	Latent heat	Molar heat	Specific heat
What refers to the measure of the disorder present in a given					
substance or system?	Enthalpy	Entropy	Heat capacity	Molar heat	Entropy
Entropy is measured in	Joule/Kelvin	Joule-Meter/Kelvin	Meter/Kelvin	Newton/Kelvin	Joule/Kelvin
What is the energy absorbed during chemical reaction under constant					
volume conditions?	Entropy	Ion exchange	Enthalpy	Enthalpy of reaction	Enthalpy
Which of the following equation is used to calculate the heats of	Gibbs Helmholtz				Gibbs Helmholtz
reaction when $\Delta G$ at two temperatutes are given?	equatioin	Clapeyron equation	Kirchoffs equation	Nernst equation	equatioin
is applicable to macroscopic systems only.	thermochemistry	thermokinetics	thermodynamics	thermochemical studies.	thermodynamics
	first law of	second law of		third law of	first law of
$\Delta E = q$ -w for an isochoric process	thermodynamics	thermodynamics	zeroth's law	thermodynamics	thermodynamics
Who proposed the Carnot cycle?	Sammy Carnot	Sonny Carnot	Sadi Carnot	Suri Carnot	Sadi Carnot
Entropy is transferred by	Work	Heat	Energy	Work and heat	Heat
The specific heat of a gas in isothermal process is	Zero	Negative	Remains constant	Infinite	Infinite
The difference between the principal specific heats of nitrogen is 300					
J/kg $\Box$ K and ratio of the two specific heats is 1.4. then the CP is	1050 J/kg °K	650 J/kg °K	750 J/kg °K	150 J/kg °K	650 J/kg °K
Which of the following variables controls the physical properties of a	-	_			
perfect gas?	Pressure	Temperature	Volume	Atomic mass	Atomic mass
A system in which state variables have constant values throughout				0.1	
the system is called in a state of	equilibrium	non- equilibrium	isothermal equilibrium	none of these.	equilibrium
In an adiabatic process can flow in to or out of the system.	no heat	heat	matter	no matter	no heat
For an adiabatic process according to first law of thermodynamics,	$\Delta E = -W$	$\Delta E = W$	$\Delta E = q - w$	$\Delta q = E - W$	$\Delta E = q - w$
The enthalpy change, $\Delta H$ of a process is given by the relation	$\Delta H = \Delta E + p \Delta v$	$\Delta H = \Delta E + \Delta n R I$	$\Delta H = \Delta E + W$	$\Delta H = \Delta E - \Delta n R I$	$\Delta H = \Delta E + p \Delta v$
The amount of heat required to raise the temperature of one mole of	1	1 1 4 4	1 1 .	1 .	1 1
the substance by 1 K is called	heat capacity	molar heat capacity	molar heat	molar capacity.	molar heat capacity
Which of the following is not correct?	H=E+PV	H-E=PV	H-E-PV=0	H=E-PV	H=E-PV
The enthalpy of a system is defined by the relation	H=E+PV Draggyurg	H=E-PV	E=H+PV	PV+E-H domaita	H=E+PV domoita
which of the following quantities is not the property of the system	Pressure	temperature	neat	density	Only one yelve of
Calidand limida harr	Only one value of	I wo value of specific	Infee value of specific	N	Only one value of
Solid and liquids have	specific neat	neat	neat	No value of specific neat	specific neat
The terms NLT D stern de ferr		Natural temperature and	Normal temperatuere		
The term N.T.P stands for	and pressurre	pressure	and pressure	pressure	and pressure
The moments of a monthing substance which increases on decreases as					
the property of a working substance which increases of decreases as	anthalny	internal anargy	ontrony	avtarnal anargy	ontrony
In an irrayaraible process there is a	loss of best	ne loss of heat	enu opy	external energy.	loss of best
	increasing the highest	decreasing the highest	increasing the lowest	degraging the lowest	decreasing the lowest
The officiency of the Cornet avale may be increased by	temporature	temperature	tomporature	temperature	tomporature
Workdone in a free expansion process is		minimum	maximum	positivo	zero
workuone in a free expansion process is	Zeit	mmmum	maximum	positive	2010
The entropy of water at 0°C is assumed to be	1	A 100	1	10	A

During which of the following process does heat rejection takes					
place in Carnot cycle?	Isothermal expansion	Isentropic expansion	Isothermal compression	Isentropic compression	Isothermal compression
The gas constant (R) is equal to the of two specific					
heats.	sum	difference	product	ratio	difference
	partial combustion of			passing air and a large	partial combustion of
	coal, coke, anthracite			amount of steam over	coal, coke, anthracite
	coal or charcoal in a	carbonisation of	passing steam over	waste coal at about	coal or charcoal in a
Producer gas is obtained by	mixed air steam blast	bituminous coal	incandescent coke	650°C	mixed air steam blast
			conversion of heat into	conversion of work into	conversion of heat into
Kelvin-Planck's law deals with	conservation of work	conservation of heat	work	heat	work
If the value of $n = 0$ in the equation $pvn = C$ , then the process is			constant pressure		constant pressure
called	constant volume process	adiabatic process	process	isothermal process	process
For a reversible adiabatic process, the change in entropy is	zero	minimum	maximum	positive	zero
For any irreversible process the net entropy change is	zero	Negative	infinity	positive	positive
For any reversible process, the change in entropy of the system and					
surroundings is	zero	Negative	infinity	positive	zero

# UNIT-II

# **SYLLABUS**

Statistical definition of temperature, pressure, entropy and chemical potential. Partition function of a system in thermal equilibrium with a heat bath.

# **Classical Theory of Radiation**

Properties of Thermal Radiation. Blackbody Radiation. Pure Temperature Dependence. Kirchhoff's Law. Stefan-Boltzmann Law and Wien's Displacement law. Saha's Ionization Formula. Saha equation for thermal ionization and its application to astrophysics.

# ENTROPY AND TEMPERATURE

Entropy and Temperature Temperature has been defined (via the zeroth law) as the observable which is the same for two systems in thermal equilibrium. It has also been seen to represent (using a microscopic point of view) the energy per degree of freedom. We can now give a precise, purely macroscopic definition of temperature via the entropy. Consider two systems in thermal contact, A and B, with some given total energy U = UA + UB and otherwise isolated from the rest of the universe. As we have discussed, the two systems will exchange energy (with U not changing) until the entropy of the combined system is as big as possible, at which point we have equilibrium. This means that the derivative of the total entropy S = SA + SB with respect to either UA or UB must vanish at equilibrium. We have  $0 = \partial SA \partial UA + \partial SB \partial UA = \partial SA \partial UA - \partial SB \partial UA$  $\partial SB \partial UB$ . The last equality above uses the fact that the total energy is fixed so that 0 = dU = $dUA + dUB \Rightarrow dUA = -dUB$ . So, we conclude that (holding fixed all other variables which the entropy may depend upon) the slope of the entropy vs. energy graph for each of systems A and B will become equal at equilibrium. This means that we can define temperature via the slope of these graphs. The precise definition is 1 T =  $\partial S \partial U N, V, \dots$ , where the notation "N, V, . . ." indicates that we hold fixed the volume and number of particles of the system. The idea here is that "equilibrium" means thermal, mechanical, and diffusive equilibrium. The latter two forms of equilibrium involve equality of pressure and chemical potential (as we shall discuss below), which we will analyze by varying the volume and number of particles of each subsystem. The entropy is to be maximized with respect to changes in each of U, V, N; we are currently considering the conditions coming from varying energy

Entropy We have seen that the equilibrium state for an isolated macroscopic thermal system is the one with the highest multiplicity. Obviously, the multiplicity of a macrostate is an important observable of the system. This is, of course, a huge number in general. To keep things manageable — and to give us other important properties, to be discussed later — we define a corresponding observable using the natural logarithm of the multiplicity times Boltzmann's constant. This is the entropy\*  $S = k \ln \Omega$ . The SI units of entropy are J/K.

## **EMISSIVE POWER**

The emissive power  $e_{\lambda}$  of a body at a given temperature for radiant energy of wavelength  $\lambda$  is defined as the energy emitted per unit area per sec.per unit range of wavelength  $\frac{b}{n} \lambda \& \lambda + d \lambda$  at the given temperature.

unit $\rightarrow$ 1 walt per square meter per Angstrom.

# **ABSORPTIVE POWER** $(a_{\lambda})$ :

The absorptive power  $a_{\lambda}$  of a body at a given temperature for radiant energy of wavelength  $\lambda$  is the ratio of radiant energy of wavelength  $\lambda$  is absorbed per unit area per second., by the body at the given temperature to the radiant energy of the same wavelength incident on unit area per second at the temperature.

For perfectly black body  $a_{\lambda}=1$ .

# Kirchoff"s law of Radiation:

The law states that the ratio of the emissive power  $e_{\lambda}$  of a body for any wavelength at a given temperature to its absorptive power  $a_{\lambda}$  for the wavelength at the temperature is constant and is equal to the emissive power  $E_{\lambda}$  of a perfectly black body at that temperature.

#### **Black Body Radiation:**

A body which completely absorbs radiation of all wavelength incidenton it is called *perfectly black boby*. since a good absorber of radiation is also a good emitter of radiation, a perfectly black body is the best possible emitter at any given temperature .The radiation emitted by such kind of body is called black body radiation, or full radiation or temperature radiation.

A perfectly black body is an ideal conception. There is no known surface which can be regarded as perfectly black. Lamp black or platinum black is the nearest approach to the perfectly black body. Lamp black can absorb about 96% of the radiant energy incident on it, &platinum black absorbs about 98%. In practice almost perfectly black body consist of a double-walled hollow metal sphere. The sphere has a small hole O. There is conical projection P opposite the hole. The inner surface of the sphere is coated with lamp black. The space between the wall is evacuated to prevent loss of heat by conduction or convention .when any radiant energy enters the space through the hole, it suffers multiple reflections. At each reflection about 96% of the incident radiant energy is absorbed .hence after few reflections all the radiant energy is absorbed by the sphere. The function of the conical projection is to prevent direct reflection of the radiant energy from the surface opposite to the hole. The hole O in the sphere acts as a perfectly black body because it absorbs all the radiant energy incident on it. When the sphere is heated black body radiation is emitted from the hole.

## **BLACK BODY RADIZTION AND THE PLANCK RADIATION LAW:**

As the temperature decreases, the peak of the black body radiation curve moves to lower intensities and longer wavelengths. The black-body radiation graph is also compared with the classical model that preceded it. In physics a black body is an object that absorbs all light that falls onto it: no light passes through it nor is reflected. Despite the name, black bodies do produce thermal radiation such as light. The term "black body" was introduced by Gustav Kirchhoff in 1862. The light emitted by a black body is called black-body radiation.

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When used as a compound adjective, the term is typically hyphenated, as in "black-body radiation", or combined into one word, as in "blackbody radiation". The hyphenated and oneword forms should not generally be used as nouns, however, In the laboratory, the closest thing to a black body radiation is the radiation from a small hole in a cavity: it 'absorbs' little energy from the outside if the hole is small, and it 'radiates' all the energy from the inside which is black. However, the spectrum (i.e. the amount of light emitted at each wavelength) of its radiation will not be continuous, and only rays will appear whose wavelengths depend on the material in the cavity (see Emission spectrum). By extrapolating the spectrum curve for other frequencies, a general curve can be drawn, and any black-body radiation will follow it. This curve depends only on the temperature of the cavity walls.



The observed spectrum of black-body radiation could not be explained with Classical electromagnetism and statistical mechanics: it predicted infinite brightness at low wavelength (i.e. high frequencies), a prediction often called the ultraviolet catastrophe.

This theoretical problem was solved by Max Planck, who had to assume that electromagnetic radiation could propagate only in discrete packets, or quanta. This idea was later used by Einstein to explain the photoelectric effect. These theoretical advances eventually resulted in the replacement of classical electromagnetism by quantum mechanics. Today, the quanta are called photons.

The intensity of radiation from a black body at temperature T is given by Planck's law of black body radiation:

Where, 
$$I(\nu) = \frac{2h\nu^3}{c^2} \frac{1}{\exp(h\nu/kT) - 1}$$

 $I(\nu)\delta\nu$  is the amount of energy per unit surface per unit time per unit solid angle emitted in the frequency range between v and v+ $\delta v$ ;

h is Planck's constant

c is the speed of light

k is Boltzmann's constant.

The wavelength at which the radiation is strongest is given by Wien's law, and the overall power emitted per unit area is given by the Stefan-Boltzmann law. So, as temperature increases, the glow color changes from red to yellow to white to blue. Even as the peak wavelength moves into the ultra-violet enough radiation continues to be emitted in the blue wavelenths that the body will continue to appear blue. It will never become invisible—indeed, the radiation of visible light increases monotonically with temperature.

The radiance or observed intensity is not a function of direction. Therefore a black body is a perfect Lambertian radiator.

Real objects never behave as full-ideal black bodies, and instead the emitted radiation at a given frequency is a fraction of what the ideal emission would be. The emissivity of a material specifies how well a real body radiates energy as compared with a black body. This emissivity depends on factors such as temperature, emission angle, and wavelength. However, a typical engineering assumption is to assume that a surface's spectral emissivity and absorptivity do not depend on wavelength, so that the emissivity is a constant. This is known as the grey body assumption. When dealing with non-black surfaces, the deviations from ideal black body behavior are determined by both the geometrical structure and the chemical composition, and

follow Kirchhoff's Law: emissivity equals absorptivity, so that an object that does not absorb all incident light will also emit less radiation than an ideal black body.

In astronomy, objects such as stars are frequently regarded as black bodies, though this is often a poor approximation. An almost perfect black-body spectrum is exhibited by the cosmic microwave background radiation. Hawking radiation is black-body radiation emitted by black holes.

# KIRCHHOFF'S LAW.

In heat transfer, **Kirchhoff's law of thermal radiation** refers to wavelength-specific radiative emission and absorption by a material body in thermodynamic equilibrium, including radiative exchange equilibrium.

A body at temperature *T* radiates electromagnetic energy. A perfect black body in thermodynamic equilibrium absorbs all light that strikes it, and radiates energy according to a unique law of radiative emissive power for temperature *T*, universal for all perfect black bodies. Kirchhoff's law states that:

For a body of any arbitrary material emitting and absorbing thermal electromagnetic radiation at every wavelength in thermodynamic equilibrium, the ratio of its emissive power to its dimensionless coefficient of absorption is equal to a universal function only of radiative wavelength and temperature. That universal function describes the perfect black-body emissive power.<sup>[1][2][3][4][5][6]</sup>

Here, the dimensionless coefficient of absorption (or the absorptivity) is the fraction of incident light (power) that is absorbed by the body when it is radiating and absorbing in thermodynamic equilibrium.

