2017-2018 ODD

SEMESTER I

L T P C

17PHP103 THERMODYNAMICS AND STATISTICAL MECHANICS 4 - - 4

Scope: Thermodynamics is an important branch of physics, which helps us to understand the different phenomena in the evolution of the universe. Also, thermodynamics is important for other parts of physics also.

Objectives: This paper gives a basic idea about the laws of thermodynamics and statistical processes.

UNIT- I

Laws of Thermodynamics: Some consequences of the laws of thermodynamics − Entropy − Calculation of entropy changes in reversible processes. The principle of increase of entropy − Thermodynamic potentials − Ehthalpy, Helmholtz and the Gibbs functions − Phase transitions − The Clausius-Clayperon equation − Van der Waals equation of state.

UNIT- II

Kinetic Theory: Distribution function and its evolution − Boltzmann transport equation and its validity − Boltzmann's H-theorem − Maxwell-Boltzmann distribution − Transport phenomena − Mean free path- Conservation laws − Hydrodynamics (No derivation).

UNIT- III

Classical Statistical Mechanics: Maxwell Boltzmann distribution law: Evaluation of constants - Maxwell's law of distribution of velocities - Most probable speed, Average speed, Root mean square speed - Principle of equipartition of energy - Partition function - Condition for applicability of M.B statistics - Non degenerate and degenerate systems - Maxwell velocity distribution in a given direction - Total internal energy of an ideal gas - Molar heat capacity of a gas at constant volume – Entropy - Helmholtz free energy - Pressure and equation of state of an ideal gas - Limitation of M.B method.

UNIT -IV

Quantum Statistical Mechanics: B.E energy distribution for energies in the range E to E + dE – Condition for B.E distribution to approach classical M.B distribution - Bose temperature - Bose Einstein condensation - Planck's law from B.E law - Fermi Dirac distribution law (no derivation) - FD law for the energies in the range E to E+dE – Fermi energy - Effect of temperature - Energy distribution curve - Free electron in a metal - Fermi temperature and Thermionic emission - Richardson Dushmann Equation - Comparison of MB,BE and FD statistics.

UNIT- V

Applications of Quantum Statistical Mechanics: Ideal Bose gas : Photons − Black body and Planck radiation − Photons − Specific heat of solids − Liquid Helium.

Ideal Fermi gas : Properties − Degeneracy − Electron gas − Pauli paramagnetism

Ferromagnetism : Ising and Heisenberg models.

TEXT BOOKS:

1. Reif F., 2008, Fundamentals of Statistical and Thermal Physics, (Reprint), McGraw Hill International Edition, Singapore.
2. Gupta and Kumar, reprint, 2014, Elements of Statistical Mechanics, Pragati Prakashan, Meerut.

REFERENCES:

1. Huang K., 2nd edition, 2014, Statistical Mechanics, Wiley Eastern Limited, New Delhi
2. Agarwal B.K. and M. Eisner, 3rd edition, 2013, Statistical Mechanics, New age international Limited, New Delhi.
3. Sears N. and L. Salinger, 2013, Thermodynamics, 3rd Ed., Narosa Publishing House, New Delhi.
4. Greiner W., L. Neise and H. Stocker, 1st edition, 2007, Thermodynamics and Statistical Mechanics, Springer Verlag, New York.
5. Singh. K. and S.P. Singh reprint 2016, Elements of Statistical Mechanics, S. Chand & Company Ltd., New Delhi.

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE
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THERMODYNAMICS AND STATISTICAL MECHANICS - LECTURE PLAN (17PHP103)

Unit No.	Topics to be covered	P.No.	No. of hours
I	Introduction about thermodynamical laws	T1-1-3,9,12-13 R1-88-92	1
	Some consequences of the laws of thermodynamics	T 1- 15-18	1
	Entropy, Calculation of entropy changes in reversible processes		1
	The principle of increase of entropy	T 1- 18-19 R1-154-155	1
	Thermodynamic potentials− Ehthalpy, Helmholtz and the Gibbs functions	T 1- 21 , 24	1
	Phase transitions The Clausius-Clayperon equation	T1-478 T 1- 27-29	1
	Van der Waals equation of state	T 1- 6-8 R1-73-74	1
	Revision		1

Textbooks:
T 1- Thermal Physics and Statistical Mechanics by S. K. Roy, New age international publishers.

Statistical Mechanics by Sathya Prakash and J.P.Agarwal- Kedar Nath Ram Nath & Co. Meerut.

Reference:
R1- Thermal Physics by S.C.Garg, R.M.Bansal, C.K.Ghosh, TataMc Grae Hill Pub., New Delhi.

Website :
www.indiastudychannel.com/resources/157686-on-introduction to thermodynamics laws.asp

Unit No.	**Topics to be covered**	**P.No.**	**No. of hours**
II	Distribution function and its evolution	T2 - 456	1
	Boltzmann transport equation and its validity	T 2 – 456 - 459	1
	Boltzmann’s H-theorem	T 2 – 458	1
	Maxwell-Boltzmann distribution Transport phenomena	T2 – 152 204-205	1
	Mean free path Conservation laws Hydrodynamics	T 2 – 195 W2 W3	1
	Revision		1

Textbooks:

T 2- Statistical Mechanics by Sathya Prakash and J.P.Agarwal- Kedar Nath Ram Nath & Co. Meerut.

Reference:
R1- Thermal Physics by S.C.Garg, R.M.Bansal, C.K.Ghosh, TataMc Grae Hill Pub., New Delhi.

Website:
W2- www.quarknet.fnal.gov/

W3 – www. astro.uni-bonn.de

Unit No.	**Topics to be covered**	**P.No.**	**No. of hours**
III	Classical statistical mechanics Maxwell Boltzmann distribution law Evaluation of constants	T 3 – 46 34-36	1
	Maxwell's law of distribution of velocities Most probable,Mean square Root mean square speeds	T2- 48 - 51	1
	Principle of equipartition of energy, Partition function, Condition for applicability of M.B statistics,	T3 - 2 –36 63-65	1
	Non degenerate and degenerate systems	T 3 – 38	1
	Maxwell velocity distribution in a given direction	T 3 – 52-53	1
	Total internal energy of an ideal gas, Molar heat capacity of a gas at constant volume, Entropy	T 3– 53-54	1
	Helmholtz free energy, Pressure and equation of state of an ideal gas	T3 – 59-60	1
	Limitation of M.B method	T 3 – 65-66	1
	Revision		1

Textbooks:
T3 – Elements of Statistical Mechanics by Miss Kamal Singh and S.P.Singh – S.Chand and Company

Reference Books:
R2- Statistical Mechanics by Agarwal .B.K. and Meisner, Wiley Eastern Limited, New Delhi

Unit No.	Topics to be covered	P.No.	No. of hours
IV	Quantum statistical mechanics B.E energy distribution for energies in the range E to E + dE,	T 3 - 78	1
	Condition for B.E distribution to approach classical M.B distribution	T3 - 80	1
	Bose temperature - Bose Einstein condensation	T 2 – 81-84	1
	Planck's law from B.E law Fermi Dirac distribution law (no derivation)	T 3 – 84 - 86	1
	FD law for the energies in the range E to E+dE, Fermi energy,	T 3 – 91-93, 95 - 97	1
	Effect of temperature , Energy distribution curve Free electron in a metal	T 3 – 97, 98-100	1
	Fermi temperature, Thermionic emission Richardson Dushmann Equation, Comparison of MB,BE and FD statistics	T 3– 101-110	1
	Revision		1

Textbooks:
T3 – Elements of Statistical Mechanics by Miss Kamal Singh and S.P.Singh – S.Chand and Company

Reference Books:
R2- Statistical Mechanics by Agarwal .B.K. and Meisner, Wiley Eastern Limited, New Delhi

Unit No.	**Topics to be covered**	**P.No.**	**No. of hours**
V	Applications of Quantum Statistical mechanics Ideal Bose gas : Photons	T3 – 304-306	1
	Black body and Planck radiation Photons	T 3 – 304-306	1
	Specific heat of solids Liquid Helium	T 4 – 319-344	1
	Ideal Fermi gas : Properties, Degeneracy, Electron gas, Pauli paramagnetism	T 2-359-362 T4 – 365-373	1
	Ferromagnetism : Ising and Heisenberg models	T 4-431-433	1
	Revision		1
	Old Question Paper Discussion		1
	Old Question Paper Discussion		1
	Old Question Paper Discussion		1

Text Books:

T4 – Elements of Statistical Mechanics by Gupta and Kumar – Pragathi Prakasham Publishers

Reference Books:
R2- Statistical Mechanics by Agarwal .B.K. and Meisner, Wiley Eastern Limited, New Delhi

Laws of Thermodynamics: Some consequences of the laws of thermodynamics − Entropy − Calculation of entropy changes in reversible processes. The principle of increase of entropy − Thermodynamic potentials − Ehthalpy, Helmholtz and the Gibbs functions − Phase transitions − The Clausius-Clayperon equation − Van der Waals equation of state.

THERMODYNAMICS

Thermodynamics is the science of studying the changes that occur within a system in relation to its interaction with its surroundings according to a series of laws formulated that are considered valid for all systems. Thermodynamics allows scientists to study the potential reactions and interactions of systems that exist only in theory, or be such that they cannot be recreated or contained in a laboratory for study.

The empirical facts of thermodynamics are comprehended in its four laws. The first law specifies that energy can be exchanged between physical systems as heat and thermodynamic work. The second law concerns a quantity called entropy, expresses limitations, arising from what is known as irreversibility, on the amount of thermodynamic work that can be delivered to an external system by a thermodynamic process.

THERMODYNAMIC SYSTEMS

An important concept in thermodynamics is the “system”. A physical system is the region of the universe under study. A system is separated from the remainder of the universe by a boundary which may be imaginary or not, but which by convention delimits a finite region. The possible exchanges of work, heat, or matter between the system and the surroundings take place across this boundary. There are five dominant classes of systems:

1. Isolated Systems – matter and energy may not cross the boundary.
2. Adiabatic Systems – heat may not cross the boundary.
3. Diathermic Systems - heat may cross boundary.
4. Closed Systems – matter may not cross the boundary.

Open Systems – heat, work, and matter may cross the boundary.

LAWS OF THERMODYNAMICS

The four main laws of Thermodynamics are,

Zeroth Law - if two systems each are in equilibrium with a third system, then they must are also be in thermal equilibrium with each other.

First Law - if heat is added to a system, some of that energy stays in the system and some leaves the system.

Second Law - no reaction is 100% efficient and all energy wants to flow and spread to areas with less energy.

Third Law - it is impossible to cool an object to absolute zero because all processes will cease before absolute zero is reached, this is commonly called the state of entropy.

ENTROPY:

Entropy is a defined function of the thermal state of a body and is not affected in any way by the manner in which a particular state is reached. The change in entropy passing from one state A to another state B is given by $S_B - S_A = \int_A^B \frac{dQ}{T}$

where dQ is the quantity of heat absorbed or rejected at a temperature T in going from state A to state B.

(i) Entropy of a system remains constant during an adiabatic change,
(ii) Entropy of a system remains constant in all reversible processes.
(iii) Entropy of a system increases in all irreversible processes.

CALCULATION OF ENTROPY:

(i) Entropy of an ideal gas

Consider n gram molecules of an ideal gas occupying a volume V at a pressure P and temperature T. Let quantity of heat dQ be given to the gas, then I law of thermodynamics is $dQ=dU+dW$. If C_v is the heat capacity of gas at constant volume, dT is rise in temperature and dV represents change in volume.

$$\text{Then, } dU = C_v dT \text{ and } dW = pdV$$

$$\Longrightarrow \quad dQ = C_v + pdV$$

From second law of thermodynamics, the change in entropy is

$$dS = dQ/T = (C_v dT)/T + pdV / T \text{ ------------ (1)}$$

If select some arbitrary state1 at temperature T_0, pressure P_0 and volume v_0 in which the entropy of the gas is change in entropy during state1 to state2 at temperature T, pressure P and volume V is given by,

$$\Delta s = s - s_0 = \int_1^2 \frac{C_v dT}{T} + \int_1^2 \frac{P\,dV}{T} \text{ ------------ (2)}$$

(a) Value of S terms of temperature and volume

From the equation of state of an ideal gas

$$PV=nRT$$

$$\Longrightarrow P = nRT / V$$

Sub. value of P in eqn (2).

$$\Delta S = \int_1^2 \frac{C_v dT}{T} + \text{nR}\int_1^2 \frac{dV.T}{V.T} \text{ ------------- (3)}$$

If Cv be assumed to constant, equ.

$$\Delta S = Cv\, log_e\, T/T_0 + \text{nR}\, log_e\, V/V_0 \text{ (state 1 and 2) --------------- (4)}$$

For a case of isothermal expansion, $T = T_0$

∴ The change in entropy of gas in the case becomes

$$\Delta S = nR\, log_e \frac{V}{V_0} \text{ --------------- (5)}$$

(b) Value of S in terms of temperature and pressure:

$$PV = nRT$$

$$V = nRT/P$$

$$\text{and } PdV + VdP = nRdT \text{ -------- (5a)}$$

So that PdV = nRdT – VdP = nRdT - $\frac{nRTdP}{P}$ using (5a)

Sub. the value PdV in eq. (2)

$$\Delta S = \int_1^2 Cv\,\frac{dT}{T} + nR\int_1^2 \left(\frac{dT}{T} - \frac{dP}{P}\right)$$

$$= C_V \log_e \frac{T}{To} + nR\left(\log_e \frac{T}{To} - log_e \frac{P}{Po}\right)$$

For an ideal gas, $C_P - C_V = nR$

$$\Delta S = C_P \log_e \frac{T}{To} + (C_P - C_V)\, log_e \frac{P}{Po}$$

For isothermal change $T=T_0$, therefore change in entropy of the gas,

$$\Delta S = (C_P - C_V)\, log_e \frac{P}{Po} = nRlog_e \frac{P}{Po} \qquad \text{----------- (7)}$$

(c) Value of S in terms of pressure and volume

$$PV = nRT$$

So that, $T = \frac{PV}{nR}$ and $dT = \frac{PdV+VdP}{nR}$

Sub. these value in equ. 2,

$$\Delta S = \int_1^2 Cv\,\frac{PdV + VdP}{dV} + nR\int_1^2 \frac{PdV}{PV}$$

$$= \int_1^2 Cv\left(\frac{dV}{V} + \frac{dP}{P}\right) + (Cp - Cv)\int_1^2 \frac{dV}{V}$$

$$= \int_1^2 \left(Cv\frac{dP}{P} + Cp\frac{dV}{V}\right)$$

$$\Delta S = Cv\, log_e\, P/Po + C_P \log_e V/Vo \qquad \text{----------- (8)}$$

(ii) Entropy of steam

Let consider mass m of ice at absolute temp. T_1, find the total gain in entropy when ice changes into steam at absolute temperature T_2.

If small amount of heat dQ is given to a substance at temperature T, the change in entropy is dS =dQ/T.

To convert mass m of ice at T_1K into water at same temperature, the amount of heat required = mL_i, where L_i is the latent heat of ice.

Change in entropy during this process = mL_i/T -------- (i)

When mass m of water at T_1 K is heated to T_2 K, the change in entropy,

$$\Delta S = \int_{T1}^{T2} \frac{dQ}{T} = \int_{T1}^{T2} \frac{mCdT}{T} = mC \log_c T_2/T_1 \qquad \text{-------- (ii)}$$

To convert mass m of water at T_2C into steam at same temperature, the amount of heat required = mL_s, where L_s is latent heat of steam.

Change in entropy during this process = mL_s/T_2 ------- (iii)

Total gain in entropy = $\frac{mLi}{T1} + mCloge\left(\frac{T2}{T1}\right) + mL_s/T_2$

PRINCIPLE OF INCREASE OF ENERGY OR DEGRADATION OF ENERGY:

The entropy of a system remains constant in reversible cyclic process but increased inevitably in all irreversible process. Since a reversible process represents a limiting ideal case, all actual process are inherently irreversible. It means that as cycle after cycle of operation is performed, the entropy of the system increase and tends to a maximum value. This is the principal of increase of entropy and may be stated as " The entropy of an isolated or self contained system either increase or remains constant according as the process it undergoes are irreversible or reversible". Analytically it may be expressed as greater than 0; where the equality sign refers to reversible processes and the inequality sign to irreversible processes. Therefore the necessary and sufficient conditions of equal brim of a self contained system is that it's entropy should be maximum and it cannot be greater than zero.

Since all physical operation in the universe are irreversible for every such operations performed, a certain amount of energy become unavailable for useful work and is added to the universe in the form of heat through friction, conduction or radiation. In this way in a distant future on account of irreversibly all energies existing in different forms will be converted into heat energy and will not be available for conversion into mechanical work i.e " The available energy of the universe is tending toward zero " it will correspond to a state of maximum entropy and all temperature difference between various bodies of the universe will be equalized due to convection etc. No heat engine will then be able to work in this state because no heat flow would be possible due to the uniformity of the temperature throughout the universe .This is called the principal of degradation of energy is conserved it is transformed into a form which is unavailable for work . Thus the energy is "running down hill" and the universe is marching toward stage of die a "head - death".