In slightly different terms, the emissive power of an arbitrary opaque body of fixed size and shape at a definite temperature can be described by a dimensionless ratio, sometimes called the emissivity, the ratio of the emissive power of the body to the emissive power of a black body of the same size and shape at the same fixed temperature. With this definition, Kirchhoff's law states:

For an arbitrary body emitting and absorbing thermal radiation in thermodynamic equilibrium, the emissivity is equal to the absorptivity.

In some cases, emissive power and absorptivity may be defined to depend on angle, as described below. The condition of thermodynamic equilibrium is necessary in the statement, because the equality of emissivity and absorptivity often does not hold when the material of the body is not in thermodynamic equilibrium.

Kirchhoff's law has another corollary: the emissivity cannot exceed one (because the absorptivity cannot, by conservation of energy), so it is not possible to thermally radiate more energy than a black body, at equilibrium. In negative luminescence angle and wavelength integrated absorption exceeds the material's emission, however, such systems are powered by an external source and are therefore not in thermodynamic equilibrium.

# STEFAN-BOLTZMANN LAW

According to Stefan's law, the total radiant heat energy that is emitted by a surface is proportional to fourth power of its absolute temperature. The same law was derived by Austrian physicist Ludwig Boltzmann in 1884 based on thermodynamic considerations which state: if E denoted radiant heat energy to be emitted by a unit area in one second and T denotes absolute temperature (in kelvin), then  $E=\sigma T4$ . The Stefan's law is applicable only to black bodies and theoretical surfaces that absorb the incident heat radiation.

For hot objects apart from ideal radiators, the law is described in the following manner.

PA=eoT4

Here,

E indicates object's emissivity which is 1 for ideal radiator

If the hot body radiates energy to cooler objects at <u>temperature</u> Tc, the rate of net radiation loss is of the form,

 $P=e\sigma A(T4-T4c)$ 

# Where,

The constant of proportionality  $\sigma$  is called the Stefan Boltzmann constant and has a value

of  $\sigma$ =5.6704×10-8wattpermetre2.K4

P denotes net radiated power

E is emissivity shows radiating area

T is radiator's temperature

Tc is surrounding temperature

The actual law states that the total energy radiated per unit surface area of a black body across all wavelengths per unit time is directly proportional to the fourth power of the black body's temperature. The expression for this is;

 $j=\sigma T4$  : For a Black Body

 $j = \varepsilon \sigma T4$ : For Real bodies with emissivity < 1

# Heat Radiation:

Thermal radiation is the transfer of energy by emitting electromagnetic waves that carry energy away from the emitting body. The radiation lies in the infrared region of the electromagnetic spectrum. The relevance that governs net radiation from hot bodies is known as Stefan-Boltzmann law.

If the surrounding is at higher i.e, Tc > T, you obtain a negative value which implies net radiative transfer to the object.

Stefan Boltzmann Law has been used to accurately find the temperature of several celestial bodies like the Sun, the Earth and the Stars.

- Sun: Stefan used a thin metal plate to approximate the energy received and radiated by the Earth. Assuming that the sun is a black body, Stefan was successfully able to incorporate Earth's received radiation into his calculation. Stefan calculated the temperature to be 5700 K which is very close to the modern value of 5778K. In contrast the values then were ranging from 1800°Cto as high as 13000000°C.
- **Stars:** By using the Luminosity of a star, its surface temperature could be found. The <u>stars</u> in this case are treated as Black Bodies. Using this not only can the temperature be found, but also the radii of very distant stars.

• Earth: Stefan calculated the temperature of the Earth by using the energy received from the sun and energy radiated by the Earth. He unfortunately failed to account for the reflection of a part of the received radiation, greenhouse effect and thereby was not able to calculate the temperature of the Earth with considerable accuracy. He calculated the average temperature of the Earth as 6°C On including such effects we come upon the correct answer of 15°C.

## WIEN'S DISPLACEMENT LAW.

It states that the black body radiation curve for different temperatures peaks at a wavelength inversely proportional to the temperature. The shift of that peak is a direct consequence of the Planck radiation law, which describes the spectral brightness of black body radiation as a function of wavelength at any given temperature. However, it had been discovered by Wilhelm Wien several years before Max Planck developed that more general equation, and describes the entire shift of the spectrum of black body radiation toward shorter wavelengths as temperature increases.

Formally, Wien's displacement law states that the spectral radiance of black body radiation per unit wavelength, peaks at the wavelength  $\lambda_{max}$  given by:

where *T* is the absolute temperature in kelvins. *b* is a constant of proportionality called *Wien's displacement constant*, equal to  $2.8977729(17) \times 10^{-3} \text{ m} \cdot \text{K}^{[1]}$ , or more conveniently to obtain wavelength in micrometers,  $b \approx 2900 \,\mu\text{m} \cdot \text{K}$ . If one is considering the peak of black body emission per unit frequency or per proportional bandwidth, one must use a different proportionality constant. However, the form of the law remains the same: the peak wavelength is inversely proportional to temperature.

# SAHA'S IONIZATION FORMULA.

The Saha ionization equation, also known as the Saha–Langmuir equation, is an expression that relates the ionization state of a gas in thermal equilibrium to the temperature and pressure.<sup>[1][2]</sup> The equation is a result of combining ideas of quantum mechanics and statistical

mechanics and is used to explain the spectral classification of stars. The expression was developed by the Indian astrophysicist Meghnad Saha in 1920, and later (1923) by Irving Langmuir.

For a <u>gas</u> at a high enough <u>temperature</u> and/or <u>density</u>, the thermal collisions of the atoms will <u>ionize</u> some of the atoms, making an ionized gas. When several or more of the electrons that are normally bound to the atom in orbits around the atomic nucleus are freed, they form an independent electron gas cloud co-existing with the surrounding gas of atomic ions and neutral atoms. In turn, this generates an <u>electric field</u>, where the motion of charges generates currents, making a localised <u>magnetic field</u>, and creates the state of matter called <u>plasma</u>.

The Saha equation describes the degree of ionization for any gas in thermal equilibrium as a function of the temperature, density, and ionization energies of the atoms. The Saha equation only holds for weakly ionized plasmas for which the <u>Debye length</u> is large. This means that the screening of the Coulomb interaction of ions and electrons by other ions and electrons is negligible. The subsequent lowering of the ionization potentials and the "cutoff" of the <u>partition function</u> is therefore also negligible.

## Saha equation its application to astrophysics. (Stellar atmospheres)

In the early twenties Ralph H. Fowler developed a very powerful method in statistical mechanics permitting a systematic exposition and working out of the equilibrium properties of matter. He used this to provide a (rigorous) derivation of the ionization formula which as described earlier Saha had obtained by extending to ionization of atoms. A significant improvement in the Saha equation introduced by Fowler was to include the effect of the excited states of atoms and ions. The maximum intensity of absorption lines was much more fruitful in giving information about physical parameters of stellar atmospheres than the criterion employed by Saha which consisted in the marginal appearance or disappearance of absorption lines.

Saha had concentrated on the marginal appearances and disappearances of absorption lines in the stellar sequence, assuming an order of magnitude for the pressure in a stellar atmosphere and calculating the temperature where increasing ionization, for example, inhibited further absorption of the line in question owing to the loss of the series electron. As Fowler and I were one day stamping round my rooms in Trinity and discussing this, it suddenly occurred to me that the maximum intensity of the Balmer lines of hydrogen, for example, was readily explained by the consideration that at the lower temperatures there were too few excited atoms to give appreciable absorption, whilst at the higher temperatures there are too few neutral atoms left to give any absorption. ..That evening I did a hasty order of magnitude calculation of the effect and found that to agree with a temperature of  $10000^{\circ}$  [K] for the stars of type A0, where the Balmer lines have their maximum, a pressure of the order of  $10^{-4}$  atmosphere was required. This was very exciting, because standard determinations of pressures in stellar atmospheres from line shifts and line widths had been supposed to indicate a pressure of the order of one atmosphere or more, and I had begun on other grounds to disbelieve this.

## **Possible Questions**

- 1) Explain Black body Radiation
- 2) Explain Krichoff's Law
- 3) Describe the applications of Saha's equation in astrophysics.
- 4) Explain Rayleigh Jean's Law.
- 5) Derive Saha's equations for Thermal ionization.
- 6) Explain Wien's Displacement Law from Plank's Law.
- 7) Describe Plank's Quantum Postulates.

#### DEPARTMENT OF PHYSICS III BSc PHYSICS (15PHU602) STATISTICAL MECHANICS

#### Unit-II

Questions	opt1	opt2	opt3	opt4	Answer
The value of gas constant (R) in S. I. units is	0.287 J/kgK	2.87 J/kgK	28.7 J/kgK	287 J/kgK	287 J/kgK
Gibb's function is expressed as,	G = H + TS	G = H / TS	G=H-TS	G = H * TS	G=H-TS
The sum of internal energy (U) and the product of					
pressure and volume (p.v) is known as	workdone	entropy	enthalpy	free energy	enthalpy
	Temperature, specific	Temperature, specific	Temperature, specific		
Internal energy of a perfect gas depends on	heats and pressure	heats and enthalpy	heats and entropy	Temperature only	Temperature only
	Only dependent on				
At critical point the enthalpy of vaporisation is	temperature	zero	minimum	maximum	zero
The term "enthalpy" comes from Greek "enthalpen"					
which means	warm	hot	heat	cold	heat
Total heat of a substance is a function of only	temperature	pressure	volume	none	none
CP and CV are the principal specific heat of a gas. In					
terms of mechanical units, CP – CV is equal to	R	R/J	R/MJ	R/M	R/MJ
Helmhotz free energy F of a system of particles is	F=U-TS	F=U/TS	F=U+TS	F=UTS	F=U-TS
defined by	1 0 15	1 0/10	1 0 10	1 015	1 0 10
of a system of particles is given by $F = U -$		free energy	helmholtz function	Gibb's free energy	
TS	Helmholtz free energy	nee energy		Glob 5 Hee energy	Helmholtz free energy
A decrease in the Helmholtz function of a system is			change in internal		
equal to:	change in temperature	external work done	energy	change in energy	external work done
In a gas the transport of momentum gives rise to the					
phenomenon of	viscosity	conduction	diffusion	volume	viscosity
Joule-Thomson effect is related to	adiabatic compression	adiabatic expansion	isothermal expansion	isothermal compression	adiabatic expansion
The specific heat of a solid is 5 cal/g/°C. Then heat					
required to raise its temperature by 20 °C is:	150 cal	25 cal	100 cal	15 cal	100 cal
P, T are $\rho$ are the pressure, absolute temperature and			~ ~	- / -	
density of an ideal gas, then:	$PT/\rho = constant$	$P \rho/T = \text{constant}$	$PT \rho = \text{constant}$	$P/\rho T = \text{constant}$	$P/\rho T = \text{constant}$
For the system of diatomic gas the number of degrees of			_		
freedom are:	2	4	5	6	6
If dQ is the amount of heat supplied and dW is the work					
done, then in isothermal process:	dQ + dW = 0	dQ - dW = 0	dQ/dW = 0	dQ * dW = 0	dQ + dW = 0
					amount oh heat
Increase in temperature of body is proportional to	amount of heat absorbed	amount of heat evolved	density of substance	average kinetic energy	absorbed
l cal =	1.2 joule	3.2 joule	4.2 joule	2 joule	4.2 joule
	Only one value of	I wo value of specific	Three value of specific	No value of specific	No value of specific
Gases have	specific heat	heat	heat	heat	heat