With an increase in entropy, the thermal agitation and hence disorder of molecules of a substance increase, i.e increase of entropy implies a transition from order to discord. Thus the principal of increase of entropy is intimately connected with the less ordered state of affairs. According to it, a system posing high entropy should be in great disorder or chaos. Thus the entropy of a substance in gaseous state is more than in liquid state, because the molecules are free to move about in great disorder in a gas than in a liquid. Moreover the entropy is more in a liquid state than in the solid state, as the molecules are more free to move in a liquid than in a solid. Hence when ice is converted into water and then into steam, the entropy and disorder of molecules increase. On the other hand when the steam is converted into water and then in to ice, the entropy and disorder of molecules continually decreased. Thus when the temperature of a system is decreased, the amount of entropy and disorder in it decreased. Entropy of the substance is therefore said to be a measure of the degree of disorder prevailing among it's molecules just as the temperature is a measure of the degree of hotness of a substance at the absolute zero of temperature the thermal motion completely disappears so that the disorder and hence the entropy tends to zero and the molecules of a substance are in perfect order i.e well arranged.

By summarizing the above arguments, say that the entropy of any isolated system increase and approaches more or less rapidly to the inert state of maximum entropy. We may recognize this fundamental law of physics to be an inherent tendency of nature to be processed from a more ordered state to a less ordered one or from a less disordered to a more disordered state or other words that the ultimate destiny of universe is not order but chaos.

THERMODYNAMIC POTENTIALS:

The thermodynamics variables such as pressure P, Volume V, temperature T and entropy S, define the stole of thermo dynamical system. A relation b/n them exists because of the two thermodynamic laws.

$$dQ = dU+PdV$$

$$dQ = TdS$$

Combining

$$TdS= dU+PdV$$

$$dU = TdS - PdV$$

Any two of above variables are independent and with the help of above relation remaining variables be determined. These relations are termed as thermodynamic potentials of thermodynamic fn.

Enthalpy or Heat content H:

Thermodynamical phenomena at constant pressure are expressed in terms of another function called enthalpy or heat content of the system.

$$H = U + PV \qquad \text{---- (1)}$$

diff. $dH=dU+PdV+VdP$

$$= (TdS-PdV) + PdV+VdP$$

$$= TdS+VdP$$

$$dH = Tds \qquad \text{------ (2)}$$

because process is carried at constant pressure. Since $Tds = dQ$, we find $dH=dQ$ enthalpy represents the quantity of heat given to the system from an external source & hence the name heat content.

Let H_i and H_f be the initial and final enthalpy,

$$H_f-H_i = Q$$

The change in enthalpy during an isobaric process equal too the heat transferred.

H has an important property in porous plug exp let P_i and V_i be the initial pressure & volume of a gas before passing through porous plug. Similarly pf and vf be the similar quantities of the gas after passing thro' the porous plug.

External work done by gas = $P_f V_f - P_i V_i$

This work done at the cost of internal energy of the because no heat exchanges b/n gas and surrounding, suppose Ui and Uf be the initial and final internal energy.

$$U_i - U_f = P_f V_f - P_i V_i$$

$$U_i + P_i V_i = P_f V_f + U_f$$

$$\text{(or)} \quad H_i = H_f$$

Thus in throttling process, the initial and final enthalpy remain same.

Taking partial diff. of H w.r. to independent variables S and P,

$$\Longrightarrow \quad \left(\frac{\partial H}{\partial P}\right)_S = V \text{ and } \left(\frac{\partial H}{\partial S}\right)_P = T \qquad \text{------ (3)}$$

As dH is perfect diff.

$$\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)$$

Using (3), we get

$$\left(\frac{\partial V}{\partial P}\right)_V = \left(\frac{\partial T}{\partial P}\right)_S \qquad \text{------- (4)}$$

Which is third thermodynamical relation

Helmholtz Function F:

On combining I & II law of thermodynamics,

$dU = Tds - dW$

suppose the temp of the system remain constant, then d(TS) = Tds

⇨ dU=d(TS)-dW

d(U-TS) = –dW

where the fn. F=U-TS

⇨ dF=-dW --------- (1)

is called Helmholtz fn. Or Helmholtz free energy, which represents that in revisable isotheral process, the work done by the system is equal to decrease in Helmholtz Fn. F is also called as work fn.

on diff. Eqn. (1), we pet

$$dF=dU-TdS-SdT$$

sub. dU=TdS-PdV

$$\Rightarrow \quad dF=TdS-PdV-TdS-SdT$$

$$= -PdV-SdT \qquad - \ (2)$$

On partial diff. Of F w.r.to independent variables T & V.

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial F}{\partial V}\right)_T = -P \qquad \text{-------} \ (3)$$

As dF is a perfect diff,

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial V}\right)$$

using eq. (3) we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

This eqn. given a relation b/n 4 thermo dynamical variable P,V,S and T. This is second thermodynamical relation

Gibbs potential (G):

If thermodynamic process is isothermal and isobaric (dp=0) then from qn.(2) we get

$$dH=T(ds)$$

$$= d\,(TS) \quad \text{[from Helmholtz fn.]}$$

$$d(H-TS) = 0$$

$$dG = 0$$

$$\text{Where } G = H - TS$$

$$G = U+PV-TS$$

is called gibb's fn. or free energy

on diff. (5), we get

$$dG = dU+PdV+VdP - TdS - SdT$$

$$= (TdS - pdv) + pdV+VdP-TdS-SdT$$

$$dG = VdP-SdT \qquad \text{----- (6)}$$

Talking partial derivatives of a w.r. to independent variable P and T, we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \text{------- (7)}$$

As dG is perfect diff ., $\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)$

This is called fourth thermodynamical relation

CLASUSIS CLAYPERON EQUATION:

Maxwell second thermo dynamical relation is

$$\left(\frac{\partial S}{\partial V}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$$

Multiply both sides by T,

$$T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

From II law of thermodynamics,

$$TdS = dQ$$

$$\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$$

$\left(\frac{\partial Q}{\partial V}\right)_T$ represent the quantity of heat absorbed or liberated per unit charge in volume at constant temp. This means that at constant temp. The heat absorbed or liberated bring out simply a change in the volume of the substance. Therefore this amount of heat absorbed or liberated at constant temp must be the latent heat and change in volume must be due to change of state. Considering a unit mass of the substance let L be the latent heat when the substance change in volume from V_1 to V_2 at constant temp. then,

$$\delta Q = L \text{ and } \delta V = V_2 - V_1$$

$$\left(\frac{L}{V_2 - V_1}\right) = T\left(\frac{\partial P}{\partial T}\right)_V$$

$$\frac{L}{V_2 - V_1} = T\frac{\partial P}{\partial T}$$

$$dP/\,dT = \frac{L}{T(V_2 - V_{1)}}$$

which is called Clausius-Clapyeron latest heat equitation

VAN DER WAAL’S EQUATION OF STATE:

Consider the volume occupied by the gas molecules negligible compared with the total volume of gas and the molecules exert no appreciable forces on one another. It is evident that both these assumptions cannot be exactly true for actual gases particularly at high pressure. In driving van der waals eqn. Of state the effect both these factor is taken into account.

Due to the finite size of molecules, the free space available for their movement is less than the actual measured volume of the gas. Also the number of collisions with the walls of containing vessel, and the pressure will be greater than the calculated by simple theory. The actual volume can be brought about by subtracting a career term b from the measured volume and using (v-b) in place of V in ideal gas equation.

Let XY be the portion of boundary wall. Consider a molecule A in the interior far from the boundary wall. It is surrounded by other molecules equally distributed in all directions. Those molecules exert attractive force on molecule A, when averaged out, over a sufficient interval of time they cancel out and net cohesion force will be zero. On the other hand the molecule B is as rear the boundary as it can go. In this case the molecular distribution is only along one side. The adhesive force between the gas molecules and the boundary walls are always must smaller than the cohesive force, between the gas molecules. The force on B due to each adjacent molecule can be resolved into components to the boundary wall. The parallel components cancel out on the average but the perpendicular components will result a field of force acting inwards on the molecules near the boundary wall. Thus whenever a molecule will strike the walls of the containing vessel at B to contribute its share towards the total gas pressure, the measured pressure P is loss than the ideal pressure calculate on the assumption that the cohesive force is P, the add a correction term P, to the measured pressure P and use $(P+P_1)$ in place of P in ideal gas.

On using both corrections in ideal gas equation, we get for a gram molecule of a gas.

$$(P+P_1)\ (V-b) = RT \qquad (1)$$

The value of P_1 is to the number of molecules striking in area of the wall in unit time & to the intensity of the field of force. Both of these factors are proportional to the density of the gas.

$$p_1=a\rho^2$$

C->constant

$$\rho \ \alpha \ 1/V$$

Hence $p_1=a/V^2$, where a is constant.

Sub. this value of p_1, in equation (1),

$$(p+a/V^2)(v-b)=RT \quad \rightarrow(2)$$

This is van der waal's equation of state. This is the simplest and the most well known equation of stove for real gas.

Another useful form of the equation of state of a real gas is

$$PV=A+B/V+C/V^2+........ \quad \rightarrow(3)$$

A,B,C,... are from of temp and are called viral coeff.

For an ideal gas it is evident that A=RT and all other viral coeff. are zero.

Van der walls equation can be but in virial form as,

Equation (2) rewritten as,

$$1=RT/((P+a/V^2)(v-b))$$

$$\text{(or)} \qquad PV=RT(l-a/PV^2)^{-1} \ (l-b/v)^{-1} \qquad \rightarrow(4)$$

The correction terms a/PV^2 & b/V are both small composed with unity provided the gas is not too much compressed. Using binomial theorem & neglecting the terms of higher power a l/V, equation V1, becomes,

$$PV=RT(l-A/PV^2)\ (l+B/V)+b^2/v^2$$

$$=RT-RT/PV.a/v+RT.b/v+RTb^2/v^2$$

Since PV=RT approx,

$$PV=RT+(RTb-a)/v+RTb^2/v^2 \quad \rightarrow(5)$$

This is van der waal's equation in virial form having only three virial coeff., A,B,&C

$$A=RT,\ B=RTb-a,\ C=RTb^2$$

PHASE TRANSITIONS

Simple substances are capable of existing in phases of three types: solid, liquid and gas. The three lines, in phase diagram separating these planes are called phase equilibrium lines. The common point A where three lines meet is called *triple point*; at this unique temperature and pressure all three phases can coexist in equilibrium with each other. Point C is the critical point at which liquid gas equilibrium line ends. The volume change ΔV between liquid and gas then approached zero; beyond C there is no further phase transition since only one fluid phase exist.

POSSIBLE QUESTIONS

6 MARKS

1. Define entropy. Define Helmholtz function.
2. State first and second law of thermodynamics.
3. What are called thermodynamic potentials?
4. Define the term drift variation and collision interaction.
5. Write down the Clausius-Clapeyron equation for latent heat.
6. Distinguish between real and ideal gas.
7. State third law of thermodynamics.
8. Calculate the entropy change in reversible processes.
9. Derive Vander Waals equation of state.
10. Derive Clausius-Clapeyron equation.
11. Obtain Helmholtz free energy Gibbs function.
12. Define the term "phase transition".
13. Obtain three different thermodynamic potentials.
14. Explain principle of increase of entropy.

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE – 641 021

DEPARTMENT OF PHYSICS

I MSc PHYSICS (17PHP103)

THERMODYNAMICS AND 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 thermodynamics	Static thermodynamics	Statistical thermodynamics	Classical thermodynamics	Classical thermodynamics
What law asserts that energy is a thermodynamic property?	First law of Thermodynamics	Second law of Thermodynamics	Third law of Thermodynamics	Zeroth law of Thermodynamics	First law of Thermodynamics
What law asserts that energy has quality as well as quantity?	First law of Thermodynamics	Second law of Thermodynamics	Third law of Thermodynamics	Zeroth law of Thermodynamics	Second law of Thermodynamics
The first law of thermodynamics is based on which of the following principles?	mass of energy	Conservation of energy		The entropy-temperature relationship	Conservation of energy
Thermodynamics is applicable to	microscopic systems only	macroscopic systems only	homogeneous systems only	heterogeneous systems only.	macroscopic systems only
Which is not true about thermodynamics ?	it ignores the internal structure of atoms and molecules	it involves the matter in bulk	it is concerned only with the initial and final states of the system	it is not applicable to macroscopic systems.	it is not applicable to macroscopic systems.
A system that can transfer neither matter nor energy to and from its 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 ______ equilibrium.	Mechanical and phase	Thermal and chemical	Thermal, mechanical and chemical	Thermal, phase, mechanical and chemical	Thermal, phase, 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 constant?	Isobaric process	Isothermal process	Isochoric or isometric process	Isovolumetric process	Isochoric or isometric process
What states that if two bodies are in thermal equilibrium with a third body, they are also in equilibrium with each other?	Zeroth law of thermodynamics	First law of thermodynamics	)Second law of thermodynamics	Third law of thermodynamics	Zeroth law of 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 reaction when ΔG at two temperatutes are given?	Gibbs Helmholtz equatioin	Clapeyron equation	Kirchoffs equation	Nernst equation	Gibbs Helmholtz equatioin
____________ is applicable to macroscopic systems only.	thermochemistry	thermokinetics	thermodynamics	thermochemical studies.	thermodynamics
$\Delta E = q - w$ for an isochoric process	first law of thermodynamics	second law of thermodynamics	zeroth's law	third law of thermodynamics	first law of 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
Gibb's function is expressed as,	$G = H + TS$	$G = H / TS$	$G=H-TS$	$G = H * TS$	$G=H-TS$
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 specific heat of a gas in isothermal process is	Zero	Negative	Remains constant	Infinite	Infinite
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	Twice the external latent heat of fusion
The difference between the principal specific heats of nitrogen is 300 J/kg □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
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 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 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
The mathematical relation for the first law of thermodynamics is	$\Delta E = q + w$	$\Delta E = 0$ for a cyclic process	$\Delta E = -q$ for an isochoric process	$\Delta E = W - q$.	$\Delta E = q + w$
For an adiabatic process according to first law of thermodynamics,	$\Delta E = -w$	$\Delta E = w$	$\Delta E = q - w$	$\Delta q = E - w$	$\Delta E = -w$
The enthalpy change, ΔH of a process is given by the relation	$\Delta H = \Delta E + p\Delta v$	$\Delta H = \Delta E + \Delta nRT$	$\Delta H = \Delta E + w$	$\Delta H = \Delta E - \Delta nRT$	$\Delta H = \Delta E + p\Delta v$
The amount of heat required to raise the temperature of one mole of 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	H=E-Pv	E=H+PV	PV+E-H	H=E+PV
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
Temperature of a gas is produced due to	Its heating value	Kinetic energy of molecules	Repulsion of molecules	Surface tension of molecules	Kinetic energy of molecules
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
Gases have	Only one value of specific heat	Two value of specific heat	Three value of specific heat	No value of specific heat	No value of specific heat
Which of the following quantities is not the property of the system	Pressure	temperature	heat	density	density
Solid and liquids have	Only one value of specific heat	Two value of specific heat	Three value of specific heat	No value of specific heat	Only one value of specific heat
The term N.T.P stands for	Nominal temperature and pressurre	Natural temperature and pressure	Normal temperatuere and pressure	Normal thermodynamic pressure	Normal temperatuere and pressure

Kinetic Theory: Distribution function and its evolution − Boltzmann transport equation and its validity − Boltzmann's H-theorem − Maxwell-Boltzmann distribution − Transport phenomena − Mean free path- Conservation laws − Hydrodynamics (No derivation).

Distribution function:

Consider a six dimensional phase space. The coordinate of a po8int in this space is represented by (x,y,z,v_x,v_y,v_z) where x,y,z are the position co-ordinates and may be denoted by r while (v_x,v_y,v_z) are velocity co-ordinate and may be denoted by v. Hence co-ordinate of a point in six dimensional phase space may be denoted by (r,v). The differential volume element about the point (r,v) in this phase space will be represented by

$$d\Gamma = dx\ dy\ dz\ dv_x dv_y dv_z = drdv.$$

If dn represents the number of particles which are in the differential volume d=drdv then the distribution function f(r,v,t) is defined by

$$dn = f(r,v,t)drdv.$$

The different lengths dr and velocities dv must be small composed with the macroscopic distances and viscosity intervals over which there are significant changes in the gross properties of the gas. On the other hand they must be sufficiently large so that there are a large number of particles contained in the differential volume element of phase space.

Boltzman Transport Equation:

Consider a system of particles acted upon by external forces. For example the system may consists of electrons in a metal that is acted upon by electric and magnetic fields. In order to device the Boltyman transport equation consider a region of six dimensional space about the point (x,y,z,v_x,v_y,v_z)i.e.(r,v). An element of volume in this six dimensional space is written as $dxdydzdv_xdv_ydv_z$ or drdv. The number of particles having coordinates within ranges r to r+dr and v to v+dv can be represented as

$$dn=f(r,v,t)drdv \quad \rightarrow(1)$$

Where f(r,v,t)is the distribution function.

At point (r,v) the variation of distribution function of with time may be caused by two independent ways:

(i) Drift-variation: The function f may vary because of the drift particles from one region of space to another. This variation pep time is represented by $(\partial f/\partial t)_{drift}$.