A pure substance which exists in a single phase has					
independent variables.	zero	one	two	three	two
Maxwell's equations consists of equations.	four	one	two	three	four
Which of the following is not a Maxwell equation?	$(\partial T/\partial V) = -(\partial p/\partial S)$	$(\partial T/\partial p) = -(\partial V/\partial S)$	$(\partial p/\partial T) = (\partial S/\partial V)$	$(\partial V/\partial T) = -(\partial S/\partial p)$	$(\partial T/\partial p) = -(\partial V/\partial S)$
The condition for exact differential is	$(\partial N/\partial y) = (\partial M/\partial x)$	$(\partial M/\partial y) = (\partial N/\partial x)$	$(\partial M/\partial y) = -(\partial N/\partial x)$	$(\partial N/\partial y) = -(\partial M/\partial x)$	$(\partial M/\partial y) = (\partial N/\partial x)$
	TdS=Cv*dT +	TdS=Cv*dT -	TdS=Cv*dT +	TdS=Cv*dT-	TdS=Cv*dT +
The first TdS equation is	$T(\partial T/\partial p)dV$	$T(\partial p/\partial T)dV$	$T(\partial p/\partial T)dV$	$T(\partial T/\partial p)dV$	$T(\partial p/\partial T)dV$
	TdS=Cp*dT +	TdS=Cp*dT -	TdS=Cp*dT +	TdS=Cp*dT -	TdS=Cp*dT -
The second TdS equation is	$T(\partial V/\partial T)dp$	$T(\partial V/\partial T)dp$	$T(\partial T/\partial V)dp$	$T(\partial T/\partial V)dp$	$T(\partial V/\partial T)dp$
	$(\partial p/\partial V)^*(\partial V/\partial T)^*(\partial T/\partial$				
Which of the following is true?	p)= infinity	p) = 0	p)= 1	p)= -1	p)= -1
What do we get on equating the first and second TdS	Cp-Cv =	Cp-Cv =	Cp+Cv =	Cp+Cv =	Cp-Cv =
equations?	$T^*(\partial T/\partial p)^*(\partial V/\partial T)$	$T^*(\partial p/\partial T)^*(\partial V/\partial T)$	$T^*(\partial p/\partial T)^*(\partial V/\partial T)$	$T^*(\partial p/\partial T) + (\partial V/\partial T)$	$T^*(\partial p/\partial T)^*(\partial V/\partial T)$
Consider the equation $Cp-Cv = -T^*(\partial p/\partial V)(\partial V/\partial T)^2$ ,	$(\partial V/\partial T)^2$ is always	$(\partial p/\partial V)$ for any	(Cp-Cv) is always		
which of the following is correct?	positive	substance is negative	positive	all	all
For an ideal gas,	Cp-Cv = R	Cp-Cv = mR	Cp=Cv	Cp=-Cv	Cp-Cv = mR
	volume expansivity =				
	$(1/V)^*(\partial V/\partial T)$ at p and				
	isothermal	isothermal	isothermal	isothermal	isothermal
The volume expansivity and isothermal compressibility	compressibility = (-	compressibility =	compressibility = (-	compressibility =	compressibility = (-
is defined as	$1/V$ )*( $\partial V/\partial T$ ) at T	$(1/V)^*(\partial V/\partial T)$ at T	$1/V$ )*( $\partial T/\partial V$ ) at T	$(1/V)^*(-\partial T/\partial V)$ at T	$1/V$ )*( $\partial V/\partial T$ ) at T
	Cp-Cv =	Cp-Cv =	Cp-Cv = T*V*(volume	Cp-Cv = T*V*(volume)	Cp-Cv = T*V*(volume
	T*V*(isothermal	T*V*(isothermal	expansivity)^2 /	expansivity) /	expansivity)^2 /
The equation $Cp-Cv = -T^*(\partial p/\partial V)(\partial V/\partial T)^2$ can also	compressibility)^2 /	compressibility) /	(isothermal	(isothermal	(isothermal
be expressed as	(volume expansivity)	(volume expansivity)	compressibility)	compressibility)	compressibility)
At constant entropy, the two TdS equations give us the					
relation	Cp+Cv = 0	Cp=Cv	Cp-Cv = mR	$Cp/Cv = \gamma$	$Cp/Cv = \gamma$
The slope of an isentrope is the slope of an					
isotherm on p-v diagram.	less than	greater than	equal to	less than or equal to	greater than
	1/(isothermal	isothermal	adiabatic	isothermal	isothermal
	compressibility	compressibility *	compressibility /	compressibility /	compressibility /
	*adiabatic	adiabatic	isothermal	adiabatic	adiabatic
Which of the following relation gives $\gamma$ .	compressibility)	compressibility	compressibility	compressibility	compressibility
According to the Clausius' theorem, the cyclic integral					
of for a reversible cycle is zero.	dW/dT	dH/dT	dQ/dT	dE/dT	dQ/dT
The efficiency of a general cycle will be the					
efficiency of a reversible cycle	equal to	less than	equal to or greater than	equal to or less than	equal to or less than
The cyclic integral of entropy is	one	zero	infinity	cannot be determined	zero
Which of the following is known as the inequality of	cyclic integral of	cyclic integral of	cyclic integral of	cyclic integral of	cyclic integral of
Clausius?	dQ/T<=0	dQ/T>=0	dW/T<=0	dW/T>=0	dQ/T<=0
If the cyclic integral of dQ/T is less than zero then the	irreversible but not				
cycle is	possible	irreversible and possible	impossible	reversible	irreversible and possible

	irreversible but not				
If the cyclic integral of dQ/T is zero then the cycle is	possible	irreversible and possible	impossible	reversible	reversible
If the cyclic integral of dQ/T is greater than zero then	irreversible but not				
the cycle is	possible	irreversible and possible	impossible	reversible	impossible
If dQ is the heat supplied at T and dQ2 is the heat					
rejected at T2, then efficiency is given by	1-(dQ2/dQ)	1-(dQ/dQ2)	(dQ/dQ2)-1	(dQ2/dQ)-1	1-(dQ2/dQ)
				fusion curve and	fusion curve and
	fusion curve and	fusion curve and	vaporization curve and	vaporization curve and	vaporization curve and
Which of the following curves meet at triple point?	vaporization curve	sublimation curve	sublimation curve	sublimation curve	sublimation curve
The slopes of sublimation and vaporization curves for					
all substances are	negative	positive	zero	infinity	positive
The slope of the fusion curve for water is	negative	positive	zero	infinity	negative
Which of the following represents the latent heat of					
vaporization at a particular pressure.	Hf-Hg	Hg-Hf	Hf+Hg	Hg+Hf	Hg-Hf
At critical pressure, value of Hg-Hf is	two	one	zero	infinity	zero
The locus of all points at which the Joule-Kelvin					
coefficient is is the inversion curve.	negative	positive	zero	infinity	zero
The region inside the inversion curve has Joule-					
Kelvin coefficient and the region outside the inversion					
curve has Joule-Kelvin coefficient.	positive, positive	negative, negative	negative, positive	positive, negative	positive, negative
For a gas being throttled, the change in temperature can					
be	positive	negative	zero	all	all
Maximum temperature drop occurs if the initial state					
lies the inversion curve.	above	on	below	zero	on
	volume expansivity = T	volume expansivity =	volume expansivity =	volume expansivity = T	volume expansivity =
	and Joule-Kelvin	(1/T) and Joule-Kelvin	(1/T) and Joule-Kelvin	and Joule-Kelvin	(1/T) and Joule-Kelvin
For an ideal gas,	coefficient = 0	coefficient = 1	coefficient = 0	coefficient = 1	coefficient = 0
The amount of heat required to raise the temperature of					
1 kg by 1°C is called as:	work capcaity	heat capacity	energy capacity	specific heat capacity	specific heat capacity
SI unit of specific heat capacity is:	kg°C	j/kg°C	j/kg°	j/g°C	j/kg°C
Which of the following has highest heat capacity?	water	air	soil	wood	water

CLASS: III BSc PHYSICS COURSE CODE:15PHU602 COURSE NAME:STATISTICAL MECHANICS BATCH-2015-2018

#### UNIT-I

UNIT: III

#### **SYLLABUS**

Quantum Theory of Radiation Radiation :-

Stefan-Boltzmann Law: Thermodynamic Proof. Radiation Pressure. Spectral Distribution of Black Body Radiation. Wien's Distribution Law and Displacement Law. Rayleigh-Jean's Law. Ultraviolet Catastrophe. Planck's Quantum Postulates. Planck's Law of Blackbody Radiation : Experimental Verification. Deduction of (1) Wien's Distribution Law, (2) Rayleigh-Jeans Law, (3) Stefan-Boltzmann Law and (4) Wien's Displacement Law from Planck's Law.

#### **STEFAN-BOLTZMANN LAW:**

#### **Thermodynamic Proof:**

Imagine a large cavity of volume V inside a blackbody held at an absolute temperature T. Heat radiating from the cavity's walls fills the cavity with a radiation field possessing energy E=E(V,T). That energy can only change in consequence of changes in the volume of the cavity and/or in the temperature of the blackbody; that is,

 $d\mathbf{E} = \left(\frac{\partial \mathbf{E}}{\partial T}\right)_{\rm V} d\mathbf{T} + \left(\frac{\partial \mathbf{E}}{\partial V}\right)_{\rm T} d\mathbf{V}, \qquad ({\rm Eq'n}\ 1)$ 

in which the subscripts on the partial derivatives represent statements to the effect that we hold the variables that they represent constant as we change the variable in the differentiation operator; so, for example, in the first term on the right side of the equality sign we hold the volume of the cavity unchanged as we vary the temperature of the blackbody and measure the consequent change in the energy of the radiation field in the cavity.

Now we invoke the master equation of classical thermodynamics,

$$TdS = dQ = dE + pdV.$$
 (Eq'n 2)

If we divide that equation by the absolute temperature and make the appropriate substitution for dE from Equation 1, we get

$$dS = \frac{1}{T} \left( \frac{\partial E}{\partial T} \right)_{V} dT + \left[ \frac{1}{T} \left( \frac{\partial E}{\partial V} \right)_{T} dT + \frac{p}{T} \right] dV.$$
(Eq'n 3)

But, as with the energy of the radiation field, we can only describe the entropy of the radiation field as a function of the volume of the cavity and the temperature of the radiation (S=S(V,T)), so we have

$$dS = \left(\frac{\partial S}{\partial T}\right)_{V} dT + \left(\frac{\partial S}{\partial V}\right)_{T} dV.$$
 (Eq'n 4)

Comparing that equation to Equation 3 leads us to infer that

 $\left(\frac{\partial S}{\partial T}\right)_{V} = \frac{1}{T} \left(\frac{\partial E}{\partial T}\right)_{V}$ (Eq'n 5)

and that

 $\left(\frac{\partial S}{\partial V}\right)_{T} = \frac{1}{T} \left(\frac{\partial E}{\partial V}\right)_{T} + \frac{p}{T}.$ 

Next we note the mathematical fact that in a second-order partial derivative with respect to two independent variables the partial differentiation operators commute with each other; that is, the order in which we carry out the differentiations has no effect upon the outcome. Thus, in this case, we have

(Eq'n 6)

(Eq'n 7)

$$\frac{\partial^2 S}{\partial V \partial T} = \frac{\partial^2 S}{\partial T \partial V},$$

which we rewrite more explicitly as

$$\frac{\partial}{\partial V}_{T} \left(\frac{\partial S}{\partial T}\right)_{V} = \frac{\partial}{\partial T}_{V} \left(\frac{\partial S}{\partial V}\right)_{T}.$$
(Eq'n 8)

Making the appropriate substitutions from Equations 5 and 6 transforms that equation into

$$\frac{1}{T} \left( \frac{\partial^2 E}{\partial V \partial T} \right) = \left[ -\frac{1}{T^2} \left( \frac{\partial E}{\partial V} \right)_T + \frac{1}{T} \left( \frac{\partial^2 E}{\partial T \partial V} \right) \right] + \frac{\partial}{\partial T} \right)_V \begin{pmatrix} p \\ T \end{pmatrix}.$$
(Eq'n 9)

We know that the radiation field in the cavity has a uniform energy density u such that E=uV. The radiation also exerts a pressure p=u/3. When we substitute those facts into Equation 9 we get

$$\frac{1}{T} \cdot \frac{du}{dT} = -\frac{u}{T^2} + \frac{1}{T} \cdot \frac{du}{dT} + \frac{1}{T} \left(\frac{1}{3} \cdot \frac{du}{dT}\right) - \frac{1}{T^2} \left(\frac{u}{3}\right),$$
(Eq'n 10)

which gives us, in turn,

$$\frac{1}{3T} \cdot \frac{du}{dT} = \frac{4}{3} \cdot \frac{u}{T^2}.$$
 (Eq'n 11)

That equation leads readily to

$$\frac{du}{u} = 4 \frac{dT}{T}$$
,

which we integrate directly to get

$$\ln(u) = 4\ln(T) + \ln\Theta, \qquad (E_0 \ln 13)$$

in which the argument  $\Theta$  of the constant of integration absorbs the factors necessary to make the arguments of the other natural logarithms pure numbers. We thus get

$$u = \Theta T^4$$
,

(Eq'n 14)

(Eq'n 12)

which expresses the Stefan-Boltzmann law.

We usually think of the Stefan-Boltzmann law as expressing the flux of radiant energy from a blackbody, not as describing the energy density of a radiation field within a resonant cavity. But if we imagine cutting a small hole in the wall of the cavity, then we see that the flow of radiation through that hole must reflect the nature of the radiation field at its source. Thus we know that the flux of thermal energy from a blackbody must conform to

$$\phi = \sigma T^4$$

(Eq'n 15)

in which the Stefan-Boltzmann constant,  $\sigma = 5.67 \times 10^{-8}$  watt per square meter per degree Kelvin raised to the fourth power.

Finally, note that, although I invoked the entropy of the radiation field in the above derivation, I did so without describing it explicitly. I noted only that we must represent the entropy of the radiation field with a function of only the volume of the cavity and the temperature of the radiation within it: we did not need to know the actual algebraic form of the function itself. If we want to make a weak chemical analogy, then we might compare the entropy in this derivation with an enzyme or a catalyst, something that mediates a chemical reaction without suffering any change itself.

Through that fact we gain a further insight into the Map of Physics. We see how Boltzmann took very little information and parlayed it into a deeper understanding of thermal radiation. Indeed, the theoretical study of blackbody radiation relied so much on almost pure mathematical reasoning that, as the Nineteenth Century turned into the Twentieth, physicists might have seen in the science of thermodynamics a plan for a full Rationalist theoretical physics. That they did not do so likely reflects the fact that thermodynamics merely describes the relationship between

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matter and energy and says nothing about the nature of matter or of forcefields or of their relationships with space and time. Now that we have begun to rationalize those deeper natures in the Map of Physics we may finally find ourselves standing on the threshold of a new age in physics.

#### WIEN'S DISTRIBUTION LAW AND DISPLACEMENT LAW

In 1893 Wilhelm Carl Werner Otto Fritz Franz Wien (1864 Jan 13 - 1928 Aug 30) devised his well-known displacement law and in 1896 he devised his less-well-known distribution law, which Max Planck used in his formal derivation of the correct formula describing blackbody radiation. Now I want to show you how to deduce those laws much as Wien did.

Imagine that we have a spherical cavity of radius R and volume V and that we have lined it with a perfectly elastic, perfectly reflecting film. And imagine that we have filled the cavity with blackbody radiation that has an absolute temperature T. Now imagine that we change the radius of the cavity and, thus, change the cavity's volume. What happens to the temperature of the radiation inside the cavity and what happens to the wavelengths of the rays that comprise the radiation?

We know right away, as did Wien, that the adiabatic expansion or compression of light does not change the light's entropy,

 $S = \frac{4}{3}V\Phi T^3, \qquad (Eq'n 1)$ 

so we also know that

 $VT^3 = constant.$  (Eq'n 2)

Replacing the volume in that equation with its description as a function of the cavity's radius and extracting the cube root of the result yields

RT = constant. (Eq'n 3)

We also know, thanks to Kirchhoff, that blackbody radiation must conform to a description in which the spectral density follows a function,  $u(\lambda,T)$ , of the wavelength and the absolute temperature only. That function describes how much of the radiation's total energy goes into the rays that have wavelengths around  $\lambda$ , so we need to know how the wavelength of any given ray changes as the radius of the cavity changes.