(ii) Collision or scattering Interactions: The function f may vary because of collision among the particles. The variation per time is represented by $(\partial f/\partial t)_{collisions}$.

Hence the rate of change of the function for may be expressed as

$$\partial f/\partial t=(\partial f/\partial t)_{drift}+(\partial f/\partial t)_{collision}$$

assumed that the number of particles in the system is conserved. If it is not so, then the term represent the generation and recombination of particles to the right hand side of equation(2).such additional terms are required in the theory of nuclear and function transistor.

To derive the Botlzman transport equation, let the particles in the differential phase space volume drdv around (r,v) move to a new position by virtue of their velocity in a short time interval dt. The velocity of the particles may change due to the external force acting upon them and the collision among themselves. Let the new position be represented by (r^1, v^1)such that

$$r' =r+vdt, \quad v' =v+adt$$

Where a is the acceleration of the particle.

Consider that no collision oceans diving the time Interval dt, then all of particles will move to the new volume dr’dv’ and write as

$$f(r+v\,dt, v+a\,dt, t+dt)dr'dv'=f(r,v,t)drdv \quad \rightarrow(3)$$

According to Lioville’s theorem,

$$dr'dv' = drdv \quad \rightarrow (4)$$

then equation (3)gives

$$f(r+vdt,\ v+adt,\ t+dt)=f(r,v,t) \quad \rightarrow (5)$$

Using Taylor series expansion on L.H.S and retaining terms linear in dt the time dt→0, above equation

$$f(r,v,t)+vdt.\ \text{grand}_r\, f + a\ dt.\ \text{grad}_v\, f+\partial f/\partial i\ dt=f(r,v,t)$$

$$v.\text{grad}_r\, f + a.\text{grad}_v\, f+ \partial f/\partial t=0 \quad \rightarrow 6$$

This is Botlzman's transport equation when no collision.

In this equation $\text{grad}_r=\Delta_r$ is the usual del operator and $\text{grad}_v= \Delta_v$ is the del operator in velocity space.

$$\Delta_r = i\frac{\partial}{\partial x} + j\frac{\partial}{\partial y} + k\frac{\partial}{\partial z}$$

$$\Delta_v = i\frac{\partial}{\partial v_x} + j\frac{\partial}{\partial v_y} + k\frac{\partial}{\partial v_z} \qquad \text{-------} \ (7)$$

$$v.\ \text{grad}_r\ f = v_x\frac{\partial}{\partial x} + v_y\frac{\partial}{\partial y} + v_z\frac{\partial}{\partial z}$$

$$\text{and } a.\ \text{grad}_r\ f = a_x\frac{\partial}{\partial x} + a_y\frac{\partial}{\partial y} + a_z\frac{\partial}{\partial z} \qquad \text{-----------}\ (8)$$

However, collisions are taken into account, then due to collisions among the particles some particles leave the volume element drdv and some ways from dr, dv, to drdv. This is equivalent to a loss or gain in the number of particles in volume element drdv. Now the change in number of particles in volume element drdv during the time interval from t to t+dt, using Liouvelle's theorem,

$$f(r+vdt,\ v+adt,\ t+dt)drdv - f(r,v,t)drdv=(\partial f/\partial t)_{\text{collision}}\ dtdrdv \quad \rightarrow (9)$$

$$\text{i.e. } \partial f/\partial t+v\text{grad}_r f+a.\text{grad}_v f=(\partial f/\partial t)_{\text{collision}}$$

This is Botlzman transport equation.

Comparing equation (2) &(9),

$$(\partial f/\partial t)_{drift}=-v.grad_r f-a.grad_v f \quad \rightarrow(10)$$

If J_{gain} & J_{loss} represents the number of particles gained and lost per unit volume element per unit time as a consequence collisions, then Botlzman's transport equation (9) may be written as

$\partial f/\partial t+v.grad_r f+a.grad_v f=J_{gain}-J_{loss} \quad \rightarrow(11)$

The collision term $\{f/t\}_{collision}$ in equation (9) or (J_{gain}-J_{loss}) in equation (11) may require special treatment. But the problem is possible to justify approximately the introduction of a parameter v_c called the relax time him or mean free time defined by the equation

$$\{\partial f/\partial t\}_{collision}=-f-f_0/\tau_c \quad \rightarrow(12)$$

Where f_0 is the distribution function in thermal equilibrium.

By definition $\partial f_0/\partial f=0$,equation(12) may be

$$(\partial f-f_0)/\partial t=f-f_0/\tau_c \quad \rightarrow(13)$$

This equation represents the rate at which distribution function approaches the equilibrium condition as being proportional to the deviation from equilibrium condition at a given time.

Eqn. (13) soln. Is

$$(f-fe)f = \quad (f-f)_{i=o} \qquad \text{------ (14)}$$

Which indicates that $(f-f_o)_i$ proportional to the distribution towards equilibrium decays exponentially .

Using eqn (12) the Boltzmann's transport eqn (9) in reaction time approximately is written as

In the steady state $\frac{\partial f}{\partial t} = 3$

Transport phenomena

The equilibrium state of a gas is the most probable state : but if the gas is not in a state of equilibrium , may have any of the following three cases:

The different parts of the ga may be have different velocities . If so these will be a relative motion of the layers of the gas with respect to one another . In such a case the layers moving faster impart momentum to the slower moving layers thro' a long chain of collisions to bring the equilibrium state. This gives rise to the phenomenon of viscosity.

2. The different parts of the gas may have diff.If so the molecules of the gas will carry kiretic energy from regions of higher temperature to the region of lower temperature to bring the eqiulilrium state. This gives rise to the phenomenon of conduction.

3. Diff parts of the gas may have diff molecular concentrations i.e . the number of molecules per unit volume. If so, the molecules of the gas will carry the mass from regions of higher concentration. Those of lower concentration of bring equilibrium state. This gives rise to the phenomenon of diffusion.

Viscosity, conduction and diffusion represent the transport of momenem , energy and mass respect .These phenomena are called themody. transport phenomena. mean free path:

Mean free path

According to kinetic theory, the molecules of a gas are moving with very large velocities, even at ordinary temp .There is no force to restrain their motion &hence the gaseous mass contained in a vessel should disappear in no time. But it is contrary to actual observations as hence there must be some factor which prevents the free escape of particles. The difficulty was solved by clausuis by ascribing to the molecules a finite small size and by introducing the idea of collisions between the molecules. If molecules were truly geometrical points, no collision would take b/n them. Actual molecules are of finite sign, rigid, perfectly elastic sphere free from mutual force action. They make frequent collision with each other and charge the magnitude and direction of their velocities. As the molecules exert no force on one another except, during collision, they move in straight lines with uniform velocity b/n two successive collisions, this str. line path being called the free path. Thus the path of the centre of mass of a small field molecule must be an irregular zig-zag having at each corner a collision with another molecule and consisting of str. line b/n them.

Thus a molecule starting from A moves along AB, suffers a collision at B with another molecule when the direction as well as magnitude of its velocity is changes and is moves along BC. After travelling a distance BC, it again suffers a collision at C and moves along CD and so on. AB, CD, DE etc., are all known as free paths and their individual length vary widely. If we follow a molecule it has traversed a great many free paths, the average of their lengths will has a definite value which is called the mean free path &is denoted by λ

Thus the mean free path is the average distances tho' with a molecule can travel though a gas without colliding with another molecule. It may be called the average free rim b/n 2 collisions. It is then a statistical quantity and the value to some extent, will depend upon the method employed in striking an average. Thus there is a certain arbitariness in on standard in defining a mean free path. However if a reference is made to a group of molecules instead to a single one and a mean value of all the free paths that are executed in a given time by all the molecules in a given volume is taken as shall get a definite quantity provided the time & volume are not too small. Thus if λ_1, λ_2, ------ λ_N are the successive free path traversed in the total time t, then

$$\lambda_1 + \lambda_2 + \lambda_3 + \ldots - \lambda_N = \tilde{v}t,$$

where ṽ is the total distance speed of molecule and N the number of collisions suffered i.e the free path traversed in time . If the mean free path, we must have

$$\lambda = \frac{\lambda 1 + \lambda 2 + \lambda 3 + \ldots - \lambda N}{N} = \frac{\tilde{v}t,}{N} = \frac{S}{N}$$

where S is the total distance travelled in N collisions

Expression for mean free path:

Let us consider a gas possessing n molecule per a let us assume only a single molecule traversing the gas with velocity and suppose other molecules to be at rest. The moving molecule will collide with all such molecules whose centres lie within distance from its centre being the molecules diameter. The space thus traversed in a second is a cylinder of base and height and hence of volume. The interior of the cylinder will enclose on the average molecules suffering impact. This expression also represents the number of collision N made by the molecule ser unit time

$$N=\pi\sigma^2 v n$$

As the distance traversed by the molecule in on second is its velocity the mean free path is given by

$$\lambda = \frac{S}{N} = \frac{v}{\pi\sigma^2 v n} = \frac{1}{\pi\sigma^2 v n} \qquad \text{------------------(1)}$$

This expression, does not represent the actual state of affairs and is generally in euro numerically because it assume that only one molecule under consideration is moving while all the other molecules standstill total await its coming. The molecules possess all possible velocities, the distribution of velocities among them being given by maxwells distribution law. Hence if a molecule moves with a absolute velocity in moving this distance it will collide with other molecule where r represents the mean relative velocity of the molecules with respect to the others. Therefore, the mean free path of that molecule is give by

$$\lambda = \frac{total\ distance\ travelled\ in\ one\ sec.}{No\ of\ collisions\ suffered\ by\ the\ mole.in\ one\ sec} = \frac{1}{\pi\sigma^2 r n}$$

But according to Maxwell's law the particular molecule under consideration may have all possible velocities and hence if is the average velocity of velocity of the molecule r the mean relative velocity of all molecules will respect to all other, the mean free path averaged over molecule of all velocities is

$$\lambda = \frac{1}{\pi\sigma^2 r n}$$

Let us now suppose that the particular molecule under consideration moves with velocity V_1. Its relative velocity with respect to another molecule of velocity V_2 making on angle with it or the relative velocity approach b/n 2 molecules is give by

$$r_2=(v_1 - v_2 \cos 0)i-(0-v_2 \sin \theta)j$$

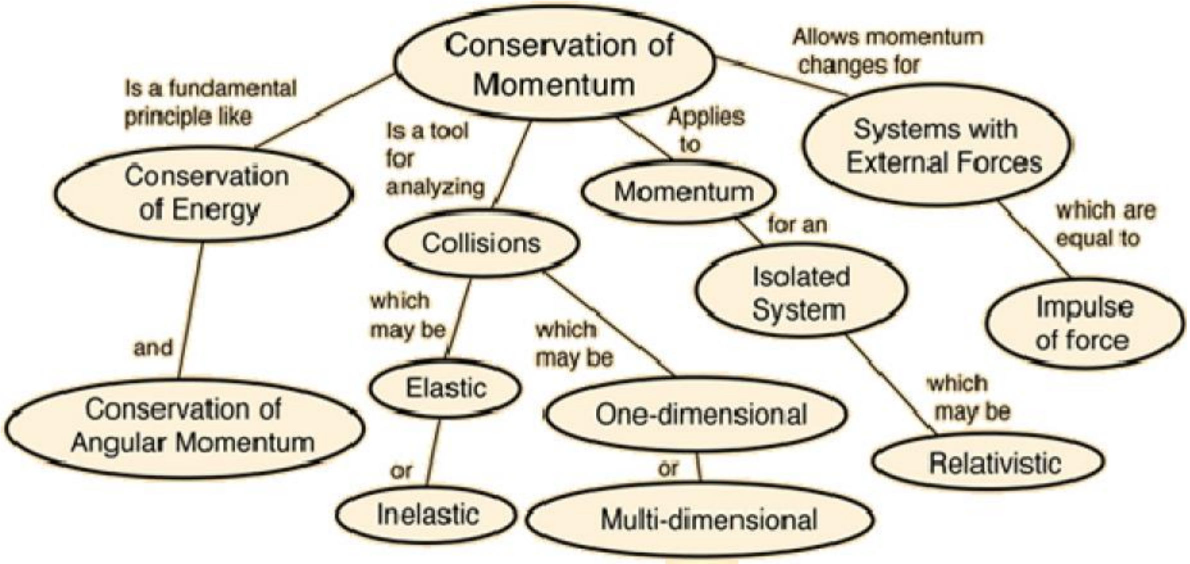
Now all the direction for velocity v_2 are equally probable. The probability that it has within the solid angle lying b/n θ andθ +d θ is ½ sin θ d θ*.

CONSERVATION LAWS

If a system does not interact with its environment in any way, then certain mechanical properties of the system cannot change. They are sometimes called "constants of the motion". These quantities are said to be "conserved" and the conservation laws which result can be considered to be the most fundamental principles of mechanics. In mechanics, examples of conserved quantities are energy, momentum, and angular momentum.

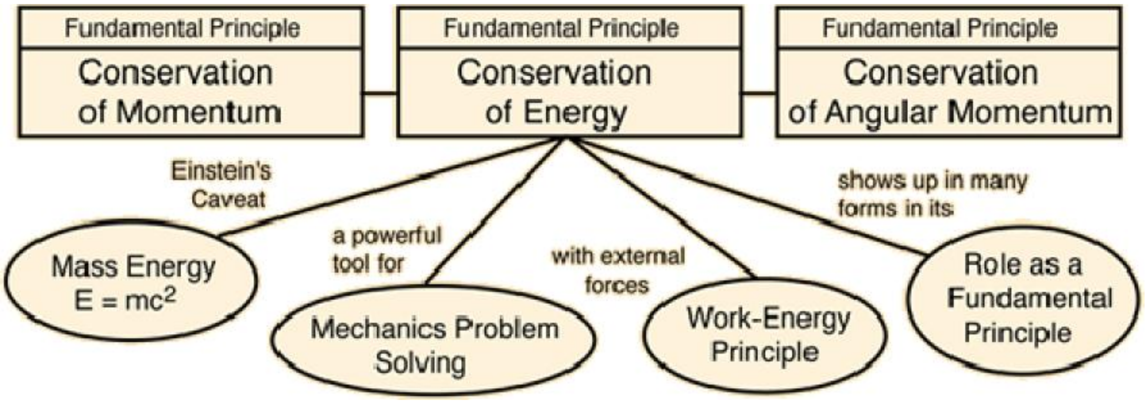
CONSERVATION OF MOMENTUM

The momentum of an isolated system is constant. The vector sum of the momenta mv of all the objects of a system cannot be changed by interactions within the system. This puts a strong constraint on the types of motions which can occur in an isolated system. If one part of the system is given a momentum in a given direction, then some other part or parts of the system must simultaneously be given exactly the same momentum in the opposite direction.



CONSERVATION OF ENERGY

Energy can be defined as the capacity for doing work. It may exist in a variety of forms and may be transformed from one type of energy to another. However, these energy transformations are constrained by a fundamental principle, the Conservation of Energy principle. One way to state this principle is "Energy can neither be created nor destroyed". Another approach is to say that the total energy of an isolated system remains constant.



HYDRODYNAMICS

Hydrodynamics is the study of fluid flow, which was also developed prior to the conclusion of the atom vs. continuum debate. It is sufficient to treat a fluid as a continuous substance. Let fluids are made of particles, can explain some fluid phenomena in terms of more fundamental physics, for instance can predict the viscosity of a gas (a macroscopic quantity) by consideration of particles, mean-free paths and so on. The state of a fluid can be described in terms of a number of ‘functions of state’, which in a simple fluid is two, for instance pressure and temperature; all other variables, for instance density or entropy, can be found from the equation of state. To include more complex fluids in terms of the mean molecular weight is not fixed, or the salinity in an ocean or water vapour concentration in the atmosphere, for example. These quantities are called intensive variables as they can be defined and measured at any particular point in space, as opposed to extensive variables such as volume or mass which are properties of a whole system. The velocity and the thermodynamic variables are functions of position r and time t.

POSSIBLE QUESTIONS

6 MARKS

1. What are the assumptions made for the kinetic theory of gases?
2. What is meant by distribution function?
3. What is meant by first order transition?
4. What is meant by mean free path?
5. Write the general form of Boltzmann's transport equation.
6. Derive Boltzmann Transport equation.
7. Derive an expression for mean free path.
8. What is called free energy path?
9. State Pauli's exclusion principle.
10. Explain the term hydrodynamics.
11. Explain about conservation laws.
12. Discuss about transport phenomena.