Assume that the cavity expands and that the expansion occurs quasi-statically; that is, that the wall of the cavity moves at a speed v that is vanishingly small relative to the speed of light. Any given ray bounces off the cavity wall, traces a chord across the cavity, bounces off the wall again, and continues on in that fashion indefinitely. At any given bounce point the trajectory of

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the ray meets the cavity's radius at an angle  $\theta$ , so we calculate the length of the chord as 2RCos $\theta$ . Any arbitrarily chosen wavefront in the ray traverses the chord in the interval

 $dt = \frac{2R\cos\theta}{c}.$  (Eq'n 4)

On each bounce the wavelength of the ray changes, in accordance with the Doppler shift, by the amount

 $d\lambda = \lambda \left(\frac{2v\cos\theta}{c}\right).$ 

But we know that v=dR/dt, so we can rewrite that equation as

 $d\lambda = \lambda \left(\frac{dR}{R}\right).$ 

If we divide that equation by  $\lambda$  and integrate it, we get

 $\ln\left(\frac{\lambda_2}{\lambda_1}\right) = \ln\left(\frac{R_2}{R_1}\right),$ 

which necessitates that

 $\frac{\lambda_2}{\lambda_1} = \frac{R_2}{R_1}$ 

for all wavelengths comprising the radiation.

When we combine that result with Equation 3 we get

 $\lambda T = w_{\star}$  (Eq'n 9)

in which w represents a pseudo-constant. If we examine the spectrum of blackbody radiation at some given temperature, then w changes with the wavelength. But if we look at the part of the radiation that has a particular wavelength while we subject the radiation to an adiabatic expansion or compression, then w remains constant and the wavelength has an inverse relationship with the radiation's temperature. That fact necessitates that we properly describe the spectral density of the radiation with a function, not of wavelength and temperature, but of wavelength multiplied by temperature; that is,

$$\mathbf{u}(\lambda, \mathbf{T}) = \mathbf{u}(\lambda, \lambda \mathbf{T}) = \mathbf{u}(\lambda, \mathbf{w}).$$
 (Eq'n 10)

(Eq'n 6)

(Eq'n 7)

(Eq'n 8)

(Eq'n 5)

That equation expresses Wien's displacement law.

But most of us did not learn Wien's displacement law in that form. The more familiar form, most often found in astronomy courses, comes from assuming (or deducing) that the spectral density function has a maximum when the wavelength has a certain value. We thus expect w to take on a unique value that would allow us to calculate the temperature at which the maximum wavelength takes on a given value. Otto Lummer and Ernst Pringsheim first determined that value in 1900 from their observations of cavity radiation. Further measurements have refined the value so that we have Wien's displacement law appearing in textbooks as

 $\lambda_{\rm m}$ T = 2897.756 micron - degree Kelvin. (Eq'n 11)

Thus, if we determine that space is filled with blackbody radiation that has its peak wavelength at 1059.5 microns, then we can infer that the radiation and, therefore, space itself has a temperature of 2.735 Kelvin. Likewise, we can calculate that the human body (T=98.6 F = 37 C = 310.15 K) radiates heat in a spectrum that has its peak at 9.343 microns, at the border between the near and far infrared regions of the electromagnetic spectrum.

So in the wild melee of electromagnetic waves flittering about within the cavity he imagined Wien discovered a simple rule. But then he re-examined his imaginary experiment and advanced the theory of blackbody radiation even further toward the goal that Kirchhoff had set.

Adiabatic expansion or compression of light does not change the entropy of the light, but it certainly changes the light's energy. We know that at any given instant the energy contained in the radiation in the cavity equals the product of the volume of the cavity and the uniform density of the energy in the cavity: E=uV. Also we know that light in an enclosure exerts a pressure p=u/3, so in a spherical cavity of radius R the light exerts upon the wall a total force of

$$F = \frac{u}{3}(4\pi R^2).$$
 (Eq'n 12)

If the radius of the wall changes by the minuscule increment of dR, then the force does upon the wall or upon the light an increment of work

$$dE = -FdR$$
  
=  $\frac{-4\pi}{3}uR^{2}dR$   
=  $-\frac{u}{3}dV$ . (Eq'n 13)

But u=E/V, so we can rewrite that equation as

$$dE = -\frac{E}{3V}dV.$$
 (Eq'n 14)
Dividing that equation by E and integrating the result gives us

$$\ln \left(\frac{E_2}{E_1}\right) = \frac{1}{3} \ln \left(\frac{V_1}{V_2}\right), \quad (Eq'n \ 15)$$

which corresponds to

$$\frac{E_2}{E_1} = \frac{\sqrt[3]{V_1}}{\sqrt[3]{V_2}} = \frac{R_1}{R_2}.$$
 (Eq'n 16)

Finally, we want to look again at the energy density of the radiation in the cavity. We have u=E/V, so we also have, as a consequence of Equation 16, the statement that

$$\frac{u_2}{u_1} = \frac{R_1^4}{R_2^4}.$$

Combining that equation with Equation 3 tells us that

$$u = \kappa T^4$$
,

which just gives us back the Stefan-Boltzmann law and verifies our work so far (insofar as the Stefan-Boltzmann law accurately describes Reality).

But that result merely gives us total energy density. We actually want to obtain a description of the spectral energy density,  $u(\lambda,T)d\lambda$ , the energy density in that part of the radiation whose wavelengths lie between  $\lambda$  and  $\lambda$ +d $\lambda$ . To that end we note that the total energy density,

$$\mathbf{u} = \int_0^\infty \mathbf{u}(\lambda, \mathbf{T}) d\lambda.$$
 (Eq'n 19)

We should properly express that equation as a function of w and note that we carry out the integration with the understanding that the temperature has the same value at all wavelengths of the blackbody radiation, so we have, combining Equations 18 and 19,

$$\frac{1}{T} \int_0^\infty \mathbf{u}(\lambda, \mathbf{w}) d\mathbf{w} = \kappa T^4.$$
 (Eq'n 20)

If we multiply that equation by T and remove the limits from the integral, we get

$$\int \mathbf{u}(\mathbf{w}) d\mathbf{w} = \boldsymbol{\kappa}'(\mathbf{w}) \mathbf{T}^5, \qquad (\text{Eq'n } 21)$$



(Eq'n 18)

(Eq'n 17)

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in which the constant that I have represented by the Greek letter kappa stands revealed as the number coming from the evaluation of a function of w in coordination with the evaluation of the integral. But now we can simply differentiate that integral with respect to w and obtain

 $\mathbf{u}(\mathbf{w}) = \mathbf{f}(\mathbf{w})\mathbf{T}^5.$  (Eq'n 22)

And at last we invoke Equation 10 to get Wien's distribution law in the form in which Max Planck used it in his 1901 paper on his derivation of the spectral density of blackbody radiation

 $\mathbf{u}(\lambda, \mathbf{T}) = \mathbf{T}^{5} \mathbf{f}(\lambda \mathbf{T}).$  (Eq'n 23)

However, some sources offer a different version of that equation,

 $u(\lambda,T) = \frac{F(\lambda T)}{\lambda^5}$  (Eq'n 24)

Clearly we can obtain that equation from Equation 23 by making the appropriate substitution from  $T=w/\lambda$  and then absorbing the fifth power of w into the unspecified function of  $\lambda T$ . We can see that form of Wien's distribution law reflected in Planck's law in the form

$$\mathbf{u}(\lambda, \mathbf{T}) = \frac{\mathbf{c}_1}{\lambda^5(\exp(\mathbf{c}_2 / \lambda \mathbf{T}) - 1)},$$
 (Eq'n 25)

in which the first radiation constant

$$c_1 = 2\pi hc^2$$
  
= 3.743x10<sup>-8</sup> W· $\mu^4$  / m<sup>2</sup>(Eq'n 26)

and the second radiation constant

$$c_2 = \frac{hc}{k}$$
  
= 14,387  $\mu$ ·K. (Eq'n 27)

As a final note I want to refer back to the imaginary experiment that led to Wien's laws. In that experiment we used a perfectly elastic, perfectly reflecting material, a material that cannot possibly exist in the real world. And yet we claim that the results of the experiment do, in fact, correctly describe Reality. On what basis can we believe such a claim?

When we bring a fantasy material into an imaginary experiment, we bring it in as what Michael Faraday called an aid to the imagination. So long as the material does not affect the application of the physical laws that we seek to clarify through the experiment, then we may ignore the fact that the material cannot exist and accept its participation in the experiment on an "as if" basis, theoretical physics in the subjunctive mood. We might then properly make an analogy with chemistry and denote our fantasy material an intellectual catalyst: like the catalyst that speeds up a chemical reaction but does not leave any part of itself in the reactants or their products, so too the fantasy material participates in our experiment without in any way distorting the laws of physics that participate in the experiment. It merely speeds up our gain of understanding the phenomenon in the experiment. As long as we make certain that our fantasy materials do not affect the laws of physics that we infer from the experiments in which we use them, then so long can we accept the results of those imaginary experiments as true to Reality.

# **RAYLEIGH-JEAN'S LAW.**

The Rayleigh-Jeans Radiation Law was a useful but not completely successful attempt at establishing the functional form of the spectra of thermal radiation. The energy density  $u_v$  per unit frequency interval at a frequency v is, according to the The Rayleigh-Jeans Radiation,

$$u_v = 8\pi v^2 k T/c^2$$

where k is Boltzmann's constant, T is the absolute temperature of the radiating body and c is the speed of light in a vacuum.

This formula fits the empirical measurements for low frequencies but fails increasingly for higher frequencies. The failure of the formula to match the new data was called *the ultravioletl catastrophe*. The significance of this inadequate so-called law is that it provides an asymptotic condition which other proposed formulas, such as Planck's, need to satisfy. It gives a value to an otherwise arbitrary constant in Planck's thermal radiation formula.

# The Derivation of the Rayleigh-Jeans Radiation Law

Consider a cube of edge length L in which radiation is being reflected and re-reflected off its walls. Standing waves occur for radiation of a wavelength  $\lambda$  only if an integral number of half-wave cycles fit into an interval in the cube. For radiation parallel to an edge of the cube this requires

 $L/(\lambda/2) = m$ , an integer or, equivalently  $\lambda = 2L/m$ 

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Between two end points there can be two standing waves, one for each polarization. In the following the matter of polarization will be ignored until the end of the analysis and there the number of waves will be doubled to take into account the matter of polarization.

Since the frequency v is equal to  $c/\lambda$ , where c is the speed of light

$$v = cm/(2L)$$

It is convenient to work with the quantity q, known as the wave number, which is defined as

 $q = 2\pi/\lambda$ and hence  $q = 2\pi\nu/c$ 

In terms of the relationship for the cube,

 $q = 2\pi m/(2L) = \pi(m/L)$ and hence  $q^2 = \pi^2(m/L)^2$ 

Another convenient term is the radian frequency  $\omega = 2\pi v$ . From this it follows that  $q = \omega/c$ .

If  $m_X$ ,  $m_Y$  and  $m_Z$  denote the integers for the three different directions in the cube then the condition for a standing wave in the cube is that

 $q^{2} = \pi^{2}[(m_{X}/L)^{2} + (m_{Y}/L)^{2} + (m_{Z}/L)^{2}]$ which reduces to  $m_{X}^{2} + m_{Y}^{2} + m_{Z}^{2} = 4L^{2}\nu^{2}/c^{2}$ 

Now the problem is to find the number of nonnegative combinations of  $(m_X, m_Y, m_Z)$  that fit between a sphere of radius R and and one of radius R+dR. First the number of combinations ignoring the nonnegativity requirement can be determined.

The volume of a spherical shell of inner radius R and outer radius R+dR is given by

$$dV = 4\pi R^{2} dR$$

$$R = (m_{X}^{2} + m_{Y}^{2} + m_{Z}^{2})^{\frac{1}{2}}$$
then
$$R = (4L^{2}v^{2}/c^{2})^{\frac{1}{2}} = 2Lv/c$$
and hence
$$dR = 2Ldv/c.$$

$$dV = 4\pi (2Lv/c)^{2} (2L/c) dv =$$

$$32\pi (L^{3}v^{2}/c^{3}) dv$$

This means that

If

Now the nonnegativity require for the combinations  $(m_X, m_Y, m_Z)$  must be taken into account. For the two dimensional case the nonnegative combinations are approximately those in one quadrant of circle. The approximation arises from the matter of the combinations on the boundaries of the nonnegative quadrant. For the three dimensional case the nonnegative combinations constitute approximately one octant of the total. Thus the number dN for the nonnegative combinations of  $(m_X, m_Y, m_Z)$  in this volume is equal to (1/8)dV and hence

$$dN = 4\pi v^2 dv$$

The average kinetic energy per degree of freedom is  $\frac{1}{2}kT$ , where k is Boltzmann's constant. For harmonic oscillators there is an equality between kinetic and potential energy so the average energy per degree of freedom is kT. This means that the average radiation energy E per unit frequency is given by

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 $dE/dv = kT(dN/dv) = 4\pi kT(L^3/c^3)v^2$ 

and the average energy *density*,  $u_v$ , is given by

$$du_{\nu}/d\nu = (1/L^3)(dE/d\nu) = 4\pi kT\nu^2/c^3$$

The previous only considered one direction of polarization for the radiation. If the two directions of polarization are taken into account a factor of 2 must be included in the above formula; i.e.,

$$du_{\nu}/d\nu = 8\pi k T \nu^2/c^3$$

This is the Raleigh-Jeans Law of Radiation. It holds empirically as the frequency goes to zero.

# **ULTRAVIOLET CATASTROPHE.**

A blackbody is an idealized object which absorbs and emits all frequencies. Classical physics can be used to derive an equation which describes the intensity of blackbody radiation as a function of frequency for a fixed temperature--the result is known as the Rayleigh-Jeans law. Although the Rayleigh-Jeans law works for low frequencies, it diverges for high frequencies is called the ultraviolet catastrophe.

Max Planck explained the blackbody radiation in 1900 by assuming that the energies of the oscillations of electrons which gave rise to the radiation must be proportional to integral multiples of the frequency, i.e.,

 $E = nh\eta$ 

Using statistical mechanics, Planck derived an equation similar to the Rayleigh-Jeans equation,  $h = 6.626 \times 10^{-34}$ 

but with the adjustable parameter  $\underline{h}$ . Planck found that for J s, the experimental data could be reproduced. Nevertheless, Planck could not offer a good justification for his assumption of energy quantization. Physicicsts did not take this energy quantization idea seriously until Einstein invoked a similar assumption to explain the photoelectric effect.

# PLANCK'S QUANTUM POSTULATES.

The basic postulates of Planck's quantum theory are:

- 1. Energy flows discontinuously in the form of small discrete packets of energy called 'quanta'. In case of light, it is called 'photon'.
- 2. Energy of each quanta is directly proportional to the frequency of radiation.

i.e.  $E \propto v$ 

or E = hv, (h is a constant known as Planck; s constant, whose value is  $h = 6.626 \times 10^{-10}$ 

<sup>34</sup> Joule sec.)

3. Total energy emitted or absorbed is always a whole number.

# EXPERIMENTAL VERIFICATION. DEDUCTION OF (1) WIEN'S DISTRIBUTION LAW,

#### Wien's displacement law

In 1894, Wilhem Wien published the derivation of his displacement law using electromagnetism and thermodynamics. The wavelength at which the radiation is strongest is given by the Wien's displacement law. When the temperature of a blackbody radiator increases, the overall radiated energy increases and the peak of the radiation curve moves to higher frequencies. Hotter objects radiate a larger fraction of their electromagnetic radiation at shorter wavelengths. This displacement of the peak of the curve is called as Wien's displacement law.

A consequence of Wien's displacement law is that the wavelength  $\lambda_{max}$  at which the intensity of the radiation produced by a blackbody is at a maximum, is a function only of the temperature

$$\lambda_{max} = \frac{b}{T}$$

where the constant b is known as Wien's displacement constant

Its value is given as  $b = 2.898 \times 10^{-3}$  meters•kelvin =  $2.898 \times 10^{6}$  nm•K

## **Deduction of Wien's Radiation Formula from Planck's Law**

Using the Planck's radiation law, in the region of low wavelengths (high frequencies), Wien's Radiation Formula can be derived as follows

$$\begin{split} \rho(\lambda,T) &= \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1} \\ & \frac{hc}{kT} >> \lambda \\ & \frac{hc}{e^{\lambda kT}} >> 1 \\ \rho(\lambda,T) &= \frac{8\pi hc}{\lambda^5} \frac{1}{\frac{hc}{e^{\lambda kT}}} = \frac{8\pi hc}{\lambda^5} e^{-hc/\lambda kT} \end{split}$$

This expression is similar to Wien's Distribution Law for constants  $C_1$  and  $C_2$  as follows

$$\rho(\lambda, T) = \frac{c_1}{\lambda^5} e^{-c_2/\lambda T}$$

## (2) RAYLEIGH-JEANS LAW,

Lord Rayleigh and J.H. Jeans (1900), using Maxwell Boltzmann doctrine of the equipartition of energy, developed a formula between the spectral energy density  $u = u(\nu, T)$  and average energy of an oscillator by treating modes of oscillations of electromagnetic waves in a box. Rayleigh-Jeans Formula is stated as follows

$$u(\nu, T) = \frac{8\pi\nu^2}{c^3}kT$$

Where k is the Boltzmann constant =  $1.3806488(13) \times 10^{-23} J/K$ , c = Speed of light, T = Temperature in Kelvins.

The Raleigh Jeans formula is discussed in detail in the section no. 1.2.2 on "Ultraviolet Catastrophe."

#### **Deduction of Rayleigh-Jean's formula from Planck's Law**

$$h\nu$$

A comparison shows that the factor  $\overline{e^{h\nu/kT}-1}$  occurs in the Planck's radiation law instead of the factor kT in the Rayleigh-Jean's formula

(small frequencies = a) For the region of long wavelengths >  $kT >> h\nu$ , ), exponential term in the Planck's radiation law is expanded  $(e^{h\nu/kT} \rightarrow 1 + h\nu/kT)$ , and only the first term is retained then Rayleigh-Jean's formula can be obtained.

$$\begin{array}{l} & \dots & \text{Planck's Law is} \quad u(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} \\ & \text{If} \quad kT >> h\nu, \dots & then \dots e^{h\nu/kT} = 1 + \frac{h\nu}{kT} \\ & u(\nu, T) = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} = \frac{8\pi\nu^2}{c^3} \frac{h\nu}{1 + \frac{h\nu}{kT} - 1} = \frac{8\pi\nu^2}{c^3} kT \end{array}$$

b) At high frequency there are a very large number of cavity modes however, the probability to emit such high energy quanta decreases exponentially according to the Boltzmann distribution. If  $kT \ll h\nu$ , there will be negligible probability for the oscillator to absorb any energy and therefore very less probability for radiation. Thus the absurd result of Ultraviolet Catastrophe is avoided.

# (3) STEFAN-BOLTZMANN LAW

In 1879 J. Stefan found experimentally an empirical relation that the total emissive power  $(j^*)$  i.e. the energy / second emitted per unit area of the surface of a blackbody for all frequencies  $(\nu)$  is directly proportional to the fourth power of its absolute temperature T (in the kelvin scale). That is

$$j^* = \sigma T^4$$

In this equation  $\sigma$  is a constant. Its value was found to be  $\sigma = 5.6074 \times 10^8$  watt metre  $^{-2} \cdot K^{-4}$ .

L. Boltzmann (1984) derived theoretically using thermodynamics and Maxwell's theory of electromagnetism and by assuming the blackbody radiation as the working substance for the ideal heat engine that the intensity (i.e. total power /unit surface area) increases with the fourth

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power of the temperature.  $\sigma$  is called as the Stefan–Boltzmann constant. The law is useful to astronomers to determine the temperature of stars from the wavelength of their radiation Lummer and Pringsheim (1897) verified experimentally the validity of the law.

In addition to Lummer and Pringsheim, Kurlbaum, Paschen, and Rubens also had performed precise experiments on thermal radiation. From these the shape of the radiation spectrum could be determined. The theory explained the reason of radiation, but it did not correctly predict the observed spectrum of emitted light. Some scientists tried to explain the distribution of energy among wavelengths in the blackbody spectrum by using the laws of classical physics. Significant laws discovered by scientists were as follows

#### Deduction of Stefan–Boltzmann law from Planck's Law

**Staring from the Planck's radiation law,** and integrating the expression over the whole spectrum, total energy density is obtained and can be expressed in the form of total power per unit surface area

$$\begin{split} u(\nu, T) &= \frac{8\pi\nu^2}{c^3} \frac{h\nu}{e^{h\nu/kT} - 1} \\ U(T) &= \frac{8\pi h}{c^3} \int_0^\infty \frac{h\nu^3}{e^{h\nu/kT} - 1} d\nu \\ U(T) &= \frac{8\pi h}{c^3} \left(\frac{kT}{h}\right)^4 \int_0^\infty \frac{(\frac{h\nu}{kT})^3 d(\frac{h\nu}{kT})}{e^{h\nu/kT} - 1} d\nu \\ \\ \text{By substituting for} \left(\frac{h\nu}{kT}\right) &= x \\ U(T) &= \frac{8\pi hk^4}{c^3h^3} T^4 \int_0^\infty \frac{x^3}{e^x - 1} \\ \\ U(T) &= \frac{8\pi^5 k^4}{15c^3h^3} T^4 \end{split}$$

$$E = \frac{cU}{4} = \frac{2\pi^5 k^4}{15c^2 h^3} T^4 = \sigma T^4$$

where the value of Stephen Boltzmann constant  $\sigma$  is given by

$$\sigma = \frac{2\pi^5 k^4}{15c^2 h^3} = 5.670400 \times 10^{-8} J s^{-1} m^{-2} K^{-4},$$

or

$$\sigma = 5.67 \times 10^{-8} W m^{-2} K^{-4}$$

The equation agrees with the Stefan–Boltzmann law  $j^* = \sigma T^4$ .

k is the Boltzmann constant, h is the Planck's constant, c is the speed of light in a vacuum.

The value of Stefan's constant  $\sigma$  was known to be  $= 5.79 \times 10^{-8} Wm^{-2} K^{-4}$  Using the values of k and c the value of h was obtained as  $6.57 \times 10^{-34} Js$  This value of h is the first calculated value of h which is quite close to the recently accepted value of h as

$$h = 6.6260755(40) \times 10^{-34} J.s$$

Thus from Planck's radiation law, other radiation laws can be derived successfully.

# (4) WIEN'S DISPLACEMENT LAW FROM PLANCK'S LAW

In 1894, Wilhem Wien published the derivation of his displacement law using electromagnetism and thermodynamics. The wavelength at which the radiation is strongest is given by the Wien's displacement law. When the temperature of a blackbody radiator increases, the overall radiated energy increases and the peak of the radiation curve moves to higher frequencies. Hotter objects radiate a larger fraction of their electromagnetic radiation at shorter wavelengths. This displacement of the peak of the curve is called as Wien's displacement law.

A consequence of Wien's displacement law is that the wavelength  $\lambda_{max}$  at which the intensity of the radiation produced by a blackbody is at a maximum, is a function only of the temperature

$$\lambda_{max} = \frac{b}{T}$$

where the constant b is known as Wien's displacement constant

Its value is given as  $b = 2.898 \times 10^{-3}$  meters•kelvin =  $2.898 \times 10^{6}$  nm•K

# **Deduction of Wien's Displacement Law from Planck's Law**

From the Planck's radiation law, Wien's Displacement Law is obtained as follows

$$\rho(\lambda, T) = \frac{8\pi hc}{\lambda^5} \frac{1}{e^{hc/\lambda kT} - 1}$$
  
For  $[\rho(\lambda, T)]_{max}$ , .....  $\lambda = \lambda_{max}$ ....and  
 $\frac{\partial \rho}{\partial \lambda} = 0$   
 $\frac{\partial \rho}{\partial \lambda} = \frac{-5}{\lambda^6} \frac{1}{(e^{hc/\lambda kT} - 1)} - \frac{\lambda^2 kT}{\lambda^5 (e^{hc/\lambda kT} - 1)^2} = 0$   
 $\frac{-5}{\lambda^6} \frac{1}{(e^{hc/\lambda kT} - 1)} - \frac{\lambda^2 kT}{\lambda^5 (e^{hc/\lambda kT} - 1)^2} = 0$   
 $5 = \frac{ch}{\lambda kT} \frac{e^{hc/\lambda kT}}{(e^{hc/\lambda kT} - 1)}$ 

$$\operatorname{Let} \alpha = \frac{hc}{\lambda kT}$$

Then above equation reduces to

$$e^{\alpha} = \frac{5}{5-\alpha}$$
$$\alpha = \ln 5 - \ln (5-\alpha)$$

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The transcendental equation can be solved graphically or numerically to obtain  $\lambda_{max} T$ 

$$\alpha = 4.965 \implies \alpha = \frac{hc}{\lambda_{max}^{kT}} = 4.965$$
$$\lambda_{max}T = \frac{hc}{k(4.965)}$$

Substituting the values of h, c, k

$$\lambda_{max}T = 2.8977685(51) \times 10^{-3}mK$$
$$\nu_{max} = \frac{c}{\lambda_{max}} = \frac{4.9663}{h}kT$$

Wien's Displacement Law can be used to determine the temperature of a blackbody by measuring the wavelength at which intensity of radiation is maximum or to determine the wavelength at which intensity of radiation is maximum if the temperature of body is known.

# **Possible Questions**

- 1) Explain Spectral Distribution of Black Body radiation.
- 2) Explain Plank's Law of Black Body Radiation.
- 3) Explain Stefan's Boltzmann's Law.
- 4) Explain Wien's Distribution Law.
- 5) Explain Wien's Displacement Law from Planck's Law

#### DEPARTMENT OF PHYSICS III BSc PHYSICS (15PHU602) STATISTICAL MECHANICS

#### Unit-III

Questions	opt1	opt2	opt3	opt4	Answer
According to kinetic theory of heat	Temperature should rise during boiling	Temperature should fall during freezing	At low temperatures all bodies are in solid state	At absolute zero there is absolute no vibration of molecules	At absolute zero there is absolute no vibration of molecules
Average kinetic energy of molecules is	Directly proportional to square root of temperature	Directly proportional to absolute temperature	Independent of absolute temperature	Inversely proportional to absolute temperature	Directly proportional to absolute temperature
The mean kinetic energy of one gram-mole of a perfect gas at absolute temperature T is	1/2 KT	1/2 RT	3/2 KT	3/2 RT	3/2 RT
The specific heat of a substance at its boiling point or melting point	Is zero	Is infinity	Is negative	Lies between 0 and 1	Is infinity
Which of the following law is applicable for the behavior of a perfect gas	Boyle's law	Charles law	Gay-lussac law	Joules law	Joules law
An ideal gas as compared to a real gas at very high pressure occupies	More volume	Less volume	Same volume	Unpredictable behavior	More volume
The unit of pressure in SI unit is	Kg/cm2	Mm of water column	Pascal	Bars	Pascal
According to kinetic theory of gases, the absolute zero temperature is attained when	Volume of the gas is zero	Pressure of the gas is zero	Kinetic energy of the molecules is zero	Mass is zero	Kinetic energy of the molecules is zero
Kinetic theory of gases assumes that the collisions between the molecules are	Perfectly elastic	Perfectly inelastic	Partly elastic	Partly inelastic	Perfectly elastic
The behavior of gases can be fully determined by	1 law	2 law	3 law	4 law	4 law
Boyle's law ie, PV = constant is applicable to gases under	All ranges of pressures	Only small range of pressures	Steady change of pressures	Atmospheric conditions	Only small range of pressures
The same volume of all gases would represent their	Densities	Specific weights	Molecular weights	Gas characteristic constants	Molecular weights
Kinetic theory of gases provide a base for	Charle's law	Charle's law and Boyle's law	Boyle's law	stefans law	Charle's law and Boyle's law
In Boyle's law what remains constant.	PV	TV	V/T	V/T	PV
An ideal gas is that which can	Be solidified	Liquefied	Not be liquefied	Not be solidified	Not be liquefied
Average kinetic energy of molecules is	Directly proportional to square root of temperature	Directly proportional to absolute temperature	Independent of absolute temperature	Inversely proportional to absolute temperature	Directly proportional to absolute temperature
Latent heat of ice is	Less than external latent heat of fusion	Equal to external latent heat of fusion	More then external latent heat of fusion	Twice the external latent heat of fusion	More then external latent heat of fusion