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DEPARTMENT OF PHYSICS

I MSc PHYSICS (17PHP103)

THERMODYNAMICS AND STATISTICAL MECHANICS

UNIT-II

Questions	opt1	opt2	opt3	opt4	Answer
Which of the following statements is TRUE for an ideal gas, but not for a real gas?	PV = nRT	An increase in temperature causes an increase in the kinetic energy of the gas	The total volume of molecules on a gas is nearly the same as the volume of the gas as a whole	No attractive forces exists between the molecule of a gas	PV = nRT
The molecules of a gas moving through space with some velocity possesses what kind of energy?	Translational energy	Spin energy	Rotational kinetic energy	Sensible energy	Translational energy
Molar specific heat at constant volume is C_v for a monoatomic gas is.	3/2 R	5/2 R	3R	2R	3/2 R
If the pressure in a closed vessel is reduced by drawing out some gas, the mean free path of the molecules.	Is decreased	Remains unchanged	Is increased	Increases or decreases according to the nature of the gas	Is increased
Cooking gas containers are kept in a lorry moving with uniform speed. The temperature of the gas molecules inside will.	Increase	Remain same	Decrease	Decrease for some, while increase for others	Remain same
Volume of gas become four times if.	Temperature become four times at constant pressure	Temperature becomes two times at constant pressure	Temperature become one fourth at constant pressure	Temperature becomes half at constant pressure	Temperature become four times at constant pressure
Molecules of a gas behave like.	Inelastic rigid sphere	Perfectly elastic rigid sphere	Perfectly elastic non-rigid sphere	Inelastic non-rigid sphere	Perfectly elastic rigid sphere
At absolute zero temperature, pressure of a gas will be	Zero	Po * 273	One atmospheric pressure	Po * 76	Zero
Boyle's law holds for an ideal gas during	Isobaric changes	Isochoric changes	Isothermal changes	Isotonic changes	Isothermal changes
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
S.I. unit of universal gas constant is	cal/°C	J/molK	J/mol	J/kg	J/molK
At constant volume, temperature is increased. Then.	Collision on walls will be less	Collisions will be in straight lines	Number of collisions per unit time will increase	Collisions will not change	Number of collisions per unit time will increase
The specific heat of a gas	Has only two values Cp and Cv	Can have any value between 0 and ∞	Has a unique value at a given temperature	Depends upon the mass of the gas	Has only two values Cp and Cv
For Boyle's law to hold the gas should be.	Perfect and of constant mass and temperature	Perfect and at constant temperature but variable mass	Real and of constant mass and temperature	Real and at constant temperature but variable mass	Perfect and of constant mass and temperature
Every gas (real gas) behaves as an ideal gas.	At high temperature and low pressure	At normal temperature and pressure	At low temperature and high pressure	low pressure	At high temperature and low pressure
According to kinetic theory of gasses at absolute zero temperature	Water freezes	Liquid helium freezes	Molecules motion stops	Liquid hydrogen freezes	Molecules motion stops
For an ideal gas Cp and Cv is	grater than one	less than one	equal to one	not equal to one	less than one
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 motion of fluids and the forces acting on solid bodies immersed in fluids and in motion relative to them is called	dynamics	hydrodynamics	statitics	mechanics	hydrodynamics
Temperature of a gas can be related to the …………….motion of the molecules	external	boundary	internal	closed	internal

Boltzmann's constant is	1.38 x 10-23 j/k	1.38 x 10-31 j/k	1.38 x 10-32 j/k	1.38 x 10-19 j/k	1.38 x 10-23 j/k
The word kinetic refers to	locomotion	vibration	motion	resonance	motion
In gases the particles are	closely packed	not free to move	regularly packed	far apart	far apart
Gases have	low density and mass	high density and mass	high density but low mass	low density but high mass	low density and mass
what does the Kinetic theory of gases describe?	small no of small particles in constant randam motion	large no of small particles in constant randam motion	large no of small particles in accelerating randam motion	large no of large particles in constant randam motion	large no of small particles in constant randam motion
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
Kinetic is a / an	latin word	roman word	greek word	arabic word	greek word
Which one of the following have the highest volume?	solid	Liquid helium freezes	gas	gel	gas
Gases are	very compressible	very little compressible	incompressible	not possible	very compressible
The three states of matter depend on	Temperature become four times at constant pressure	force	potential energy	biomass	Temperature
The term fluids is used for	liquid only	gases only	liquid and gass	gel only	liquid and gas
Why are liquids and gases termed as fluids? Because	they can flow	they have irregular shape	they have randomly moving	they are compressible	they can flow
The Brownian Motion was discovered by the scientist	albert brown	John brown	robert brown	issac brown	John brown
If the car tires are hot, the pressure of gas molecules in them would be	high	low	same as before heating	may be high or low	high
Gas can exert	pressure on wall	force on the base	pressure in solid	force in liquid	pressure on wall
The random motion of smoke or gas particles in the air is termed as	brueian motion	brownian motion	radom motion	static	brownian motion
All of the following are basic assumptions of the kinetic theory except:	matter is composed of very tiny particles	when individual particles collide, they undergo no exchange of kinetic energy	the total kinetic energy of colliding particles remains constant	the particles of matter are in continual motion	when individual particles collide, they undergo no exchange of kinetic energy
For a gas, which pair of variables are inversely proportional to each other (if all other conditions remain constant)?	P,T	P,V	V,T	n,V	P,T
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 term N.T.P stands for	Nominal temperature and pressure	Natural temperature and pressure	Normal temperature and pressure	Normal thermodynamic pressure	Normal temperature and pressure
M.B. distribution can be applicable to _________	identical molecule	indistinguishable molecule	gas	liquid	identical molecule

Maxwell –Boltzmann Momentum Distribution Law for an Ideal Gas:

The Maxwell –Boltzmann equation for distribution of energy among the molecules of an ideal gas is

$$n(E)dE=\frac{2\pi N}{(\pi KT)^{3/2}}Ee^{1/2}e^{-E/KT}dE \qquad \text{--------------------(1)}$$

All the energy of the gas in the form of K E of its molecules .Therefore

$$E=\frac{1}{2}mv^2=(\frac{(mv)^2}{2m}=\frac{p^2}{2m} \qquad \text{-----------------------(2)}$$

Taking differential of this eqn..

$$dE=\frac{p}{m}dp \qquad \text{-----------------------(3)}$$

sub..the expression for E and dE in eq(1), the number of molecules n(p)dp whose momentum lie between p and p+dp is

$$n(p)dp=\frac{2\pi N}{(\pi KT)^{3/2}}.(\frac{p^2}{2m})^{1/2}.e^{-p2/2mKT}.(\frac{p}{m})dp$$

$$=\frac{4\pi N}{(2\pi mKT)^{3/2}}.p^2e^{-p2/2mKT}.dp \qquad \text{---------------------(4)}$$

This eq. is known as Maxwell –Boltzmann law of distribution of momenta among the molecules of an Ideal Gas.

Evaluation of constant:

The total number N of the particles in the system is given by

$$N = \Sigma_r n_r = \sum_r e^{-\alpha} g_r e^{-Er/kT}$$

$$= e^{-\alpha}\Sigma_r\, g_r e^{-Er/kT}$$

$$=A\ \Sigma_r\, g_r e^{-Er/kT} \qquad \text{-------- (1)}$$

Where $A=e^{-\alpha}$

From eq. (1) $A = \frac{N}{\sum_r g_r \; e^{\frac{-Er}{kT}}}$

For continuous variation of energy of free particles of an ideal gas, g_r is replaced by g(E) dE, E_r is replaced by E and the sign of summation is replaced by the sign of integration.

$$A = \int_0^\infty \frac{N}{g(E)dE \; ^{\frac{-Er}{kT}}} \qquad \text{----------- (2)}$$

The limits of integration are taken from 0 to ∞ because energy of the particles of an ideal gas is entirely kinetic and so they can have any K.E. The value of g(E) dE for particles with no spin is given by

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

The integral in eq. (2) is evaluated as follows:

$$I = \int_0^\infty g(E)\, e^{-E/kT} dE$$

$$= 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty E^{1/2}\, e^{-E/kT} dE$$

Let E/kT = x, then E=kTx

Therefore dE = kTdx

$$I = 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (kTx)^{\frac{1}{2}}\, e^{-\frac{x}{kT}} (kT) dx$$

$$= 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (x)^{\frac{1}{2}} e^{-x} dx$$

$$= 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (x)^{\frac{3}{2}-1}\, e^{-x} dx$$

The integral on the R.H.S of this equation is a gamma-function defined as

$$\int_0^\infty (x)^{n-1}\, e^{-x} dx = \Gamma\ (n)$$

Therefore $\int_0^\infty (x)^{\frac{3}{2}-1}\, e^{-x}\,dx = \Gamma(3/2) = ½\,\sqrt{\pi}$

$I = 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \times ½\,\sqrt{\pi}\; = V\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}$

Sub. the value of this integral in eq. (2),

$$A = e^{-\alpha} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \qquad \text{-------- (3)}$$

The constant A i.e., $e^{-\alpha}$ is called degeneracy parameter

$$\text{Taking log on both sides, } -\alpha = \log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right] \qquad \text{------------ (4)}$$

Maxwell –Boltzmann speed Distribution Law:

The Maxwell –Boltzmann equation for distribution of energy among the molecules of an ideal gas is

$$n(E)dE = \frac{2\pi N}{(\pi KT)^{3/2}} E^{1/2} e^{-E/KT} dE \qquad \text{----------------------(1)}$$

A classical ideal gas is defined as an assembly of non-interacting molecules, each distinguishable from the other. Therefore, the molecules have no internal degrees of freedom, all the energy of the gas in the form of kinetic Energy of the molecules.

$$E = \frac{1}{2}mv^2 = \frac{1}{2}m(v^2_x + v^2_y + v_z^2) \qquad \text{--------------------------(2)}$$

$$dE = mvdV \qquad \text{--------------------------(3)}$$

Substitute the expression for E and dE in eq(1), the number of molecules n(v)dv whose speeds lie in between v and v + dv is given by

$$n(v)dv = \frac{2\pi N}{(\pi KT)^{3/2}} \left(\frac{1}{2}mv^2\right)^{1/2} e^{-mv2/2KT} mv\, dv$$

$$= 4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2} v^2 e^{-mv2/2KT} dv \qquad \text{-------------------(4)}$$

This eq. is known as the Maxwell of Maxwell –Boltsmann law of distribution speeds among the molecules of a gas .In this equation n(v) is the number of molecules per unit speed range .Therefore , the unit of n(v) is molecules /(m/sec).

Discussion of the law:

The curves for n(v) plotted against v at three different temperatures T_1,T_2,T_3 where $T_1<T_2<T_3$

From the distribution curves we get the following conclusions.

(1)At any temperature there is no molecules having zero speed.

(2) As the speed increases the no of molecules in a given speed interval Δv increases upto a certain maximum value.

(3) As the speed further increases beyond v_p , n(p) decreases exponentially towards zero. It means according to classical physical a molecules can have a infinite speed.

(4) As the temperature increases, v_p increases, and the range of speed is greater .Hence the curve become broad.

(5) At the given temperature the area under the distribution curves is equal to the total number of molecules in the gas .Thus

$$N=\int_0^\infty n(v)dv$$

Since the area must be same at all the temperature, the distributive curve must flatten as the temperature rises.

Most Probable, Average and root: Mean square speed

Most Probable speed, v_p:

The most probable speed of the molecules is that speed at which the number of molecules per unit range of speed is maximum.

From the M-B distribution law for the molecular speeds the number of molecules per unit range of speed is given by

$$n(v) = 4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} v^2 e^{\frac{-mv^2}{2kT}} \qquad \text{--------- (1)}$$

Taking logarithm of both sides of this equation

$$\log n(v) = \log\left[4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2}\right] + 2\log v - \frac{mv^2}{2kT}$$

by dif.this equation with the respect v,

$$\frac{1}{n(v)}\frac{dn(v)}{dv} = 0 + \frac{2}{v} - \frac{mv}{KT}$$

$$\frac{dn(v)}{dv} = -n(v)\left[\frac{mv}{kT} - \frac{2}{v}\right] \qquad \text{--------- (2)}$$

At the most probable speed $v = v_p$ the number of molecules n(v) is maximum

$$\left[\frac{dn(v)}{dv}\right]_{v_p} = 0$$

From eq. (2)

$$\frac{mv_p}{kT} - \frac{2}{v_p} = 0$$

From this eq. $$v_p = \sqrt{\frac{2kT}{m}} \qquad \text{----------- (3)}$$

$$= 1.414\sqrt{\frac{kT}{m}}$$

Average speed:

The number of molecules whose speeds lie between v and v+dv is n (v) dv. The total speeds of these molecules is v n (v)dv, and the total number the molecules is N. Since the molecules is distributed among all velocities from 0 to ∞, the average speed is given by

$$\tilde{v} = \frac{1}{N}\int_0^\infty v\, n\,(v)\, dv \qquad ------(4)$$

$$= \frac{1}{N}\int_0^\infty v\, 4\pi N\, \left(\frac{m}{2\pi kT}\right)^{3/2}\, v^2\, e^{\frac{-mv2}{2kT}} dv$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^3\, e^{\frac{-mv2}{2kT}} dv \qquad ----------- (5)$$

Let $mv^2 / 2kT = x$

Then $v = \left(\frac{2kT}{m}\right)^{1/2} x^{1/2}$

$$dv = \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) x^{-1/2}\, dx$$

Sub. these values in eq. (5),

$$\tilde{v} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \left(\frac{2kT}{m}\right)^{3/2} x^{3/2}\, e^{-x} \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) x^{-1/2}\, dx$$

$$= 2/\sqrt{\pi}\left(\frac{2kT}{m}\right)^{\frac{1}{2}} \int_0^\infty x\, e^{-x} dx$$

$$= \left(\frac{8kT}{m}\right)^{\frac{1}{2}} \int_0^\infty x^{2-1}\, e^{-x} dx \qquad ----------- (6)$$

The integral term in gamma function defined by

$$\int_0^\infty x^{n-1}\, e^{-x} dx = \Gamma\ (n)$$

$$\int_0^\infty x^{2-1}\, e^{-x} dx = \Gamma\ (2) = 1.\Gamma\ (1) = 1.1 = 1$$

Hence, $\tilde{v} = \sqrt{\frac{8kT}{\pi m}}$ -------- (7)

$$= 1.596\sqrt{\frac{kT}{m}}$$

Root mean square

The number of molecules whose speed is between ν and ν + dν is n (ν) dν. The sum of the squares of the speeds of these molecules is ν^2 n (ν) dν, and the total number of molecules is N. Since the total number of molecules is distributed among all these from 0 to ∞, the mean square speed is given by

$$\tilde{v}^2 = \frac{1}{N}\int_0^\infty v\, n\,(v)\, dv \qquad \text{--------- (8)}$$

$$= \frac{1}{N}\int_0^\infty v^2\, 4\pi N \left(\frac{m}{2\pi kT}\right)^{3/2} v^2\, e^{\frac{-mv2}{2kT}} dv$$

$$= 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty v^4\, e^{\frac{-mv2}{2kT}} dv \qquad \text{----------- (9)}$$

Let $mv^2 / 2kT = x$

Then $v = \left(\frac{2kT}{m}\right)^{1/2} x^{1/2}$

$$dv = \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) x^{-1/2}\, dx$$

Sub. these values in eq. (5),

$$\tilde{v}^2 = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \left(\frac{2kT}{m}\right)^2 x^2\, e^{-x} \left(\frac{2kT}{m}\right)^{\frac{1}{2}} \left(\frac{1}{2}\right) x^{-1/2}\, dx$$

$$= \frac{4}{\sqrt{\pi}} \left(\frac{kT}{m}\right) \int_0^\infty x^{\frac{5}{2}-1}\, e^{-x} dx \qquad \text{----------- (10)}$$

The integral term in gamma function defined by

$$\int_0^\infty x^{\frac{5}{2}-1}\, e^{-x} dx = \Gamma\,(5/2) = 3/2 \times ½ \times \sqrt{\pi} = \frac{3\sqrt{\pi}}{4}$$

$$\text{Hence, } \tilde{v}^2 = \frac{4}{\sqrt{\pi}} \left(\frac{kT}{m}\right) \frac{3\sqrt{\pi}}{4} = \frac{3kT}{m}$$

$$v_{rms= \sqrt{\tilde{v}2}} = \sqrt{\frac{3kT}{m}} \qquad \text{-------- (11)}$$

$$= 1.732\sqrt{\frac{kT}{m}}$$

Thus $\nu_p < \tilde{\nu} < v_{rms}$

Principles of Equipartition of Energy:

The total energy of a particle of a system in thermodynamic equilibrium can be expressed as the sum of independent squared terms in position and momentum coordinates. For example, the K.E. E of a free particle of mass , m which has velocity v and momentum p can be expressed as

$$E = \frac{p_{.}{}^2 + p_y{}^2 + p_z{}^2}{2m} \qquad \text{------------ (1)}$$

For a particle of mass m moving with simple harmonic motion along the x-axis, the total energy

$$E = \frac{p_x{}^2}{2m} + \frac{1}{2}Cx^2 \qquad \text{---------------- (2)}$$

where C is the force constant per unit displacement from the mean position. Each independent squared term in the expression for the energy of a particle is said to give rise to one degrees of freedom of the particles. Thus a free particle has three degrees of freedom, and a particle moving with a linear simple harmonic motion has two degrees of freedom.

The principle of equipartition of energy is stated as follows:

When a system in a thermodynamic equilibrium at absolute temperature T, the mean value of each quadratic term in either a position or a momentum coordinate, which occurs in the total energy of the particle is (1/2)kT.

The principle may also be stated as follows:

When a system is in thermodynamic equilibrium at absolute temperature T, the mean energy of a particle in the system is distributed equally among its various degrees of freedom and for each of them it is (1/2)kT.

The principle was first deduced by Maxwell in 1959 for the energy of translational motion of a free particle. Boltzmann later showed that the principle is true for the energies of the rotation and vibration also. Rigorous proof's from statistical mechanics were given later by other workers.

Proof of the Principles:

We will prove the principle by finding the mean value of the term $\frac{p_x}{2m}$ in the expression for the energy of a particle in a linear S.H.M. along the X-axis.

The mean value of $\frac{p^2}{2m}$ at equilibrium is given by

$$\left\langle\frac{p^2}{2m}\right\rangle = \frac{\int\int\int\int\int\int\frac{p^2}{2m}\, e^{-\frac{E}{kT}}\, dxdydzdp_xdp_ydp_z}{\int\int\int\int\int\int e^{-\frac{E}{kT}}\, dxdydzdp_xdp_ydp_z}$$

Where E is the total energy.

Writing the exponential term as

$$e^{-\frac{E}{kT}} = e^{-\left(\frac{p_x{}^2}{2m}+Eo\right)/kT}$$

$$= e^{-\frac{p_x{}^2}{2mkT}} + \; e^{-Eo/kT}$$

Where E_0 is the contribution to the total energy due to all the coordinates and momenta expect P_x, we get

$$\left\langle\frac{p_x{}^2}{2m}\right\rangle = \frac{\int\frac{p_x{}^2}{2m}e^{-\frac{p_x{}^2}{2mkT}}\; dp_x\int\int\int\int\int\; e^{-\frac{Eo}{kT}}\, dxdydzdp_ydp_z}{\int e^{-\frac{p_x{}^2}{2mkT}}\; dp_x\int\int\int\int\int e^{-\frac{Eo}{kT}}\, dxdydzdp_ydp_z}$$

Cancelling the five –fold integral in the numerator and denominator, we obtain

$$\left\langle\frac{p_x{}^2}{2m}\right\rangle = \frac{1}{2m}\frac{\int_{-\infty}^{\infty}p_x{}^2e^{-\frac{p_x{}^2}{2mkT}}\; dp_x}{\int_{-\infty}^{\infty}e^{-\frac{p_x{}^2}{2mkT}}\; dp_x} \qquad \text{-------- (3)}$$

Let, $\frac{p_x{}^2}{2mkT} = u^2$

So that $p_x = \sqrt{(2mkT)}\ u$

$dp_x = \sqrt{(2mkT)}\ du$

$$\text{hence, } \langle\frac{p_x{}^2}{2m}\rangle = \frac{1}{2m}\frac{\int_{-\infty}^{\infty}(2mkT)\, u^2 e^{-u^2}\quad \sqrt{(2mkT)}\, du}{\int_{-\infty}^{\infty} e^{-u^2}\quad \sqrt{(2mkT)}\, du}$$

$$= kT\ .\ \frac{\int_{-\infty}^{\infty} u^2 e^{-u^2}\quad du}{\int_{-\infty}^{\infty} e^{-u^2}\quad du} \qquad \text{-----------} \ (4)$$

now evaluate the integral in the numerator.

$$I = \int_{-\infty}^{\infty} u^2 e^{-u^2}\quad du = \int_{-\infty}^{\infty} u.\,(ue^{-u)^2}\quad du$$

Integrating by parts, we obtain

$$I = u\int u\, e^{-u^2}\quad du - \int\left[\frac{du}{du}.\int u\, e^{-u^2}\quad du\right]du$$

$$= -\tfrac{1}{2}\ \ ue^{-u^2}\ \ \Big] + 1/2\int_{-\infty}^{\infty} e^{-u^2}\quad du$$

It can be shown that the first term is zero at both the limits. Hence $\int_{-\infty}^{\infty} u^2 e^{-u^2}\quad du = \tfrac{1}{2}$ $\int_{-\infty}^{\infty} e^{-u^2}\quad du$. Sub this in eq. 4, $\langle\frac{p_x{}^2}{2m}\rangle = \frac{1}{2}kT$ --------- (5)

By a similar proof we can shoe that the mean value (1/2)C x^2 is (1/2) kT. Thus the mean energy of one- dimension harmonic oscillator is

$$\langle\frac{p_x{}^2}{2m}\rangle + \langle\frac{1}{2}C\, x^2\rangle = \tfrac{1}{2}\, kT + \tfrac{1}{2}\, kT = kT$$

In the case of a free particle of the total K E

$$E = \frac{p_{.}{}^2 + p_y{}^2 + p_z{}^2}{2m}$$

The mean energy is

$$\langle\frac{{p_x}^2}{2m}\rangle + \langle\frac{{p_y}^2}{2m}\rangle + \langle\frac{{p_z}^2}{2m}\rangle = \frac{1}{2}kT + \frac{1}{2}kT + \frac{1}{2}kT = \frac{3}{2}kT$$

Limitation of the principle of equipartition of Energy:

Theoretical values of the specific heat capacities of substances calculated from the equipartition of energy show that they should be independent of the temp..But the experimental result shows that the conclusion is not true. The effect of temperature on the specific heat capacity is considerable. The specific heat capacity increases with increase in temperature, and it decreases when the temperature is lowered. At low temperatures its rate of decrease with decrease of temperature is large both for solids and gases. The effect cannot be explained in any way by classical mechanics and the equipartition principle.

Partition function Z

$$N = e^{-\alpha}\Sigma_r g_r e^{-E/kT}$$

$$= A\sum_r g_r e^{-E/kT} \qquad \text{--------- (1)}$$

Where $A = e^{-\alpha}$

The summation in eq. (1) is taken over all integrals of r corresponding to all possible energy states of the particles. The summation term is called the partition function or the sum over states and is denoted by the symbol Z. Thus

$$Z = \sum_r g_r e^{-E/kT} \qquad \text{------------- (2)}$$

Now in terms of Z, eq. (1) is written as $N = AZ = e^{-\alpha}Z$ ------------ (3)

Using this relation the Maxwell-Boltzmann distribution law $n_r = e^{-\alpha}g_r e^{-E/kT}$

Is written in the form

$$n_r = N/Z \text{ x } g_r e^{-Er/kT} \qquad \text{----------- (4)}$$

the multiplier α can be expressed as follows

$$e^{-\alpha} = N/Z$$

$$-\alpha = \log (N/Z) = -\log (Z/N) \qquad \text{-----------------} (5a)$$

$$\alpha = -\log (N/Z) = \log (Z/N) \qquad \text{------------------} (5b)$$

Evaluation of Z

$$Z = N/A = \frac{N}{\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}}$$

$$= V \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \qquad \text{------------} (6)$$

This equation gives the value of the partition function for an ideal gas consisting of mono atomic having no spin

Condition for applicability of the Maxwell-Boltzmann statistics

The M-B statistics is applicable to a system of identical particles which do not interact with each other directly except during their collisions. The condition whether neutral particles in a system will interact with each other or not determined by calculating their de Broglie wavelength.

If the wavelength is smaller than the mean distance between the particles, then the particles will not interact. Thus if λ is the de Broglie wavelength and d the mean distance between the particles, the condition for application of M-B statistics is $\lambda < d$ ------- (1)

To express this condition in terms of the degeneracy parameter $e^{-\alpha}$ the expression for d and λ.

The volume per particle = V/N

Therefore the mean distance d between the particles is

$$d=(V/N)^{1/3} \qquad \text{--------} (2)$$

The mean K.E. of the particles is (3/2) kT. Therefore, the corresponding momentum p is given by

$$\frac{p^2}{2m} = \frac{3}{2}kT$$

$$p = \sqrt{(3mkT)}$$

$$\text{and } \lambda = h/p = h / \sqrt{(3mkT)}$$

$$= \left(\frac{h^2}{3mkT}\right)^{1/2} \qquad \text{-------- (3)}$$

Sub. the values of d and λ in condition (1),

$$\left(\frac{h^2}{3mkT}\right)^{1/2} < \left(\frac{V}{N}\right)^{1/3}$$

$$\text{Or} \quad \left(\frac{h^2}{3mkT}\right)^{3/2} < (V/N)$$

$$\text{Or} \left(\frac{h^2}{3mkT}\right)^{\frac{3}{2}} (N/V) < 1$$

Multiplying by $(3/2\pi)^{3/2}$,

$$(3/2\pi)^{3/2} \text{ x } \left(\frac{h^2}{3mkT}\right)^{\frac{3}{2}} \left(\frac{N}{V}\right) < (3/2\pi)^{3/2}$$

$$\left(\frac{h^2}{3mkT}\right)^{\frac{3}{2}} \left(\frac{N}{V}\right) < 0.33$$

$$\text{Or} \qquad e^{-\alpha} << 1$$

$$\text{Or} \qquad A<<1$$

Non –degenerate and degenerate systems:

If the number of particles ,n_r in an energy level E_r is much less than the number of quantum states, g_r available in the same energy level i.e,, if $n_r << g_r$the system of particles is said to be non degenerate.

If n_r is greater than g_r i.e, if $n_r > g_r$ the system is said to be degenerate.

If n_r is much greater than g_r,i.e,, if $n_r >> g_r$ the system is said to be strongly degenerate.

The degeneracy parameter A($e^{-\alpha}$) is given by

$$A = e^{-\alpha} = \frac{n_r}{g_r e^{-\beta E}}$$

If we consider the ground state as a zero, then

$$A = e^{-\alpha} = \frac{n_0}{g_0}$$

Therefore in terms of A is foregoing conditions are as follows:

1.If A<<1, the system is non-degenerate.

2. If A>1, the system is degenerate.

3. If A >>1,the system is strongly degenerate.

Maxwell velocity distribution in a given direction:

In a system of an ideal gas the number of molecules having velocity components in the range between $v_x$and v_x+dv_x, v_y and v_y+dv_y and v_z and v_z+dv_z is given by

$$n\,(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = [f\,(v_x, v_y, v_z)]\,[g(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z] \qquad \text{-------} \ (1)$$

The first term on the R.H.S of this equation is the distributed function for the velocity components, i.e., it is the number of molecules each having the velocity components v_x v_y v_z per quantum state in the energy level E. The second term is the number of quantum states within the velocity space $dv_x\, dv_y\, dv_z$. These terms are obtained as follows.

$$f(E) = \frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2} e^{-E/kT} \qquad \text{------- (2)}$$

Assuming that each molecule has only three degrees of freedom due to its motion of translation, the K.E of each molecule is given by

$$E = ½\, mv^2$$

$$= ½\, m\,(v_x^2 + v_y^2 + v_z^2) \qquad \text{------- (3)}$$

From eq. (2), $f(v_x, v_y, v_z) = \frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2} e^{-m(v_x 2 + v_y 2 + v_z 2)/kT}$ ----------- (4)

The volume of one quantum state in the momentum space is h^3/V, where V is the physical volume of the system.

Therefore the number of quantum states in volume $dp_x\, dp_y\, dp_z$ of momentum space.

$$= V/h^3\, dp_x\, dp_y\, dp_z$$

$$= m^3V/h^3\, dv_x\, dv_y\, dv_z$$

$$\text{Hence } g(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = m^3V/h^3\, dv_x\, dv_y\, dv_z \qquad \text{--------- (5)}$$

Sub. Eq. (4) and (5) into (1)

$$n(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = \frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2} m^3V/h^3\, e^{-m(v_x 2 + v_y 2 + v_z 2)/kT}\, dv_x\, dv_y\, dv_z$$

Simplifying this equation,

$$n(v_x, v_y, v_z)\, dv_x\, dv_y\, dv_z = N\left(\frac{m}{2\pi KT}\right)^{3/2} x\, e^{-m(v_x 2 + v_y 2 + v_z 2)/kT}\, dv_x\, dv_y\, dv_z \qquad \text{-------- (6)}$$

Now the number $n(v_x)\, dv_x$ of molecules, having x component of velocity in the range between v_x and v_x+dv_x is obtained by integrating eq. (6) over all possible values of v_y and v_z.

$$n(v_x)\, dv_x = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}[n(v_x, v_y, v_z) dv_x]\, dv_y\, dv_z$$

$$= N\left(\frac{m}{2\pi KT}\right)^{3/2} e^{-mv_x 2/2kT}\int_{-\infty}^{\infty} e^{-mvy2/2kT} \int_{-\infty}^{\infty} e^{-mvy2/2kT}$$

The definite integrals are standard integrals, the value of each being

$$[(2\pi kT)/m]^{1/2}$$

Sub. this value in above equation ,

$$n\,(v_x)\,dv_x = N\,\left(\frac{m}{2\pi KT}\right)^{3/2}\left(\frac{2\pi KT}{m}\right)\,e^{-mv_x^2/2kT}\,dv_x$$

$$= N\,\left(\frac{m}{2\pi KT}\right)^{1/2}\,e^{-mv_x^2/2kT}\,dv_x \qquad \text{----------} \ (7)$$

This equation gives the number of molecules having x component of velocity in the range between v_x and v_x+dv_x. Eq. (7) shows that the velocity component v_x is distributed symmetrically about the value $v_x = 0$.

Total internal energy of an ideal gas

The total internal internal energy of an ideal gas is given by

$$U = \int_0^\infty E\, n(E)dE \qquad \text{--------} \ (1)$$

$$= \int_0^\infty E\,\left[\frac{2\pi N}{(\pi kT)^{3/2}}\,E^{\frac{1}{2}}e^{-\frac{E}{kT}}dE\right]$$

$$= \frac{2\pi N}{(\pi kT)^{3/2}}\,\int_0^\infty\,\left[E^{\frac{3}{2}}e^{-\frac{E}{kT}}dE\right] \qquad \text{-----------} \ (2)$$

Let E/kT = x, so that E = kTx

Therefore dE = kTdx

Sub. These values in eq. (2) get

$$-\frac{2\pi N}{(\pi kT)^{3/2}}\,(kT)^{3/2}kT\,\int_0^\infty x^{3/2}\,e^{-x}\,dx$$

$$= \frac{2NkT}{\sqrt{\pi}}\,\int_0^\infty x^{\frac{5}{2}-1}\,e^{-x}dx \qquad \text{-------} \ (3)$$

The integral is the gamma function

$$\Gamma\,(5/2) = 3/2\ \Gamma\,(3/2) = 3/2 \times ½ \times \sqrt{\pi} = 3\sqrt{\pi}\,/\,4$$

Sub. This value in eq. (3) ,

$$U = \frac{2NkT}{\sqrt{\pi}} \times \frac{3\sqrt{\pi}}{4} = \frac{3}{2}NkT \qquad \text{----------- (4)}$$

From this equ. The average internal energy per molecule is given by $U / N = \frac{3}{2}kT$ ------ (5)

For 1 mole of an ideal gas, N is Avagadro 's number and the value of U is given by eq. (4) is the total internal energy of one mole of an ideal gas.

Molar Heat Capacity of a gas at Constant Volume:

The molar heat capacity C_v, of a gas at constant volume is defined as the quantity of heat required to raise the temperature of 1 mole of the gas through 1 degree, at constant volume.

According to the definition

$$C_v=\left(\frac{\partial U}{\partial T}\right)_V$$

$$=\frac{\partial}{\partial T}\left(\frac{3}{2}NKT\right)=\frac{3}{2}NK \qquad \text{-------------------(1)}$$

$$C_v=\frac{3}{2}N\left(\frac{N}{R}\right)=\frac{3}{2}R \qquad \text{--------------------(2)}$$

Where R is the gas constant for one mole.