The specific heat of a substance at its boiling point or melting point	Is zero	Is infinity	Is negative	Lies between 0 and 1	Is infinity
Which of the following properties of gas molecule the one that is same for all ideal gases at a particular temperature is	Mass	velocity	momentum	kinetic energy	Mass
Mean kinetic energy of perfect gas is	proposional to T	inverse proposional to T2			proposional to T
The word kinetic refers to	locomotion	vibration	motion	resonance	motion
what does the Kinetic theory of gases describe?	sinan no or sinan	large no or sman	Targe no or sman	Targe no or targe	Targe no or sman
which experiment shows how kinetic theory works?	g by freefall	brownian motion	pin hole camera	refration of light	brownian motion
what forces are assumed to exist between particles in a gas	attractive	repulsive	both	no force	no force
Average kinetic energy of molecules is	Directly proportional to square root of temperature	Directly proportional to absolute temperature	Independent of absolute temperature	Inversely proportional to absolute temperature	Directly proportional to absolute temperature
A gas is taken in a sealed container at 300 K. it is heated at constant volume to a temperature 600 K. the mean K.E. of its molecules is	Halved	Doubled	Tripled	Quadrupled	Doubled
The mean kinetic energy of one gram-mole of a perfect gas at absolute temperature T is	1/2 KT	1/2 RT	3/2 KT	3/2 RT	3/2 RT
If for a gas $(R/Cv) = 0.670$ this gas is made up of molecules which are	Diatomic	Mixture of diatomic and polyatomic	Mono atomic	Polyatomic	Mono atomic
A sample of an ideal gas occupies a volume V at a pressure P and absolute temperature T, the mass of each molecules is m. the expression for the density of gas is ( $k = Boltzmann$ constant)	mKT	P/KT	p/KTV	Pm/KT	Pm/KT
Unit of thermal conductivity is	W/s/m/k	J/k	m/k.	J/s/m/k	J/s/m/k
Viscosity is transfer	energy	mass	momentum	force	momentum
In steady state, rate of flow of heat through any cross section of slab is directly proportional to	length	Temperature difference	area	force	Temperature difference
does not require bulk motion	viscosity	conduction	diffusion	none	diffusion
According to kinetic theory of gasses at absolute zero temperature	Water freezes	Liquid helium freezes	Molecules motion stops	Liquid hydrogen freezes	Molecules motion stops
A gas which obeys kinetic theory perfectly is known as	Monoatomic gas	Diatomic gas	real gas	perfect gas	perfect gas
How many degrees of freedom do non linear triatomic gas molecules has?	2	6	3	5	6
If a gas has n degree of freedom, ratio of principal specific heats of the gas is	1+2/n	2n	1-2/n	#REF!	1-2/n
O <sub>2</sub> is a molecule and has translational degrees of freedom	Monatomic, three	Diatomic, three	Monatomic, one	Diatomic, one	Diatomic, three
The degree of freedom for diatomic gas is:	4	6	5	3	5
On which of the following factors, does the average kinetic energy of gas molecules depend?	Pressure	Velocity of gas molecules	Absolute temperature	Volume of the gas	Absolute temperature

The mean free path is the	average distance covered by a molecule between two successive collisions	length of the container that contains the gas	mean of the square of the average distance between two successive collisions	square of the average distance between two successive collisions	square of the average distance between two successive collisions
The average distance a molecule can travel without colliding is called	Average distance	mean free path	mean drift	mean distance	mean free path
How many degrees of freedom for triatomic gas molecules has?	2	6	3	5	6
Specific heat capacity of a substance is equal to	amount of heat	A. amount of heat	A. amount of heat	A. amount of heat	amount of heat required to
Specific heat capacity of a substance is equal to	mass of substance ×	heat capacity/mass	mass of substance/	heat capacity+mass	heat capacity/mass of
Increase in temperature of body is proportional to	amount oh heat	amount of heat	density of substance	average kinetic	amount oh heat absorbed
Kinetic theory of gases assumes that the collisions between the molecules are	perfectly elastic	perfectly inelastic	partly elastic	partly inelastic	perfectly elastic
Kinetic energy of the molecules in terms of absolute temperature (T) is proportional to	Т	j	J2	Vr	Т
Specific heat of air at constant pressure is equal to	0.17	0.21	0.24	1.41	0.24
The ratio of two specific heats of air is equal to	0.17	0.21	0.24	1.41	1.41
The specific heat of air increases with increase in	temperature	pressure	both pressure and temperature	variation of its constituents	temperature
Specific heat of metals can be expressed as	$T^3$	$AT + BT^2$	$AT^2 + BT^3$	$AT + BT^3$	$AT + BT^3$
The specific heat capacity of a substance is equal to	mass of the substance × heat capacity	heat capacity/mass of the substance	mass of the substance / heat capacity	mass of the substance	heat capacity/mass of the substance
Specific heat capacity of glass is	635 J kg <sup>-1</sup> °C <sup>-1</sup>	670 J kg <sup>-1</sup> °C <sup>-1</sup>	705 J kg <sup>-1</sup> °C <sup>-1</sup>	740 J kg <sup>-1</sup> °C <sup>-1</sup>	670 J kg <sup>-1</sup> °C <sup>-1</sup>
The specific heat capacity of a substance is equal to	the amount of heat required to raise the temperature of a 1 kg of a substance by 1 K	the amount of heat required to raise the temperature of a substance by 1 K	the amount of heat required to change the phase of a substance from solid to liquid without any chan	the amount of heat required to change the phase of a substance from liquid to gas without any change	the amount of heat required to raise the temperature of a 1 kg of a substance by 1 K
Specific heat capacity of mercury is	120 J kg <sup>-1</sup> °C <sup>-1</sup>	140 J kg <sup>-1</sup> °C <sup>-1</sup>	160 J kg <sup>-1</sup> °C <sup>-1</sup>	180 J kg <sup>-1</sup> °C <sup>-1</sup>	140 J kg <sup>-1</sup> °C <sup>-1</sup>
The amount of heat required to raise temperature of a substance by 1°C is called as:	work capcaity	heat capacity	energy capacity	specific heat capacity	heat capacity
Heat capcity does not depends on	change in temperature	mass of body	nature of substance	height of substance	height of substance
Heat brings change	physical	chemical	reversible	periodic	chemical
The amount of heat required to raise the temperature of 1 kg by 1°C is called as:	work capcaity	heat capacity	energy capacity	specific heat capacity	specific heat capacity
SI unit of specific heat capacity is:	kg°C	j/kg°C	j/kg°	j/g°C	j/kg°C
Which of the following has highest heat capacity?	water	air	soil	wood	water

#### UNIT: IV

# UNIT-IV

# **SYLLABUS**

#### **Bose-Einstein Statistics**

Bose-Einstein distribution law. Thermodynamic functions of a Completely Degenerate Bose Gas. Bose-Einstein condensation, properties of liquid He (qualitative description). Radiation as photon gas. Bose's derivation of Planck's law.

# **BOSE-EINSTEIN DISTRIBUTION LAW.**

# Bose Einstein energy distribution for energies in the range E to E + dE:

The molecules of an ordinary gas have spin angular momentum equal to an integral multiple of ħ. It means that the molecules are bosons and they will obey the Bose-Einstein statistics. The energy distribution law for a system of identical molecules is obtained as follows.

The number n (E) dE of the molecules having energies in the range from E to E+dE is given by

n(E) dE = f(E) g(E) dE ----- (1)

where f(E) is the energy distribution function, and g (E)dE is the number of quantum states available in the energy range.

Substituting the expression for f (E) in equation (1), obtained

$$n(E)dE = \frac{g(E)dE}{e^{\alpha}e^{E/kT}-1} \qquad (2)$$

g (E) dE is given by, g (E) dE = 
$$2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

Substituting this equ. in (2)

n(E) dE = 
$$2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \cdot \frac{E^{\frac{1}{2}}dE}{e^{\alpha}e^{E/kT}-1}$$
 ------ (3)

This is Bose Einstein energy distribution law given by the number of particles with energies between E and E +dE.

The constant  $e^{\alpha}$  appears in the distribution law cannot be less than or equal to 1 because

(i) if  $e^{\alpha}$  is <1, then for E = 0

$$n(E)dE = \frac{g(E)dE}{e^{\alpha}e^{E/kT} - 1}$$

 $n(0)dE = \frac{g(0)dE}{e^{\alpha}-1} = \text{negative quantity}$ 

which is impossible.

(ii) if 
$$e^{\alpha} = 1$$
, then for  $E = 0$ 

$$n(0)dE = \frac{g(0)dE}{1-1} = \infty$$

Which is also impossible. Therefore  $e^{\alpha}$  must be greater than 1.

# Condition for B-E distribution to approach classical M-B distribution:

The B-E distribution is given by

n(E) dE = 
$$2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \cdot \frac{E^{\frac{1}{2}}dE}{\frac{1}{A}e^{E/kT} - 1}$$
 ----- (1)

If 1 in the denominator is neglected in comparison with the first term, this distribution will approach the M-B distribution:

n(E) dE = 
$$2\pi V \left(\frac{2m}{h^2}\right)^{3/2} AE^{1/2} e^{-E/kT} dE$$
  
=  $2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{N}{V} \left(\frac{h^2}{2\pi m k T}\right)^{3/2} E^{1/2} e^{-E/kT} dE$   
=  $\frac{2\pi N}{(\pi k T)^{3/2}} E^{1/2} e^{-E/kT} dE$ 

The condition for this is that

$$\frac{1}{A}e^{E/kT} >> 1$$

i.e. 
$$\frac{A}{eE/kT}e^{E/kT} \ll 1$$

For all values of the energy,  $e^{E/kT}$  is greater than or equal to 1. Therefore the condition is

A<<1.

## **BOSE-EINSTEIN CONDENSATION:**

At the Bose temperature molecules  $T_B$ , molecules just start reaching the zero-energy state(E=0) from the higher energy state(E>0). If the temperature of the gas is lowered below  $T_B$ , the number of molecules in the zero-energy state will increase, and the number in the higher energy states will decrease. Suppose that in thermal equilibrium at the temperature  $T < T_B, n_0$  is the number of molecules in the non zero- energy state and  $N_e$  is the number in the higher energy states. Then

$$N_{e=}N-n_0$$

-----(3)

The zero –energy state occupation number is given by

 $n_0 = \frac{g_0}{\frac{1}{A} - 1}$ ------ (4)

where  $g_0$  is the number of allowed states at energy E=0

N<sub>e</sub> is given by, N<sub>e</sub>=2.612V(
$$\frac{2\pi mKT}{h2}$$
)<sup>3/2</sup>-----(5)

and N is given by N=2.612V $\left(\frac{2\pi m KT}{h2}\right)^{3/2}$ 

div. eq. (5) by eq. (1)

$$\frac{Ne}{N} = \left(\frac{T}{TB}\right)^{3/2}$$

Or

 $N_e = N (T/T_B)^{3/2}$  -----(6)

where T<T<sub>B</sub>

From eq.(3) & eq.(6)  $n_0 = N - N_e$ 

 $= N[1 - (\frac{T}{TB})^{3/2}]$  (7)

These eq.shows that as T approaches absolute zero of temperature  $N_e \rightarrow 0$  and  $n_0 \rightarrow N$ 

Thus all the molecules of B-E gas tend to condense into the zero energy states of the gas at absolute zero this phenomenon is called Bose-Einstein condensation. The temperature at which  $n_0 = N_e = N/2$  obtained by sub.  $N_{e=}N/2$  in eq. (6).

$$\frac{N}{2} = N(\frac{T}{TB})^{3/2}$$
$$T = (\frac{1}{2})^{2/3} T_B$$
$$= 0.63 T_B$$

The molecules of an ideal B-E gas exist in two phases at  $T < T_B$ 

- i. a gaseous phase consisting of  $N_e$  molecules distributed among the energy states higher than the ground state,and
- ii. a condensed phase consisting of  $n_0$  molecules occupying the ground state.

The molecules in the condensed phase do not contribute to the internal energy, specific heat capacity, entropy, etc.

The transition of the molecules  $atT_B$  to the ground state is a sudden of phenomenon. In this phenomenon there is a decrease in volume of the momentum space by the volume of the space which  $n_0$  molecules had occupied before their transition to the zero-energy state. This differs from the usual type of vapor condensation process in which there is a decrease in the physical volume.

The transition of liquid <sub>2</sub>He<sup>4</sup>-I to superfluid liquid <sub>2</sub>He<sup>4</sup>-II at the observed temperature 2.18K can be expanded by Bose-Einstein condensation process.

#### UNIT: IV

# PROPERTIES OF LIQUID HE (QUALITATIVE DESCRIPTION).

Liquid Helium Kamerlingh Onnes discovered liquid Helium (2 4 He) in 1911. It liquefies at a temperature of 4.2 K. Recall that the freezing point of water is T = 273 K = 0 C. There are some interesting properties of liquid helium, but we must first review some basic thermodynamics. **Heat Capacity**: The change in the heat energy Q of a system equals the change in temperature T of the system times a proportionality constant C called the heat capacity:

## $\Delta Q = C \Delta T$

The heat capacity has units of energy per unit temperature. A large heat capacity implies that a large change in the energy of an object translates into only a small change in temperature. The heat capacity of an object will depend on the density of a material as well as the volume. For example, an ocean has a much larger heat capacity than a bucket of water. So it would be nice to factor out the mass dependence and have a constant which is intrinsic to the type of material: **Specific Heat:** The specific heat c is defined by the relation:

## $\Delta Q = c m \Delta T$

In other words, c C m °. It has the dimensions of energy per unit temperature per unit mass. It is approximately constant for similar materials of different volumes.

**Super fluids:** Liquid helium below the critical temperature exhibits some remarkable properties. First of all, one observes that above the transition temperature liquid helium boils vigorously, but below it the liquid is absolutely calm. The first phase is referred to as the normal phase, or liquid helium I; and the second phase below the critical temperature is referred to as the superfluid phase, or liquid helium II. The reason that the second phase is referred to as a superfluid is that it exhibits very little viscosity (resistance to flow). Liquid helium II has a high rate of capillary PHY3101 Modern Physics Lecture Notes Spin 3 D. Acosta Page 3 4/3/00 flow, and a thin film can crawl up the sides of a container. Imagine pouring a Coke into a glass and watching it flow up and over the rim of the glass!

## **RADIATION AS PHOTON GAS.**

First, consider a cubic box with each side of length L that is filled with electromagnetic (EM) radiation (a so-called 'photon gas') that forms standing waves whose allowable wavelengths are restricted by the size of the box. We will assume that the waves do not interact and therefore can be separated into the three orthogonal Cartesian directions such that the allowable wavelengths are: where ni is an integer greater than zero, and i represents one of the three Cartesian directions—x, y, or z. From quantum mechanics, the energy

# E(n) = (n+1/N)

of a given mode (i.e., an allowable set nx ,ny ,nz ) can be expressed as where h is Planck's constant ( $6.626 \times 10$  ? 34J s). The number N represents the number of such modes, or photons, of the given energy. Importantly, unlike electrons, an unlimited number of modes, or photons, of a given energy can exist; thus, photons are governed by Bose-Einstein statistics.