Entropy:

According to Boltzmann's relation, the entropy S of an isolated system of non-interacting particles in equilibrium is given by

$$S = k \log W_{max} \qquad \text{------- (1)}$$

Where W_{max} is the maximum number of statistically independent ways of distributing the particles among the quantum states. From the M-B count,

$$\log W = N \log N - N + \Sigma_r n_r (\log g_r - \log n_r + 1)$$

$$= N \log N - N + \Sigma_r n_r \log (g_r/n_r) + N$$

$$= N \log N - \Sigma_r n_r \log (n_r/g_r)$$

For maximum value of W

$$n_r/g_r = e^{-(\alpha+\beta E_i)}$$

Therefore, $\log W_{max} = N \log N + \Sigma_r n_r (\alpha+\beta E_r)$

$$= N \log N + \alpha \Sigma_r n_r + \beta \Sigma_r n_r E_r$$

$$= N \log N + \alpha N + \beta U \quad \text{-----------} (2)$$

Where U is the total internal energy

Sub. $\beta = 1/kT$ and $\alpha = \log (Z/N)$

Where Z is the partition function,

$$\log W_{max} = N \log N + N \log \frac{Z}{N} + \frac{U}{kT}$$

$$= \frac{U}{kT} + N \log Z \quad \text{----------} (3)$$

Sub. this value of $\log W_{max}$ in eq. (1),

$$S = U/T + Nk \log Z \quad \text{----------}(4)$$

For an ideal gas, $U = \frac{3}{2} NkT$ and $Z = V \left(\frac{2\pi mKT}{h^2}\right)^{\frac{3}{2}}$

According to M-B count , the entropy of an ideal gas is

$$S = \frac{3}{2} Nk + Nk \log\left[V\left(\left(\frac{2\pi mKT}{h^2}\right)^{\frac{3}{2}}\right)\right] \quad \text{--------} (5)$$

Helmholtz Free Energy:

The Helmholtz Free Energy F of a system of particles is defined by

$$F=U-TS \quad \text{----------------}(1)$$

The entropy of a system is given by

$$S=\frac{U}{T}+NK+NK\log\frac{Z}{N}$$

Subs this value in eq (1)

$$F=U-T[\frac{U}{T}+NK+NK\log\frac{Z}{N}]$$

$$=-NKT(log\frac{Z}{N}+1) \qquad ----------(2)$$

$$=-NKT[\log Z-\log N+1] \qquad ----------- (3)$$

Eq(3) can be expressed in

$$F=-NKT\log Z+NKT\log N-NKT$$

$$=-NKT\log Z+KT(N\log N-N)$$

$$=-NKT\log Z+KT\log N!$$

Pressure and Equation of State of an Ideal gas:

The Helmholtz free energy F is

$$F=U-TS$$

Taking differential

$$dF=dU-TdS-SdT \qquad --------------------(1)$$

from the first and second law of thermodynamics for a reversible process we get

$$dU=TdS-PdV$$

$$\text{or } dU-TdS=-pdV \qquad -----------------(2)$$

Therefore eq (1)

$$dF=-pdV-SdT \qquad -----------------(3)$$

This equation shows that F is a function of the independent variable V and T

$$F=f(V,T)$$

Therefore

$$dF=\left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial V}\right)_V dT \qquad \text{---------------------(4)}$$

Equating the co efficient of dV in eq(3) and (4) we get

$$P=-\left(\frac{\partial F}{\partial V}\right)_T \qquad \text{------------------------(5)}$$

An expression for F is

$$F=-NKT\,[\log Z - \log N + 1]$$

From eq(5) we get

$$P=NKT\left(\frac{\partial \log Z}{\partial V}\right)_T \qquad \text{----------------------(6)}$$

For an ideal monatomic gas the partition function z is given by

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

By taking log to base e

$$\log Z = \log V+\frac{3}{2}\log\left(\frac{2\pi mKT}{h^2}\right)$$

By diff. partially we get

$$\frac{\partial \log Z}{\partial V}=\frac{1}{V}$$

subs this value in eq(6)

$$P=\frac{NKT}{V} \qquad \text{----------------------(7)}$$

In this equation K is Boltzmann’s constant ($1.38\text{x}10^{-23}$J/K),and for 1 mole of a gas N is Avogardro’s number($6.023\ \text{x}10^{23}$/mol).Therefore, for one mole the product NK is the same for all gases. This constant is called molar gas constant denoted by the symbol R. So for 1 mole of a gas eq(7) in the form

$$PV=RT \qquad \text{---------------------}(8)$$

This equation for one mole of an ideal gas is called the equation of state for the gas. The numerical value of R is

$$R=Nk=(6.023 \text{ X}10^{23}/\text{mol})(1.38 \text{ x}10^{-23} \text{ J/K})$$

$$=8.31 \text{ J/mol K}$$

Limitations of Maxwell-Boltzmann Method:

The method has several limitations, some of them are

1. It is applicable to only isolated gas of identical molecules in equilibrium ,for which the following conditions are satisfied.
    - i. The mean potential energy due to interaction b/w the molecules is very small compared to their mean K E.
    - ii. The gas is dilute i.e, the number of molecules per unit volume is small, so the average separation b/w the moleculesis large and hence individual molecules can be distinguished.

Therefore, important results ,such as the expression for u,c_v and p, obtained by this method are the same as those delivered by applying a simple kinetic theory.

2. The expression for the Maxwell-Boltzmann count does not give the correct expression for the entropy of an ideal gas, and leads to Gibbs'paradox. To resolve the Paradox the expression must be divided by N!.
3. In the expression for the entropy of an ideal gas

$$S=NK\log[(\frac{2\pi mKT}{h^2})e^{5/2}]$$

if we put T=0, we get

$$S=NK\log 0=-\infty.$$

Thus the expression for S does not satisfy the third law of thermodynamics which may be started as follows: Every substance has afinite positive entropy, but an absolute zero of temperature the entropy may become zero, and it becomes zero in case of perfectly crystalline solid.

4. It cannot be applied to a system of indistinguishable particle. If we apply the Maxwell – Boltzmann distribution law of thermonic emission , we get the following expression for the emission current density

$$J=A_0T^{1/2}e^{-\frac{\Phi}{KT}}$$

which is not correct .The correct Expression which has been verified as

$$J=A_cT^2e^{-\frac{\Phi}{KT}}$$

POSSIBLE QUESTIONS

6 MARKS

1. What is meant by partition function?
2. What are called boson?
3. Define molar heat capacity of a gas.
4. Define degenerate and non-degenerate system.
5. Explain the principle of equipartition of energy.
6. Derive an expression for pressure and the equation of state of an ideal gas.
7. What are the limitations of M-B statistics?
8. Obtain Helmhotz free energy.
9. Obtain an expression for most probable, average and root mean square speeds.
10. Explain the limitations of M.B. method.
11. Calculate total internal energy of an ideal gas.
12. Evaluate constant value of M.B. statistics.
13. Explain M.B. distribution law.
14. What are the conditions for applicability of M.B. statistics?

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DEPARTMENT OF PHYSICS

I MSc PHYSICS (17PHP103)

THERMODYNAMICS AND STATISTICAL MECHANICS

UNIT-III

Questions	opt1	opt2	opt3	opt4	Answer
Which is called as degeneracy parameter?	e^{α}	e^{β}	$ce^{-\alpha}$	$e^{+\beta}$	$e^{-\alpha}$
Partition function is denoted by the symbol____	Z	A	M	N	Z
Mean distance d between the particles is _____	$(N/V)^{1/3}$	$(V/N)^{1/3}$	$(N/V)^{3}$	$(V/N)^{3}$	$(V/N)^{1/3}$
If A<<1, the system is _________	non- degenerate	degenerate	strongly degenerate	weekly degenerate	non- degenerate
If A>1, the system is _________	non- degenerate	degenerate	strongly degenerate	weekly degenerate	degenerate
If A>>1, the system is _______	non- degenerate	degenerate	strongly degenerate	weekly degenerate	strongly degenerate
The number of quantum states is represented by _____	n_r	g_r	E_r	N	g_r
The degeneracy parameter A = _________	Z	e^{α}	$e^{-\alpha}$	e^{β}	$e^{-\alpha}$
In M.B. distribution, the unit of n(v) is ______	m/ sec	mol/sec	mol/m/sec	sec	mol/m/sec
v_p = ___	$\sqrt{(2kT/m)}$	$1.414\sqrt{kT}$	$1.732\sqrt{(kT/m)}$	$3.414\sqrt{kT}$	$\sqrt{(2kT/m)}$
Average speed is represented by ___	v_p	v	Av	v_{rms}	v_p
Which of the following is correct for a perfect gas?	$v<v_p<v_{rms}$	$v_p<v<v_{rms}$	$v<v_{rms}<v_p$	$v>v_p>v_{rms}$	$v_p<v<v_{rms}$
Root mean square = ________	$\sqrt{(2kT/m)}$	$1.414\sqrt{kT}$	$1.732\sqrt{(kT/m)}$	$3.414\sqrt{kT}$	$1.732\sqrt{(kT/m)}$
Average speed = _________	$1.596\sqrt{(kT/m)}$	$1.414\sqrt{kT}$	$1.732\sqrt{(kT/m)}$	$3.414\sqrt{kT}$	$1.596\sqrt{(kT/m)}$
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 β = ______	kT	k	T	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
The mean energy of principle of equipartition of energy is ______	kT	3/2 kT	2/3 kT	½ kT	3/2 kT
A free particle has __________ degrees of freedom.	1	2	3	4	3
A particle moving with a linear simple harmonic motion has ___ degrees of freedom.	1	2	3	4	2
Helmhotz free energy F of a system of particles is defined by _______.	F=U-TS	F=U/TS	F=U+TS	F=UTS	F=U-TS
The specific heat at constant volume is	the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant pressure	the amount of heat required to raise the temperature of 1 kg of water through one degree	the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant volume	any one of the above	the amount of heat required to raise the temperature of unit mass of gas through one degree, at constant volume
The gas constant (R) is equal to the __________ of two specific heats.	sum	difference	product	ratio	difference
The quantum statistics reduces to classical statistics under the following condition	$\rho\lambda^3 = 1$	$\rho\lambda^3 >> 1$	$\rho\lambda^3 << 1$	$\rho\lambda^3 = 0$	$\rho\lambda^3 >> 1$
Specific heat of metals can be expressed as ___	T^3	$AT + BT^2$	AT^2+BT^3	$AT + BT^3$	$AT + BT^3$
Boltzmann entropy probability relation is given by _______	$S=k \log_e \omega$	$S = k/\log_e \omega$	$S = k+\log_e \omega$	$S = k-\log_e \omega$	$S=k \log_e \omega$
Enthalpy and internal energy have relation ______	H= U –PV	H= U/PV	H=U+PV	H=UPV	H=U+PV
In quantum physics identical particles are ______	a) indistinguishable	distinguishable	symmetric	anti-symmetric	indistinguishable
The zero point energy of one dimensional oscillator is _____	2h	½ h	1/3 h	3h	½ h
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
_________of a system of particles is given by $F = U - TS$	Helmholtz free energy	free energy	helmholtz function	Gibb’s free energy	Helmholtz free energy
For non-degenerate system	$A= 1$	$A<< 1$	$A> 1$	$A>= 1$	$A<< 1$
The spin of the photon is	0	1	2	½	1
B.E distribution function is given by	$\{1/(e^{\alpha + \beta E}) \}$	$\{1/(e^{\alpha + \beta E}) + 1\}$	$\{(e^{\alpha + \beta E}) - 1\}$	{1/(ea + bE) – 1}	$\{(e^{\alpha + \beta E}) - 1\}$
The degeneracy parameter $e^{-\alpha} =$	$N/V (h^2 / 2\pi mkT)^{1/2}$	$N/V (h^2 / 2\pi mkT)^{3/4}$	$N/V (h^2 / 2\pi mkT)^{3/2}$	$N/V (h^2 / 2\pi mkT)^3$	$N/V (h^2 / 2\pi mkT)^{3/2}$
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
As temperature increases, the most probable __________also increases	frequency	wavelength	energy	velocity	velocity
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
The correct expression for J = __________	$A_C T^2 e^{-\varphi/kT}$	$A_C T e^{-\varphi/kT}$	$A_C T^{1/2} e^{-\varphi/kT}$	$T^2 e^{-\varphi/kT}$	$A_C T^2 e^{-\varphi/kT}$
The value of gas constant R= _____	8.13K/mol	7.013 mol/K	8.31 mol/JK	8.31 J/mol K	8.31 J/mol K
Partition function is denoted by the symbol____	Z	A	M	N	Z
Mean distance d between the particles is _____	$(N/V)^{1/3}$	$(V/N)^{1/3}$	$(N/V)^3$	$(V/N)^3$	$(V/N)^{1/3}$
In M.B. distribution, the unit of n(v) is ______	m/ sec	mol/sec	mol/m/sec	sec	mol/m/sec
$v_p =$ ___	$\sqrt{(2kT/m)}$	$1.414\sqrt{kT}$	$1.732\sqrt{(kT/m)}$	$3.414\sqrt{kT}$	$\sqrt{(2kT/m)}$
Root mean square = ________	$\sqrt{(2kT/m)}$	$1.414\sqrt{kT}$	$1.732\sqrt{(kT/m)}$	$3.414\sqrt{kT}$	$1.732\sqrt{(kT/m)}$
The equation for total internal energy of one mole of an ideal gas is _______	$U/N = 3/2\ kT$	$U/N = 3/2$	$U/N = kT$	$U/N = 2/3\ kT$	$U/N = 3/2\ kT$
M.B. law cannot be applicable to ______ particles.	distinguishable	Indistinguishable	isolated	Isobaric	Indistinguishable
The mean energy of principle of equipartition of energy is ______	kT	3/2 kT	2/3 kT	½ kT	3/2 kT

Quantum Statistical Mechanics: B.E energy distribution for energies in the range E to E + dE – Condition for B.E distribution to approach classical M.B distribution - Bose temperature - Bose Einstein condensation - Planck's law from B.E law - Fermi Dirac distribution law (no derivation) - FD law for the energies in the range E to E+dE – Fermi energy - Effect of temperature - Energy distribution curve - Free electron in a metal - Fermi temperature and Thermionic emission - Richardson Dushmann Equation - Comparison of MB,BE and FD statistics.

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

$$n(E)\, dE = f(E)\, g(E)\, dE \quad \text{---------------} \quad (1)$$

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

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

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

Substituting this equ. in (2)

$$n(E)\, dE = 2\pi V\, (\frac{2m}{h^2})^{3/2} . \frac{E^{\frac{1}{2}}dE}{e^{\alpha}e^{E/kT} - 1} \quad \text{-------} \; (3)$$

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

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

(i) if e^{α} is <1, then for E = 0

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

$n\,(0)dE = \frac{g\,(0)dE}{e^{\alpha}- 1}$ = 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^{α} must be greater than 1.

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

The B-E distribution is given by

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

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

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

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

$$=\frac{2\pi N}{(\pi kT)3/2}\ E^{1/2}\ e^{-E/kT}\ dE$$

The condition for this is that

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

$$\text{i.e. } \frac{A}{E/kT}\ e^{E/kT} << 1$$

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

$$A<<1.$$

Limiting Case of Bose-Einstein Statistics:

For an ideal Bose-Einstein distribution the degeneracy parameter A(=e^{α})cannot be greater than 1;its maximum value can be 1.If the temperature of the gas is decreased, the value of A increases from a low value towards 1.At a certain temperature T_B, the value of A becomes just less than 1,and then there is no change in the value below T_B .At T_B some proportion of the molecules start reaching the zero-energy state. This critical temperature is called the Bose temperature.

Expression for the Bose Temperature:

In the ideal Bose-Einstein gas of spinless molecules in the thermal equilibrium at the temperature T, the tot al number of N molecules is given by

$$N= 2\pi V\left(\frac{2mkT}{h^2}\right)^{3/2}\int_0^2 \frac{x^{1/2}}{e^{\alpha}e^{x}-1}\,dx$$

Where

$$x=E/kT$$

The value of integral

$$N= 2\pi V\left(\frac{2mkT}{h^2}\right)^{3/2}\frac{\sqrt{\pi}}{2}\left[\frac{1}{e^{\alpha}}+\frac{1}{2^{\frac{3}{2}}e^{2\alpha}}+\frac{1}{3^{\frac{3}{2}}e^{3\alpha}}+\ \dots\dots\right]$$

Substituting the value $e^{1/A} = e^{-\alpha} = A$

$$N= V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\left[\frac{A}{1}+\frac{A^2}{2^{\frac{3}{2}}}+\frac{A^3}{3^{\frac{3}{2}}}+\ \dots\dots\right]$$

At Bose Temperature $T=T_B$,

$$N=V\left(\frac{2\pi mkTB}{h^2}\right)^{3/2}\left[1+\frac{1}{2^{\frac{3}{2}}}+\frac{1}{3^{\frac{3}{2}}}+\ \dots\dots\right]$$

The series in the square bracket is the Riemann Zeta function whose value is 2.612.

$$N=V\left(\frac{2\pi mkTB}{h^2}\right)^{3/2}\times 2.612$$

$$=2.612\ V\left(\frac{2\pi mkTB}{h^2}\right)^{3/2} \quad \text{--------(1)}$$

Where

$$T_B=\left(\frac{h^2}{2\pi mk}\right)\ (N / 2.612\ V)^{3/2} \quad \text{---------(2)}$$

For all known Bose-Einstein gas, the Bose temperature T_B is very low. For ex, for helium $({}_2He^4)T_B= 3.15$ K

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

$$N_e=N- n_0 \quad \text{-------------------- (3)}$$

The zero –energy state occupation number is given by

$$n_0=\frac{g0}{\frac{1}{A}-1} \quad \text{-------------------- (4)}$$

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

N_e is given by, $N_e=2.612V\left(\frac{2\pi mKT}{h2}\right)^{3/2}$ -------------------- (5)

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

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 $T<T_B$

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

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

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 at T_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 ${}_2He^4$-I to superfluid liquid ${}_2He^4$-II at the observed temperature 2.18K can be expanded by Bose- Einstein condensation process.

Planck's law of radiation from Bose-Einstein distribution law:

According to planck's radiation law the energy of radiation of wavelength in the range between λ and λ+dλ emitted per unit volume by a perfectly black body at absolute temperature T is given by $U(\lambda)d\lambda = \frac{8\pi hc}{\lambda^5} \frac{d\lambda}{e^{\frac{hc}{kT}} - 1}$

Derivation of law

According to the Bose- Einstein distribution law the number of Bosons having energies between E and E+dE is

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

where g(E) dE is the number of quantum stage of energies E and E +dE.

Let T be the absolute temp. of a black body chamber of volume v. The chamber is supposed to be filled with photons each having energy hν .They move in all possible directions with the speed of light C. Each photon has unit spin angular momentum equal to h(h/2π).Hence photons are bosons and use B.E distribution law to derive Planck's law of radiation.

1. *Constant α*:

Photons of different energies are absorbed and re-emitted by the walls of the chamber at constant temp.

In this process a higher energy photon is converted into a number of low energy photons and vice-versa. Though the total energy of the photons remain constant, the total no of photons present in enclosure is not constant. Therefore the condition $\sum_r n_r$ = N or $\sum_r dn_r = 0$ is not applicable for the distribution and hence the multiplier α is zero, i.e $e^{-\alpha}$ is equal to 1.

2. *Expression for g(E)dE:*

The number of quantum states corresponding to the momenta in the range between p and p+dp for particles with no spin is given by

$$g(p)\,dp = \frac{4\pi V p^2 dp}{h^3}$$

each photon has unit spin angular momentum, there are two allowed quantum states for each photon. Hence photons of the same energy can have the two different directions of polarization circularly clockwise and circularly anti-clockwise. Taking the spin in two account for photonswe have

$$g(p)\,dp = \frac{2\ x\ 4\pi V p^2 dp}{h^3}$$

$$= \frac{8\pi V p^2 dp}{h^3} \qquad \text{---------} \ (2)$$

For photons of frequency ν.

Energy, $E = mc^2 = h\nu$ and momentum $p = mc = mc^2/2 = h\nu/c$

By sub these values in equ. (2), $g(\nu)\,d\nu = \frac{8\pi V \nu^2 d\nu}{C^3}$ -------- (3)

Sub. the values of α and g(E) dE in eq. (1)

$$n(\nu)\,d\nu = n\,(E)dE$$

$$= \frac{8\pi V}{c^3}\ \nu^2 d\nu / e^{h\nu/kT} - 1 \qquad \text{--------} \ (4)$$

This equ. Gives the number of photons of frequencies between ν and ν + dν in the enclosure of volume v at temp T.

Now the energy per unit volume of the enclosure,of the photons of frequencies between ν and ν + dν is

$$U(\nu)d\,\nu = \frac{h\nu n(\nu)\ \nu}{\nu}$$

$$== \frac{8\pi h}{c^3}\nu^3 \ d\nu / e^{h\nu/kT} -1 \qquad \text{------------------(5)}$$

This is this the plancks law of radiation in terms of frequency ν

*Eq*n(5) can be transformed in terms of the wavelength λ by using the relations

$$\nu=\frac{c}{\lambda}, \ d\nu=-\frac{c}{\lambda^2}d\lambda$$

The energy u(ν)d ν contained in a frequency interval between ν and ν + dν is equal to the contained in a corresponding wavelength interval b/n λ and λ+ d λ.

$$U(\lambda)d\lambda=u(\nu)d\nu$$

$$= \frac{8\pi h}{c^3}\frac{\left(\frac{c}{\lambda}\right)3\left(-\frac{c}{\lambda^2}d\lambda\right)}{eh\nu/kT -1}$$

Omitting the negative sign we get,

$$U(\lambda)d\lambda=\frac{8\pi hc}{\lambda^5}d\lambda / e^{h\nu/kT} -1 \quad \text{-------------------------------- (6)}$$

This is the planck’s law of radiation in terms of wavelength λ

Fermi –Dirac distribution law:

In F-F statistics, the condition are:

(i) The particles are indistinguishable from each other i.e., there is no restriction between different ways in which n_i particles are chosen.

(ii) Each sublevel or cell may contain 0 or one particle. Obviously g_i must be greater than or equal to n_i.

(iii) The sum of energies of all particles in the different quantum groups taken constitutes the total energy of the system.

The Fermi – Dirac statistics is given by

$$n_i= \frac{g_i}{e^{(\alpha+\beta\epsilon i)}+1}$$

Fermi-Dirac energy distribution for energies in the range E to E + dE:

The number of particles having energies in the range between E and E+dE is given by

$$n(E)\,dE = f(E)\,g(E)\,dE \qquad \text{---------- (1)}$$

where g(E) dE is the number of quantum states of energy between E and E +dE.

Sub. The expression for f(E) in eq. (1), then

$$n\,(E)dE = \frac{g(E)dE}{e^{\frac{Er-Ef}{kT}}+1} \qquad \text{---------- (2)}$$

For particles like electrons of spin angular momentum ±1/2 ħ, there are two possible spin orientation. For a system of such particles g(E) dE is given by

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

sub. the value of g (E) dE in eq. (2), get

$$n\,(E)\,dE = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{E^{\frac{1}{2}}\,dE}{e^{(E-\,E_F)/kT}+1} \qquad \text{------------- (3)}$$

This is Fermi-Dirac distribution law giving the number of particles with energies between E and E+dE.

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

At T=0, when E <E_{Fo},

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

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

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

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

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

This means that at temperature T>0, the probability for occupation of a quantum states at the Fermi level is ½. At temperature T>0, 50% of the quantum states at the Fermi level are occupied and 50% are empty.

Effect of temperature on Fermi Energy:

The Fermi energy E_F of an electron gas at temperature T is related to the value E_{Fo} at T=0 by the equation

$$E_F = E_{F_0}\left[1 - \frac{\pi^2}{12}\left(\frac{kT}{E_{F_0}}\right)^2\right]$$

It is seen that as T is increased E_F decreases. But the rate of decrease with temperature is very small over a large range of temperature. The temperature at which E_F becomes zero is very large. For free electrons in metallic copper this temperature is of the order of 90 x 30^3K. So the temperature dependence of E_F over practical range of temperature be neglected and E_F at temperature T may be considered as constant equal to E_F.

Energy distribution curve:

The Fermi –Dirac energy distribution law is

$$n(E)dE = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{E^{\frac{1}{2}}\, dE}{e^{(E-E_{Fo})/kT}+1} \qquad \text{----------} (1)$$

(1) Curve at T = 0. At T = 0, when $E<E_{Fo}$, then

$$e^{(E-E_{Fo})/kT} = e^{-\infty} = 0$$

From eq. (1)

$$n(E)dE = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2} dE$$

$$\text{or} \quad n(E) = CE^{1/2} \qquad \text{----------} (2)$$

where C is constant.

At T = 0, when $E=E_{Fo}$, then

$$e^{(E-E_{Fo})/kT} = e^{\infty} = \infty$$

Therefore under this condition n(E) = 0.Thus the curve representing eq. (2) is a parabola which ends abruptly at $E = E_{Fo}$.

(2) Curve at T>0:

At T>0, when $E<<E_{Fo}$ the exponential term in the denominator of equ. (1) can be neglected in comparison with 1. So the region ($E<<E_{Fo}$) is the same parabola. Then as E approaches E_{Fo}, the curves falls towards the axis of E and intersects the line $E=E_{Fo}$ at the point P. When $E>E_{Fo}$ the curve approaches the axis asymptotically showing that at a higher temperature a few electrons have energy greater than E_{Fo}

Fermi energy E_{Fo} for free electrons in a metal:

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

$$N = \int_0^{\infty} n(E)\, dE$$

$$= \int_0^{\infty} f(E)\, g(E) dE$$

$$= \int_0^{E_{F_0}} f(E)g(E)\, dE + \int_{E_{F_0}}^{0} f(E)g(E)\, dE \quad \text{--------} (1)$$

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.

$$N = \int_0^{E_{F_0}} g(E)\, dE$$

$$= 4\pi V\,(2m/h^2)^{3/2} \int_0^{E_{F_0}} E^{1/2}\, dE$$

$$= 4\pi V\,(2m/h^2)^{3/2}\ \ 2/3\ E_{Fo}^{3/2}$$

$$= \frac{8\pi}{3} V \left(\frac{2mE_{F_0}}{h^2}\right)^{3/2}$$

From this equation,

$$\left(\frac{2mE_{F_0}}{h^2}\right)^{3/2} = 3N / 8\pi V$$

$$E_{F_0} = \frac{h^2}{2m}\left(\frac{3N}{8\pi V}\right)^{2/3} \quad \text{-------- (2)}$$

$$E_{F_0} = \frac{h^2}{2m}\left(\frac{3n}{8\pi}\right)^{2/3} \quad \text{-------- (3)}$$

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.

Fermi Temperature:

The Fermi temperature $T_h$is defined as the ratioof the Fermi energy E_{Fo}at absolute zero to Boltzmann's constant k. Thus

$$T_F = E_{F0}/k \qquad \text{------ (1)}$$

Relation between T_F and the density of the free electron in a metal

$$T_F = E_{F0}/k$$

$$= \frac{h^2}{2mk}\left(\frac{3n}{8\pi}\right)^{2/3}$$

$$= \frac{h^2}{2mk}\left(\frac{3}{8\pi}\right)^{2/3} (n)^{2/3}$$

Sub. the numerical value of h, m and k

$$T_F = \left(\frac{(6.63\ x\ 10^{-34})2}{2\ x\ 9.11\times 10^{-31} \times 1.38 \times 10^{-23}}\right) \text{x} \left(\frac{3}{8\pi}\right)^{2/3} (n)^{2/3}$$

$$= 4.23 \text{ x } 10^{-15}\ (n)^{2/3} \quad \text{------ (3)}$$

Relation between the degeneracy parameter A and T_F

The degeneracy parameter A is $A = N/V\left(\frac{h^2}{2\pi mkT}\right)^{3/2}$ ---------- (4)

From eq. 2 the density n = N/V of the free electron is given by

$$n = N/V = 8\pi/3 \left(\frac{2mkT}{h^2}\right)^{3/2} \text{ ----------- (5)}$$

Sub. this value in eq. (4)

$$A = \frac{8\pi}{3}\left(\frac{2mkT}{h^2}\right)^{3/2}\left(\frac{h^2}{2mkT\pi}\right)^{3/2}$$

$$= \frac{8}{3\sqrt{\pi}} (T_F / T)^{3/2} = 1.5 (T_F / T)^{3/2}$$

$$\text{Therefore } T_F / T = (A/1.5)^{2/3} \text{ ----------------- (6)}$$

This eq.shows that the degeneracy condition that A>1 is equivalent to $T_F>1$

The value of T_F for the free electrons in metal is very large. For the free electrons in copper T_F 8.15×10^4k. This value is much higher than room temp.so that the free electrons gas in copper is highly degenerate.

Interpretation of the Fermi Tempertaure:

The temp.T of an ideal gas whose mean molecular K E is equal to the mean energy of the free electron in a metal at absolute zero is given by

$$3/2\ kT = U_0 = 3/5\ E_{Fo}$$

$$\text{Or } T = 2/5\ (E_{Fo}/k) = 2/5T_F$$

It means that if free electron gas is considered to obey the classical statistics a piece of copper would have to be heated to a temp. 2/5 times the Fermi temp.for the metal is

$$2/5\times8.15\times10^4=4.07\times10^4\text{k}$$

Thermionic Emission:

According to the Fermi-Dirac statistics the free electrons in the highest energy level in a metal at absolute zero have the Fermi energy E_{Fo}. But they are not emitted spontaneously from the metal because of attractive forces of other charges at the surface. Therefore, to enable an electron having maximum energy E_{Fo} in the metal at zero K to escape from the surface to vacuum a certain minimum amount of energy Φ_o must be important to it. This energy is called the work function of the metal at 0K. At a higher temp. these energies are denoted by E_F and Φ.

On heating a metal to a high temp. T a free electron with energy E_{Fo} may acquire an additional kinetic energy equal to the work function Φ of the metal. Then its total kinetic energy inside the metal is (E_{F0} +Φ). The electron with this K.E inside the metal will just escape into vaccun from the metal surface, and will have 0K.E. on emergence. Hence this energy is the P.E. of the electron at rest outside the metal. This P.E. is called surface barrier of the metal. It is denoted by $E_{S.}$ Thus $E_S = E_{Fo} + \Phi$.

The Fermi-Dirac shows that if a metal is heated to a high temp. only those electron in the shaded portion of the curve will have K.E. > than Es and hence they can escape from the metal surface. Thus when a metal is heated to a high temp. T a free electron will occur total K.E. > surface barrier potential energy Es will be emitted from the metal. This phenomenon is called thermionic emission.

Richardson – Dushmann Equation:

Let E_x be the total K.E of an electron at temp. T in the positive x-direction. An electron having x-components of its velocity in the range between ν_x and $\nu_x + d\nu_x$ will escape from the metal surface in the positive x-direction if $\frac{1}{2} m\nu_x^2 \geq Es$.

$$\text{If } E_x \geq Es$$

$$\text{Or } E_x \geq E_{Fo} + \Phi \qquad \text{----------------} \; (2)$$

The number of electrons per unit volume with the x-component of their velocity in the range ν_x and $\nu_x + d\,\nu_x$ is $\frac{n\,(\nu_x) d\nu_x}{V}$

The number of such electrons escaping from the metal surface per unit area per second is

$$\frac{\nu_x n\,(\nu_x) d\nu_x}{V}$$

The current density dJ due to these electrons that is the current per unit area i.e., the charge passing normally through unit area per second is given by

$$dJ = \frac{q\,\nu_x n(\nu_x)d\nu_x}{V} \quad \text{--------(3)}$$

where q – electronic charge. The total current density J is given by

$$J = \frac{q}{V}\int_{E_x=E_s}^{\infty} \nu_x n(\nu_x)d\nu_x \quad \text{----------- (4)}$$

The function $n(\nu_x)d\nu_x$ is given by Fermi-Dirac law of distribution of velocity in the x-direction

$$n(\nu_x)d\nu_x = V\left(\frac{4\pi m^2 kT}{h^3}\right)e^{E_{F0}/kT}.e^{\frac{-m\nu_x{}^2}{2kT}}\,d\nu_x$$

In this equation, we sub. $\frac{1}{2}m\nu_x{}^2 = E_x$

$$m(\nu_x)d\nu_x = dE_x$$

$$d\nu_x = 1/m\nu_x\, dE_x$$

$$\text{Hence, } n(\nu_x)d\nu_x = V\left(\frac{4\pi m^2 kT}{h^3}\right)e^{E_{F0}/kT}.e^{\frac{-E}{kT}}\,(1/m\nu_x)dE_x$$

Or

$$\nu_x n(\nu_x)d\nu_x = V\left(\frac{4\pi mkT}{h^3}\right)e^{\frac{E_{F_0}}{kT}}.e^{\frac{-E}{kT}}\,dE_x$$

Sub. this equation in equ. (4)

$$J = q\left(\frac{4\pi mkT}{h^3}\right)e^{\frac{E_{F_0}}{kT}}\int_{Es}^{\infty} e^{\frac{-Ex}{kT}}dE_x \quad \text{-------- (6)}$$

The value of the integral is

$$\int_{Es}^{\infty} e^{\frac{-Ex}{kT}}dE_x = \left[-kTe^{\frac{-Ex}{kT}}\right]_{Es}^{\infty}$$

$$= kTe^{\frac{-Es}{kT}}$$

$$= kTe^{-(E_{F0} + \Phi)/kT} \quad \text{-------- (7)}$$

Sub. this value in eq. (6) and simplifying

$$J = \left(\frac{4\pi k^2 mq}{h^3}\right)T^2\, e^{-\Phi/kT} \quad \text{-------- (8)}$$

which is written as $J = A_0T2^2e^{-\Phi/kT}$ -------- (9)

Where $A_0 = \left(\frac{4\pi k^2 mq}{h^3}\right)$ = universal constant = 1.204×10^6 A/m^{2}K^2

Eq.(9) is known as Richardson's or Dushman's or the Richardson- Dushmann eq. It was first derived by O.W. Richardson in 1901 and later the theory of its derivation were perfected by S.Dushman in 1923.

The eq. is based on the assumption that all the electrons having energy equal to or greater than the surface potential barrier or emitted but quantum mechanical theory shows that an electron having energy $E_x \geq E_s$ may not escape from the metal surface it may be reflected back, and that the probability of escape for such an electron is (1-r) where r is the reflection coefficient which is a function of (ν_x). But in thermionic emission velocity range of the emitted electrons is not large, in this process r can be considered as constant over the small velocity range.

$$J = A_0(1-r)T^2 e^{-\Phi/kT} \qquad \text{----------------------(10)}$$

Comparison of M-B, B-E and F-D Statistics:

Quantity	M-B	B-E	F-D
Particles	Distinguishable	Indistinguishable called bosons	Indistinguishable called Fermions
Spin	-	0,1,2,-------	½, 3/2, 5/2, ------
Wave function	-	Symmetric under interchange of two bosons	Antisymmetric under interchange of two bosons
Number of particles per energy state	No upper limit	Bosons don’t obey Pauli exclusion principle: No upper limit to the no. of particles per quantum state.	Fermions obey Pauli exclusion principle: Max. of one particles per quantum state.
Distribution function f(E)	$\frac{N}{V}\frac{h^2}{(2\pi mkT)^{3/2}}e^{-E/kT}$	$\frac{1}{e^{\alpha}e^{\frac{E}{kT}} - 1}$	$\frac{1}{e^{\frac{(E-Ef)}{kT}} + 1}$

POSSIBLE QUESTIONS

6 MARKS

1. Give three differences between M-B, F-D and B-E statistics.
2. Explain Bose temperature and Bose-Einstein condensation
3. Which kind of particles is called as fermions?
4. What is called Bose- Einstein condensation?
5. Derive Richardson Dushmann equation.
6. Define Fermi energy.
7. Define the term Bose temperature.
8. What are called fermions?
9. Obtain Planck’s law of radiation from Bose- Einstein distribution law.
10. Explain energy distribution curve of FD statistics.