# **Possible Questions**

- 1) Explain Bose Einstein Condensation.
- 2) Explain Properties of Liquid Helium.
- 3) Describe Bose Einstein Distribution Law.
- 4) Explain Bose Derivation of Palnk's Law.
- 5) Describe Thermodynamic function for completely degenerate Bose gas.

#### DEPARTMENT OF PHYSICS III BSc PHYSICS (15PHU602) STATISTICAL MECHANICS

Unit-IV

Questions	opt1	opt2	opt3	opt4	Answer
			A can exchange neither	A can exchange both	A can exchange neither
In a micro canonical ensemble, a system A of fixed volume is in	A can exchange only	A can exchange only	energy nor particles with	energy and particles with	energy nor particles with
contact with a large reservoir B. Then	energy with B	particles with B	B	B	B
			A can exchange neither	A can exchange both	D
In a canonical ensemble, a system A of fixed volume is in	A can exchange only	A can exchange only	energy nor particles with	energy and particles with	A can exchange only
contact with a large reservoir B. Then	energy with B	particles with B	B	B	energy with B
			A can exchange neither	A can exchange both	A can exchange both
In a grand canonical ensemble, a system A of fixed volume is in	A can exchange only	A can exchange only	energy nor particles with	energy and particles with	energy and particles with
contact with a large reservoir B. Then	energy with B	particles with B	В	B	В
Those substances which have so far not been resolved by any				,	
means into other substances of simpler form are called	atom	molecules	element	compounds	element
The sum of internal energy (U) and the product of pressure and					
volume (p.v) is known as	workdone	enthalpy	entropy	gidds	enthalpy
What is the relation between the second second	thermodynamic	thermodynamic	thermodynamic		thermodynamic
what is the relation between thermodynamic	probability increases with	probability decreases with	probability does not	zero	probability increases with
probability (W) and entropy?	entropy	entropy	change with change in		entropy
At the most probable state of a system the entropy of the system	· · · · · · · · · · · · · · · · · · ·				· · · · · · · · · · · · · · · · · · ·
is	maximum	minimum	constatut	zero	maximum
If the two parts A and B in a system are considered to be in					
equilibrium and having thermodynamic probabilities $W_{\Lambda}$ and	$W = W_A W_B$	$W = W_A + W_B$	$W = (W_{A} + W_{P}) / 2$	$W = \sqrt{(W_A - W_B)}$	$W = W_A W_B$
$W_{\rm p}$ , what will be the thermodynamic probability of the system?	··· ··· A · ··· B	··· ··· A ··· B	··· (·· A ··· b) / =	······································	AB
What is the entropy chosen at the triple point of water?	zero	less than zero	more than zero	constant	zero
At the state of perfect order $(W = 1)$ of pure crystalline	entropy at 0 °C	entropy at absolute zero	entropy at the freezing	constant	entropy at absolute zero
substance how is the zero entropy defined?	temperature	temperature	point of the substance	none	temperature
The process which decreases the entropy of the universe is	reversible	irreversible	isochoric	impossible	impossible
When the potential gradient in a process is infinitesimal or zero.				1	
what will be the change in entropy of the universe?	entropy decreases	entropy increases	no change in entropy	zero	no change in entropy
What is the entropy transfer associated with work?	positive entropy transfer	negative entropy transfer	no entropy transfer	zero	no entropy transfer
Specific heat of metals can be expressed as	T <sup>3</sup>	$AT + BT^2$	$AT^2 + BT^3$	$AT + BT^3$	$AT + BT^3$
What is the entropy change (dS <sub>iso</sub> ) of an irreversible isolated	10 0	10 > 0	10 < 0	10:	10 > 0
(dQ=0) process?	$dS_{iso} = 0$	$dS_{iso} \ge 0$	$dS_{iso} \leq 0$	dS1so=constant	$dS_{iso} > 0$
What is the entropy change $(dS_{iso})$ of a reversible isolated	10 0	10 0	10 0	10	10 0
(dO=0) process?	$dS_{iso} = 0$	$dS_{iso} > 0$	$dS_{iso} < 0$	dS1so=constant	$dS_{iso} = 0$
An ensemble usually refers to an equilibrium density distribution that	time	valaaity	motion	maga	time
does not change with	ume	velocity	motion	mass	time
In the ensemble, we assume peq to be uniform	microcanonical	macrocanonical	canonical	none	microcanonical
In molecular simulations, the microcanonical ensemble is usually					
referred to as the ensemble	VE	NV E	macrocanonical	N/VE	NV E
A canonical ensemble represents the possible states of a					
mechanical system in equilibrium with a heat bath at	Chemical	phase	thermal	mechanical	thermal
a fixed temperature					
The canonical ensemble was first described byin 1884	Kelvin	Joule	Gibbs	Boltzmann	Boltzmann
The concept of ensemble put forward by	Einstein	Gibbs	Bose	Dirac	Gibbs

An ice cube in water or common salt in a water solution can be considered as members of a ensemble	microcanonical	canonical	grand canonical	macro canonical	grand canonical
The entropy of the combined system will be given by	S0=S1+S2	S0=S1-S2	S0=S1*S2	S0=S1/S2	S0=S1+S2
The relation between entropy and probability is	S=f(x)	$S=f(\Omega)$	$S=f(-\Omega)$	$S=-f(\Omega)$	$S=f(\Omega)$
Water molecules in a tea pot is an example of	microcanonical	canonical	grand canonical	macro canonical	canonical
The members of grand canonical can exchange	heat only	work only	mass only	heat and work	heat and work
Which canonical has idealised concept?	microcanonical	no canonical	grand canonical	macro canonical	microcanonical
The members of canonical ensemble can exchange	heat only	work only	mass only	thermal energy	thermal energy
Which ensemble do not interact with surroundings?	microcanonical	canonical	grand canonical	macro canonical	microcanonical

#### DEPARTMENT OF PHYSICS III BSc PHYSICS (15PHU602) STATISTICAL MECHANICS

#### Unit-V

Questions	opt1	opt2	opt3	opt4	Answer
M.B. distribution can be applicable to	identical molecule	indistinguishable molecule	gas	liquid	identical molecule
The number of quantum states is represented by	n <sub>r</sub>	gr	E <sub>r</sub>	N	g <sub>r</sub>
The degeneracy parameter A =	Z	e <sup>α</sup>	e <sup>-a</sup>	e <sup>β</sup>	e <sup>-α</sup>
In M.B. distribution, the unit of $n(v)$ is	m/ sec	mol/sec	mol/m/sec	sec	mol/m/sec
The equation for total internal energy of one mole of an ideal gas is	U/N = 3/2  kT	U/N = 3/2	U/N = kT	U/N = 2/3  kT	U/N = 3/2  kT
The value of $\beta = $	kT	k	Т	1/kT	1/kT
At absolute zero temperature the entropy may become	Infinity	positive	Zero	Negative	Zero
The value of entropy becomes zero in perfectly	liquid	crystalline solid	gas	inert gas	crystalline solid
M.B. law cannot be applicable to particles.	distinguishable	Indistinguishable	isolated	Isobaric	Indistinguishable
In dilute gas, the number of molecules per unit volume is	large	very small	infinity	small	small
In dilute gas, the average separation between the molecules is	large	very small	Infinity	small	large
In classical physics identical particles are	indistinguishable	distinguishable	symmetric	anti-symmetric	distinguishable
The dimensions of the phase space depends upon the of the system.	entropy	heat content	degrees of freedom	enthalpy	degrees of freedom
B.E distribution function is given by	$\{1/(e^{a+bE})\}$	$\{1/(e^{a+bE})+1\}$	$\{(e^{a+bE})-1\}$	$\{1/(ea + bE) - 1\}$	$\{(e^{a+bE})-1\}$
The degeneracy parameter $e^{-a} =$	N/V $(h^2 / 2pmkT)^{1/2}$	N/V $(h^2 / 2pmkT)^{3/4}$	N/V $(h^2 / 2pmkT)^{3/2}$	$N/V (h^2 / 2pmkT)^3$	N/V $(h^2 / 2pmkT)^{3/2}$
Maxwell first developed theory	Equipartition	partition	classical	quantum	classical
According to classical mechanics a molecule can have	finite speed	infinite speed	variable speed	constant speed	infinite speed
B.E distribution law is used to derive of radiation	Plank's law	Weiss law	Widemann- Franz law	All the above	Plank's law
Wave function of the system of identical Bosons is	Asymmetric	linear	non-linear	symmetric	symmetric
M.B. distribution can be applicable to	identical molecule	indistinguishable molecule	gas	liquid	identical molecule
In M.B. distribution the mean P.E. is than/ to K.E. of ideal gas.	larger	very large	small	equal	small
When T=0, the value of entropy $S = $ in M.B. distribution.	infinity	negative infinity	zero	one	negative infinity
M.B. law cannot be applicable to particles.	distinguishable	Indistinguishable	isolated	Isobaric	Indistinguishable
B.E distribution law is used to derive of radiation	Planck's law	Weiss law	Widemann Franz law	Rayleigh's law	Planck's law
Wave function of the system of identical Bosons is	asymmetric	linear	non-linear	symmetric	symmetric
Which of the following obey Pauli exclusion principle?	M.B. statistics	B.E. statistics	F.D. statistics	Einstein's equation	F.D. statistics
Which of the following do not obey Pauli exclusion principle?	M.B. statistics	B.E. statistics	F.D. statistics	Einstein's equation	B.E. statistics
In B.E. distribution, the constant $e^{\alpha}$ must be	greater than 1	smaller than 1	equal to 1	zero	greater than 1
The molecules obey B.E. statistics are	photons	phonons	fermions	bosons	bosons
is the energy distribution function.	f(E)	g(E)	n(E)	f	f(E)
is the number of quantum states	f(E)	g(E)	n(E)	f	g(E)
In B.E. energy distribution, if $e^{\alpha} = 1$ , for E=0, then n(0) dE =	postive infinity	negative infinitive	1	0	postive infinity
In B.E. energy distribution, if $e^{\alpha} < 1$ , for E=0, then n(0) dE =	postive infinity	negative infinitive	1	0	negative infinitive
For an ideal B.E. distribution the degeneracy parameter A cannot be	greater than 1	smaller than 1	equal to 1	zero	greater than 1
For all known B.E. gases, T <sub>B</sub> is very	high	low	small	0	low

E E		1		-1	-1
E.Fermi developed the statistics for	photons	DOSONS	phonons	electrons	electrons
In B.E statistics the particles are identical and indistinguishable. These	Bosons	fermions	leptons	baryons	Bosons
particles are called as	-	a	-		a
Particles with half-integral spin are called as	Bosons	fermions	leptons	baryons	fermions
Fermions obey principle	Heisenberg	Le-chatlier	Pauli	Haber	Pauli
Condition for B.E distribution to approach M.B distribution is $1/A(e^{bE})$	A<=1	A<<1	A>>1	A>>1	A<<1
>>1 i.e	11 · 1	21 · · 1	21 <sup></sup> 1		
In B.E statistics the particles are identical and indistinguishable. These particles	Bosons	fermions	leptons	baryons	Bosons
The Bosons has	spin 1	zero or half-integral spin	zero or whole number	zero	zero or half-integral spin
The examples for Bosons	photons	electrons	neutrons	protons	photons
Particles with half-integral spin are called as	bosons	Fermions	leptons	electrons	leptons
The examples for Fermions	Photons	phonons	electrons	antiparitcles	electrons
The spin of the photon is	0	1	2	1/2	1
In F.D statistics the particles are identical and indistinguishable. These	Earmiona	hagang	nhotona	Irmmtona	Formiona
particles	remnons	DOSOIIS	photons	kiyptolis	remnons
B.E distribution function is given by	$\{1/(ea + bE)\}$	$\{1/(ea + bE) + 1\}$	$\{(ea + bE) - 1\}$	$\{1/(ea + bE) - 1\}$	$\{1/(ea + bE) - 1\}$
Fermi energy Ef =	- aKT	aKT	-1/ aKT	1/ aKT	- aKT
Fermi-Dirac distribution function FD(E) =	$\{1/(ea + bE) + 1\}$	{1/( ea + bE) - 1}	{( ea + bE) - 1}	$\{-1/(ea + bE) + 1\}$	$\{1/(ea + bE) + 1\}$
In terms of Fermi energy F.D distribution function is fFD(E) =	$\{-1/(eE + EF) + 1\}$	$\{1/(eE - EF) + 1\}$	$\{1/(eE + EF) + 1\}$	$\{1/(eE + EF) - 1\}$	$\{1/(eE + EF) + 1\}$
B.E statistics is used to find the among identical	energy distribution	frequency distribution	both a and b	mass distribution	energy distribution
According to B.E distribution law the number of Bosons having energies	$g(E)dE/{(ea + bE) + 1}$	$g(E)dE/{(ea + bE) - 1}$	$g(E)dE/{(ea + bE) - 1}$	$g(E)dE/{(ea + bE) - 1}1/2$	$g(E)dE/{(ea + bE) - 1}1/2$
Wave function of the system of identical Bosons is	Unsymmetric	linear	symmetric	zero	symmetric
The molecule of an ideal B.E gas in two phases at	T = TB	T > TB	T < TB	T <= TB	T < TB
Which type of statistics is used to describe the electron contribution to specific heat?	MB statistics	BE statistics	FD statistics	Classical statistics	FD statistics

CLASS: III BSc PHYSICS COURSE CODE:15PHU602 COURSE NAME:STATISTICAL MECHANICS

# UNIT: V

BATCH-2015-2018

## UNIT-V

#### **SYLLABUS**

Fermi-Dirac Statistics Fermi-Dirac Distribution Law. Thermodynamic functions of an ideal Completely Degenerate Fermi Gas. Fermi Energy. Electron gas in a Metal. Specific Heat of Metals. White Dwarf Stars. Chandrasekhar Mass Limit.

#### FERMI-DIRAC STATISTICS

In quantum statistics, a branch of physics, Fermi–Dirac statistics describe a distribution of particles over energy states in systems consisting of manyidentical particles that obey the Pauli exclusion principle. It is named afterEnrico Fermi and Paul Dirac, each of whom discovered the method independently (although Fermi defined the statistics earlier than Dirac).<sup>[1][2]</sup>

Fermi–Dirac (F–D) statistics apply to identical particles with half-integer spin in a system with thermodynamic equilibrium. Additionally, the particles in this system are assumed to have negligible mutual interaction. That allows the many-particle system to be described in terms of single-particle energy states. The result is the F–D distribution of particles over these states which includes the condition that no two particles can occupy the same state; this has a considerable effect on the properties of the system. Since F–D statistics apply to particles with half-integer spin, these particles have come to be calledfermions. It is most commonly applied to electrons, which are fermions withspin 1/2. Fermi–Dirac statistics are a part of the more general field of statistical mechanics and use the principles of quantum mechanics.

# FERMI-DIRAC DISTRIBUTION LAW.

The Fermi-Dirac distribution applies to fermions, particles with half-integer spin which must obey the Pauli exclusion principle. Each type of distribution function has a normalization term multiplying the exponential in the denominator which may be temperature dependent. For the Fermi-Dirac case, that term is usually written:



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The significance of the Fermi energy is most clearly seen by setting T=0. At absolute zero, the probability is =1 for energies less than the Fermi energy and zero for energies greater than the Fermi energy. We picture all the levels up to the Fermi energy as filled, but no particle has a greater energy. This is entirely consistent with the Pauli exclusion principle where each quantum state can have one but only one particle.

$$f(E) = \frac{1}{e^{(E - E_F)/kT} + 1}$$

#### FERMI ENERGY.

The Fermi energy at absolute zero of temperature is denoted by  $E_{Fo}$  and this is considered as a constant over a large range of temperature.

The Fermi function is,

 $f(E) = \frac{1}{e^{\left(E - E_{F_0}\right)/kT} + 1}$ 

At T=0, when E < E<sub>Fo</sub>,

 $f(E) = \frac{1}{e^{-\infty} + 1} = \frac{1}{0 + 1} = 1$  (1)

and at T = 0, when  $E > E_{Fo}$ ,

$$f(E) = \frac{1}{e^{\infty} + 1} = \frac{1}{\omega + 1} = 1$$
 (2)

Equ. 1 and 2 shows that at T=0, the function f(E) is constant equal to 1 for all values of energies upto  $E_{Fo}$  it falls to zero. That is at T=0, it is a step function.

Thus at absolute zero of temperature all possible quantum states of energy less than  $E_{Fo}$  re occupied and all those of energy more than  $E_{Fo}$  are empty.

Accordingly the Fermi energy  $E_{Fo}$  is defined as the energy of the highest occupied level at absolute zero. At any other temperature T>0, when  $E=E_{Fo}$ , the Fermi energy is

$$f(E) = \frac{1}{e^{\left(E - E_{F_0}\right)/kT} + 1} = \frac{1}{e^{0/kT} + 1} = 1/2$$

This means that at temperature T>0, the probability for occupation of a quantum states at the Fermi level is  $\frac{1}{2}$ . At temperature T>0, 50% of the quantum states at the Fermi level are occupied and 50% are empty.

# ELECTRON GAS IN A METAL

The total number N of the free electrons in a metal of volume V is given by

$$N = \int_0^\infty n(E) dE$$
  
=  $\int_0^\infty f(E) g(E) dE$   
=  $\int_0^{E_{F_0}} f(E)g(E) dE + \int_{E_{F_0}}^0 f(E)g(E) dE$  ------ (1)

At T = 0, when  $E \le E_{F_0}$ , then f (E) =1 and at T=0, when  $E \ge E_{F_0}$  then f(E) = 0. Hence in equ. (1)the second integral is zero and in the first integral f (E) = 1.

$$N = \int_0^{E_{F_0}} g(E) dE$$
  
=  $4\pi V (2m/h^2)^{3/2} \int_0^{E_{F_0}} E^{1/2} dE$   
=  $4\pi V (2m/h^2)^{3/2} 2/3 E_{F_0}^{3/2}$   
=  $\frac{8\pi}{3} V \left(\frac{2mE_{F_0}}{h^2}\right)^{3/2}$ 

From this equation,

When n = N/V = no.of free electrons per unit volume, i.e., the free electron density.

The values of  $E_{Fo}$  calculated from eq. (3) for a number of metals are of the order of several electron volts. This fact is a very important difference between classical statistics and Fermi-Dirac statistics. According to classical statistics all electron in a metal at absolute zero would have zero energy.

## SPECIFIC HEAT OF SOLIDS

#### Law of Dulong and Petit

According to Dulong and Petit's law, the product of atomic weights and specific heat at constant volume is constant. This constant is known is atomic heat. Its values as calculated theoretically on the basis of kinetic theory of matter comes out to be 5.96. Since atomic weight of an element is constant, its specific heat must be constant. i.e., the value of the specific heat of various elements should be same at all temperatures. This is however, contrary to the experimentally observed facts. It has been found by experiments that the specific heat of all substances varies with temperature.

It was experimentally found by Nernst and Lindemann that the specific heat of a substance decreases with decreases in temperature and tends to be zero at absolute zero. On the other hand, the specific heat increases with increase in temperature and tends to a maximum value. Carbon, Boron and Silicon, whose atomic heat at ordinary temperature (20°C) are 1.76, 2.75 and 4.98 respectively, show an increase in these values towards 6 as their temperature is raised and finally the atomic heat of these substances becomes 6 at high temperature, but it is less than 6 at low temperature. The variation of specific heat in metals like lead, tin and platinum is very small.

The experimental observation of specific heat at low temperature indicate that specific heat decreases slowly with decrease of temperature and below a certain temperature, characteristic of each element the specific heat decreases rapidly tending finally to zero value at the absolute zero of temperature. This shows that Dulong and Petit's law is in god agreement with experimental observation at higher temperatures and deviates from experiments as the temperature decreases.

The <u>specific heat</u> of copper is 0.093 cal/gm K (0.389 J/gm K) and that of lead is only 0.031 cal/gm K(0.13 J/gm K). Why are they so different? The difference is mainly because it is expressed as energy per unit mass; if you express it as energy per mole, they are very similar. It

is in fact that similarity of the molar specific heats of metals which is the subject of the Law of Dulong and Petit. The similarity can be accounted for by applying <u>equipartition of energy</u> to the atoms of the solids.

From just the translational degrees of freedom you get 3kT/2 of energy per atom. Energy added to solids takes the form of atomic vibrations and that contributes three additional degrees of freedom and a total energy per atom of 3kT. The specific heat at constant volume should be just the rate of change with temperature (temperature derivative) of that energy.

Energy per mole =  $3kTN_A$   $N_A = Avogadro's number$ 

The Law of Dulong & Petit  $C_v = \frac{\partial}{\partial T} (3kTN_A) = 3kN_A / mole = 24.94J / mole K$ 

## **Einstein's Contribution to Specific Heat Theory**

**Einstein's theory of specific heat:** The first attempt to explain the variation of specific heat with temperature was made by Einstein in 1907 on the basis of quantum theory. According to quantum theory, heat is radiated in the form of discrete particles known as photons. Each photon has energy equal to hv where h is the Planck's constant and v is the frequency of the heat radiations.

To explain the variation of specific heat with temperature, Einstein assumed:

- (i) A solid is constituted of atoms. These atoms are at rest under the action of their mutual attractions and repulsions at absolute zero of temperature. The energy of the solid in this state is zero. When the solid is heated, the atoms are set into simple harmonic vibrations about their positions of equilibrium. The frequency of these vibrations is one and the same, characteristic of the particular solid concerned.
- (ii) Each atom of a solid has 3 degrees of freedom like a molecule of monoatomic gas.
- (iii) The mean energy per degree of freedom is not kT as given by equipartition law, but as calculated by Planck by the application of quantum theory.

The value of v giving god fit for a particular solid is represented by  $v_E$  and is called **Einstein's Frequency for that solid**. $\theta$  corresponding to  $v_E$  is represented as  $\theta_E$  and is called **Einstein's temperature**.

This is Einstein's equation for the atomic heat of solid at constant volume. The equation represents that the atomic heat is a function of temperature. The characteristic of experimentally observed variation of specific heat of solids are as follows:

- At high temperature, the atomic heat approaches the constant value 3R as given by Dulong and Petit's law.
- (ii) The atomic heat decreases with decrease of temperature and tends to zero at absolute zero of temperature.
- (iii) The experimental curves drawn temperature versus atomic heat show that the curves have the same form for al substances.

These facts can be explained on the basis of Einstein's equation.

(i) At high temperatures, hv/kT approaches very small values and so we have
 Thus, according to Einstein's equation, the atomic heat approaches 3R which is in agreement
 with experiments and Dulong and Petit's law.

 When the value of temperature tends to zero, hv/kT tends to infinity and hence 1 may be neglected in the expression

Then the equation becomes

Thus according to Einstein's equation, the atomic heat tends to zero as temperature tends to absolute zero. Also, according the Einstein's equation, atomic heat decreases with decrease of temperature.

(iii) According to Einstein's equation, the atomic heats of different elements differ only because of differences in the characteristic frequency v. At corresponding temperatures, such that the value of the ratio v/T are the same, then according to Einstein's equation, the atomic heat will be the same for al elements. Thus the experimental curves have the same form for al substances.

Thus Einstein's theory predicts the correct values of atomic heats for various elements as observed experimentally, i.e., the Einstein's theory is in good agreement with experimental results.

The Law of Dulong and Petit assumed that Maxwell-Boltzmann statistics and equipartition of energy could be applied even at low temperatures. Einstein recognized that for a quantum harmonic oscillator at energies less than kT, the Einstein-Bose statistics must be applied. This was the same conclusion that was drawn about blackbody radiation. The statistical distribution of energy in the vibrational states gives average energy:

$$\langle E \rangle = \frac{h\upsilon}{e^{h\upsilon/kT} - 1}$$

where this frequency is the frequency of a quantum vibrator. There are three degrees of freedom per vibrator, so the total energy is

$$E_{oscillators} = \frac{3hvN_A}{e^{hv/kT} - 1}mole^{-1}$$

In the Einstein treatment, the appropriate frequency in the expression had to be determined empirically by comparison with experiment for each element. The quantity  $h\nu/k$  is sometimes

called the Einstein temperature. Although the general match with experiment was reasonable, it was not exact.

$$C_{V} = \frac{\partial E}{\partial T} = \frac{3N_{A}k\left(\frac{hv}{kT}\right)^{2}e^{hv/kT}}{\left(e^{hv/kT}-1\right)^{2}}mole^{-1}$$

Debye advanced the treatment by treating the quantum oscillators as collective modes in the solid which are now called "phonons". The High Temperature Limit of the Einstein Specific Heat Einstein's introduction of <u>quantum behavior</u> showed why the specific heat became temperature dependent at low temperatures, and it had a high temperature limit which agreed with the <u>Law of Dulong and Petit</u>. To show this, note that for high temperatures, a <u>series expansion</u> of the exponential gives

$$e^{h\upsilon/kT} \approx 1 + \frac{h\upsilon}{kT}$$

The Einstein specific heat expression then becomes

$$C_{v} = \frac{\partial E}{\partial T} = \frac{3N_{A}k\left(\frac{hv}{kT}\right)^{2}\left(1 + \frac{hv}{kT}\right)}{\left(\frac{hv}{kT}\right)^{2}}mole^{-1}$$

This reduces to the Law of Dulong and Petit.

$$C_V = 3N_A k \left(1 + \frac{hv}{kT}\right) \approx 3N_A k \ mole^{-1}$$

# Debye's theory of Specific heats

Though the Einstein's theory predicts almost correctly the variation of specific heat with temperature, it was observed that in the case of some elements like copper, aluminium, iron etc., the atomic heat at low temperature decreases more rapidly than that predicted by Einstein's theory. This disagreement is due to the assumption that the vibrations of all the atoms are simple harmonic and have one and the same frequency. In fact, the vibrations of an atom must be complex, because it is under the field of force of a large number of other vibrating atoms. Moreover, in Einstein's theory, v and hv/k have been obtained empirically and cannot be verified from any other independent physical data. Debye, therefore, modified Einstein's theory which gives excellent agreement with experiment over the whole observable temperature range.

Debye assumed that any solid is capable of vibrating elastically in many different modes, the frequency varying from on mode to another, and the number of modes of vibration of solids is limited in number.

When a continuous solid is subjected to elastic vibrations, two kinds of vibrations are produced.

(i)

Transverse vibrations, and (ii) Longitudinal vibrations.

The number of modes of longitudinal vibrations per unit volume with frequencies between v and v + dv.

## Liquid Helium:

As an application of B-E. statistics, the qualitative nature of the superfluid transition of liquid helium at 2.2 K were investigated. Ordinary helium consists almost entirely of neutral atoms of the isotope  $_2$ He<sup>4</sup>. As the total angular momentum of this atoms is 0.

Helium exhibits peculiar properties at low temperatures.

- (i) Helium gas at atmospheric pressure condenses at 4.3 K into a liquid of very low density about  $0.124 \text{ gm}/\text{cm}^3$
- (ii) Further cooling about 0.82 K doesnot freeze it and its believed that it remains all the way down to absolute 0. The solid state of helium does not form unless it is subjected to an external pressure of atleast 23 atm.
- (iii) For He<sup>1</sup> in liquid phase there is another phase transition called  $\lambda$  transition which divides the liquid state into two phases He I and II. K. Onnes while liquefying helium noted that about 2.2 K, density appeared to pass through abrupt maximum and then decreasing slightly. Investigations also revealed that critical temperature at 2.186 K. It represents a transition to a new state of matter known as liquid He II.
  - a) Heat conductivity is very large in the order of  $3.10^6$  times greater.
  - b) Co-efficient of velocity gradually diminishes as the temperature is lowered and appears to be approaching 0 at absolute 0 temp.
  - c) Specific heat measurements by Kessom show that specific heat curve is discontinuous at 2.186 K. The shape of the specific heat curve resembles the shape of the letter  $\lambda$  and this peculiar transition is called  $\lambda$  transition and the discontinuity temp. 2.186 K is called  $\lambda$  point. Kesson concluded that transition He I  $\rightarrow$ He II at  $T_{\lambda}$  is second order transition. The transition temp. decreases as the pressure is increased.

## Possible Questions

- 1) Explain Fermi Dirac Distribution Law.
- 2) Explain Electron gas in a metal.
- 3) Explain Specific Heat of Metals
- 4) What is White Dwarf Star.
- 5) Explain Chandrasekhar Mass Limit.
- 6) Explain Fermi Dirac Statistics.