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE – 641 021					
DEPARTMENT OF PHYSICS					
I MSc PHYSICS (17PHP103)					
THERMODYNAMICS AND STATISTICAL MECHANICS					
UNIT-IV					
Questions	**opt1**	**opt2**	**opt3**	**opt4**	**Answer**
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
The variable W in an equilibrium stands for	minimum probability distribution	probability distribution	maximum probability distribution	constant probability distribution	maximum probability distribution
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^{α} must be _________	greater than 1	smaller than 1	equal to 1	zero	greater than 1
The molecule of an ordinary gas have spin angular momentum equal to an integral multiple of ________	h	ħ/2π	ħ	h/2π	ħ
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^{α} =1, for E=0, then n(0) dE =	postive infinity	negative infinitive	1	0	postive infinity
In B.E. energy distribution, if e^{α} <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_B is very _______	high	low	small	0	low
The value of Reimann Zeta function is ______	6.212	1.612	2.126	2.612	2.612
A gaseous phase consisting of Ne molecules distributed among the energy states ____ than the ground state.	higher	lower	equal to	very smaller	higher
The transition of liquid $_2He^4$-I to superfluid liquid $_2He^4$-II is observed at _________	8.12 K	2.18 K	1.82 K	1.28 K	2.18 K
For an ideal B.E. gas the condensation temperature is T_B. Find the temperature at which the number of molecules in the zero energy state (E=0) is 7/8 times the total number of molecules in the gas.	$T=T_B$	$T=4T_B$	$T=1/4\ T_B$	$T=4/3\ T_B$	$T=1/4\ T_B$
E.Fermi developed the statistics for _______	photons	bosons	phonons	electrons	electrons
At T=0, when $E<E_{F0}$, the Fermi energy is given by ________	one	infinity	negative infity	zero	one
At T=0, when $E<E_{F0}$, the Fermi energy is given by ________	one	infinity	negative infity	zero	zero
For free electrons in metallic copper the temperature is of the order of _________	90×10^{3} K	90×10^{-3} K	90×30^{3} K	90×30^{-3} K	90×30^{3} K
For free electrons in copper, T_F = ________	8.15×10^{2}K	8.15×10^{-2} K	8.15×10^{-4} K	8.15×10^{4}K	8.15×10^{4}K
The value of T_F free electrons in a metal is _____	very large	very small	zero	infinity	very large
The free electron gas in copper is _______	highly degenerate	degenerate	weekly degenerate	non-degenerate	highly degenerate
Surface potential barrier energy of the metal is denoted by ________________	E_P	E_S	S	S_E	E_S
Richardson explain his theory in the year ______	1801	1701	1901	1921	1901
Spin value of bosons are in the order of _________	0,1,2,…….	0, 2,4,6,………..	½, 3/2, 5/2,……	1/3, 3/3, 5/3,…………	0,1,2,…….

S.Dushmann explained his theory in the year _______	1801	1701	1923	1921	1923
Spin value of fermions are in the order of _________	0,1,2,…….	0, 2,4,6,………..	½, 3/2, 5/2,……	1/3, 3/3, 5/3,…………	½, 3/2, 5/2,……
The value of β is given by	3 KT	KT	1/KT	4KT	1/KT
In B.E statistics the particles are identical and indistinguishable. These particles are called as	Bosons	fermions	leptons	baryons	Bosons
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 $1/A(e^{\beta E}) >> 1$ i.e	A<=1	A<<1	A>>1	A>>1	A<<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	½	1
In F.D statistics the particles are identical and indistinguishable. These particles	Fermions	bosons	photons	kryptons	Fermions
B.E distribution function is given by	$\{1/(e\alpha + \beta E) \}$	$\{1/(e\alpha + \beta E) + 1\}$	$\{(e\alpha + \beta E) - 1\}$	$\{1/(e\alpha + \beta E) - 1\}$	$\{1/(e\alpha + \beta E) - 1\}$
Fermi energy Ef =	$- \alpha KT$	αKT	$-1/ \alpha KT$	$1/ \alpha KT$	$- \alpha KT$
Fermi-Dirac distribution function FD(E) =	$\{1/(e\alpha + \beta E) + 1\}$	$\{1/(e\alpha + \beta E) - 1\}$	$-1/ \alpha KT$	$\{-1/(e\alpha + \beta E) + 1\}$	$\{1/(e\alpha + \beta E) + 1\}$
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}
When T = 0 and E < Ef , then fFD(E) =	0	1	½	3	1
The degeneracy parameter e-□ =	N/V (h2 / 2pmkt)1/2	N/V (h2 / 2pmkt)3/4		N/V (h2 / 2pmkt)3	N/V (h2 / 2pmkt)3
The maximum value of degeneracy parameter in B.E statistics is	One	two	three	four	One
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	$g(E)dE/\{(e\alpha + \beta E) + 1\}$	$g(E)dE/\{(e\alpha + \beta E) - 1\}$	$g(E)dE/\{(e\alpha + \beta E) - 1\}$	$g(E)dE/\{(e\alpha + \beta E) - 1\}1/2$	$g(E)dE/\{(e\alpha + \beta E) - 1\}1/2$
According to Plank's law of radiation, the energy of the photon is	Constant	same	not distinct	vary	Constant
For an isolated system the total energy in a B.E. distribution law is used to derive _______ of radiation	A<=1	A<<1	A>>1	A=1	A<<1
Wave function of the system of identical Bosons is	Unsymmetric	linear	symmetric		symmetric
The molecule of an ideal B.E gas in two phases at	T = TB	T > TB	T < TB	T <= TB	T < TB
The __________consists of no molecules occupying ground state	condensed phase	liquid phase	gaseous phase	inert gas	gaseous phase
_________of same energy can have two different directions of polarization	Planck's law	Weiss law	Franz law		Planck's law
At __________the molecule just reach the zero energy state	Bohr temperature	Kelvin temperature	Neel temperature	Curie temperature	Bohr temperature

Applications of Quantum Statistical Mechanics: Ideal Bose gas : Photons − Black body and Planck radiation − Photons − Specific heat of solids − Liquid Helium.
Ideal Fermi gas : Properties − Degeneracy − Electron gas − Pauli paramagnetism
Ferromagnetism : Ising and Heisenberg models.

EMISSIVE POWER

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

unit → 1walt per square meter per Angstrom.

ABSORPTIVE POWER(a_λ):

The absorptive power a_λ of a body at a given temperature for radiant energy of wavelength λ is the ratio of radiant energy of wavelength λ 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_λ of a body for any wavelength at a given temperature to its absorptive power a_λ for the wavelength at the temperature is constant and is equal to the emissive power E_λ of a perfectly black body at that temperature.

Black Body Radiation:

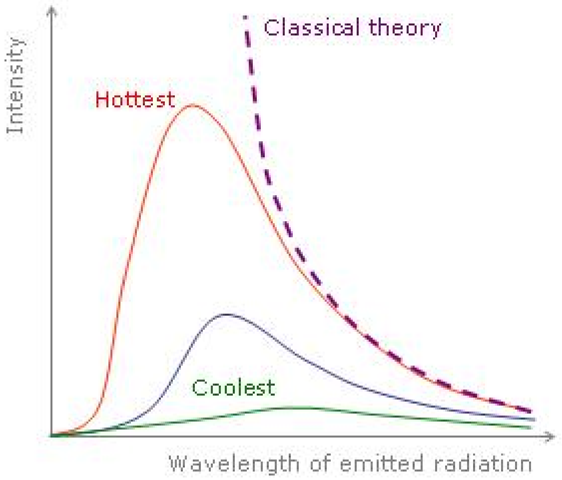
A body which completely absorbs radiation of all wavelength incident on it is called *perfectly black boby*. since a good absorber of radiation is also a good emitter of radiation , a perfectly black body is the best possible emitter at any given temperature .The radiation emitted by such kind of body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

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 one-word 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:

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

Where,

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

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.

SPECIFIC HEAT OF GASES

When a gas is heated, there is in general, an increase in volume as well as pressure in addition to the rise in temperature. For simplicity either the pressure or volume may be kept constant while temperature rises. Therefore, a gas has two specific heats. (i) Specific heat at constant volume, and (ii) Specific heat at constant pressure. The specific heat of a gas at constant volume is the amount of heat required to raise the temperature of 1 gm of the gas through 1°C, the volume being kept constant. It is denoted by c_v. The specific heat of a gas at constant pressure is the amount of heat required to raise the temperature of 1 gm of the gas through 1°C, the pressure being kept constant. It is denoted by c_p. In the former case, the whole heat supplied increases the internal energy of the gas. As a result the temperature rises by 1°C.

In the latter case the gas is allowed to expand against a constant pressure and in doing s it does external work in addition to the work done in increasing the temperature by 1°C; i.e., the internal energy, as in the former case. Hence the specific heat at constant pressure c_p is greater than the specific heat at constant volume c_v by an amount equal to the thermal equivalent of the external work done by the gas, i.e., by the amount of heat that must be used up to do this external work.

Therefore, $c_p - c_v = Q = W$,

Where, Q s the amount of heat used to do the extra work and W the external work done in the same units as of Q.

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 $_2He^4$. 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 gm / 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^1 in liquid phase there is another phase transition called λ 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 λ and this peculiar transition is called λ transition and the discontinuity temp. 2.186 K is called λ point. Kesson concluded that transition He I →He II at T_λ is second order transition. The transition temp. decreases as the pressure is increased.

Electron Gas

A metal can be considered to be composed of a system of fixed positive nuclei and a no. of mobile electrons referred to us the electron gas.

To study the properties of an electron gas at low temperature in the region. For electrons s=1/2 so $g_z = 2s+1 = 2$.

$$\varepsilon_f = h^2/2m \left(\frac{3n}{4\pi .V.2}\right)^{2/3}$$

$$= h^2/8m \left(\frac{3n}{\pi .2}\right)^{2/3} \qquad \text{----- (1)}$$

$$E_a = 3/5\ n\ \varepsilon_f \qquad \text{----------- (2)}$$

In the limit T → 0

Which means that in the limit every one of the states is occupied fully up to the energy level ε_f whereas all the states above this energy level are empty. For electrons m = 9.1×10^{-28}gm, and g =2.

$$\frac{1}{D} = \frac{h^2}{2\, x\, 9.1\, x\, 10^{-28}\, kT}\left(\frac{3n}{8\pi V}\right)^{2/3}$$

A typical metal atomic weight 100 and density 10 so that the volume of gm. atom of 10cc. and the number of electrons assuming one free electron from atom is 6.02×10^{23}. Then

$$\frac{1}{D} = \frac{(6.62\, x\, 10^{-27})^2}{2\, x\, 9.1\, x\, 10^{-28}\, x\, 1.38\, x\, 10^{-18}\, x\, T}\left(\frac{3x\, 6.02\, x\, 10^{23}}{8\, x\, 3.14\, x\, 10}\right)^{2/3}$$

$$= 10^5/\, 1.5T$$

Which means degeneracy is sufficiently high. It shows clearly that for electron gas, a classical statistics is not valid and can be applied only at temperature of the order of $10\ ^5$K. Therefore at low and other ordinary working temperatures, it is necessary to use Fermi- Dirac statistics to study the electron gas in the metals. At low temperature electronic contribution to the specific heat of metals is given by the equ.

$$C_v = \tfrac{1}{2}\, nk\, \pi^2\, (kT/\, \varepsilon_f)$$

$$D = (kT/\, \varepsilon_f)$$

$$C_v = \tfrac{1}{2}\, nk\, \pi^2\, D$$

Using this value find the value of 1/D,

$$C_v = \tfrac{1}{2}\, nk\, \pi^2 \times 1.5 \times 10^{-5} \times T$$

$$\text{Sub. } nk = R$$

$$= 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$= 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$\pi^2 = 10$$

$$C_v = \tfrac{1}{2} \times 1.5 \times 10^{-5} \times 2 \times 10 \times T$$

$$= 1.5 \times 10^{-4} \times T \text{ cal/gm. atom}$$

Pressure of the electron gas can be obtained by,

$$P_o = \frac{2}{5}\, \frac{n\varepsilon f}{V}$$

$$= \frac{2}{5V}\ \frac{h^2}{2m}\left(\frac{3n}{4\pi V gs}\right)^{2/3}$$

$$= \frac{nh^2}{20mV}\left(\frac{3n}{\pi V}\right)^{2/3} \text{ using } gs = 2$$

For a metal of atomic weight 100 and density 10

$$P_o \tilde{\ } 10^5 \text{ atoms}$$

Which means at normal temperature the pressure of gas is sufficiently high.

Degeneracy

(i) Weak degeneracy: At $T > T_F$ (i.e., at intermediate temperatures) the Fermi gas is said to be slightly degenerate. In this case $kT > \in_F (0)$, then $\in_F$ is negative or α is positive and $A < 1$.

For $A < 1$, we can write

$$\frac{1}{\frac{1}{A}e^{\alpha}+1} = \left(\frac{1}{A}e^{\alpha}+1\right)^{-1} = Ae^{x}(1+Ae^{-x})^{-1}$$

$$= Ae^{-x}(1-Ae^{-x}+a^2e^{-2x} - ....)$$

$$\text{Therefore, } f_1(x) = \frac{2}{\sqrt{\pi}}\ \int_0^{\infty} x^{1/2}\,dx/\frac{1}{A}e^{\alpha}+1$$

$$= \frac{2}{\sqrt{\pi}}\left[A\int_0^{\infty} e^{-x}x^{1/2}dx - A^2\int_0^{\infty} e^{-x}x^{1/2}dx - A^3\int_0^{\infty} e^{-x}x^{1/2}dx - ....\right]$$

$$= A - A^2/2^{3/2} + A^3/3^{3/2} - .... \quad (1)$$

$$\text{Similarly, } f_2(\alpha) = A = A^2/2^{5/2} + A^3/3^{5/2} - .... \quad (2)$$

Using these values of $f_1(\alpha)$ and $f_2(\alpha)$, equations (10) and (12) take the form

$$n = g_s\,.\,V/h^3\,(2\pi mkT)^{3/2}\,[A-A^2/2^{3/2}+A^3/3^{3/2}] \quad ----------- (3)$$

$$E = 3/2\ g_s\,.\,V/h^3\,(2\pi mkT)^{3/2}\,[A-A^2/2^{3/2}+A^3/3^{3/2}] \quad ----------- (4)$$

Dividing eq. (4) by (3),

$$E/n = 3/2\ kT\,[1+A^2/2^{5/2}-A^3/3^{5/2}] \quad ------------- (5)$$

To the first approximation We can write

$$n = g_s\,.\,V/h^3\,(2\pi mkT)^{3/2}\,A$$
$$E = 3/2\ g_s\,.\,V/h^3\,(2\pi mkT)^{3/2}\,kT.A$$

$$E/n = 3/2\ kT \text{ or } E = 3/2\ nkT \qquad \text{-------------} (6)$$

which is well known relation for a perfect gas in classical statistics.

A comparison of equations (5) and (6) shows that ideal Fermi-Dirac gas deviates from perfect gas behaviour and this derivation is called degeneracy. It is obvious that degeneracy is the function of A. Greater is the value of A, more marked will be the degeneracy. Hence for A<1or $T>T_F$, the Fermi gas slightly degenerate.

Case (ii) strong degeneracy. When α is large and negative $A=e^{-\alpha} >> 1$. As degeneration increases will increases of A, therefore in this case degeneracy becomes more prominent. Further to the first approximation; from en. (3)

$$A \approx 1/g_s \,.\, n/V\, h^3/(2\pi mkT)^{3/2}$$

This eqn. shows that the gas will be strongly degenerate at low temperature and high particles densities n/v. The evaluation of integrals $f_1(\alpha)$ and $f_2(\alpha)$ under these conditions is complicated.

This case of strong degenerate at low temperature ranges:

(a) At absolute zero i.e when T= 0
(b) When T is above absolute zero, but A>> 1.

Case (a) At absolute zero i.e. when T=0. When T →0 A→0. In this case the Fermi-dirac gas is completely degenerate.

At T=0,

$$f(\in) = \frac{1}{\frac{1}{A}e^{\epsilon/kT}+1} = \frac{1}{e^{\frac{(\epsilon-\epsilon_F)}{kT}}+1} = 1 \text{ for } 0 \leq \epsilon \leq \epsilon_F(0)$$

$$= 0 \text{ for } \epsilon > \epsilon_F(0)$$

where $\epsilon_F(0)$ is given by eqn. (18)

Now the **total internal energy of perfect Fermi- dirac gas at** T=0 **i.e. zero point energy of Fermi gas is**

$$E_0 = 3nh^2/10m\,[3n/4\pi Vg_s]^{2/3} = 3/5\, n\, \epsilon_F\,(0) \qquad \text{----------} (8)$$

Now the pressure at T=0 is given by

$$P_0 = 1/3\, E_0/V$$
$$= 1/5nh^2/V_m\, (3n/4\pi g_s V)^{2/3} \qquad \text{---------} (9)$$

Form equations (8) and (9) it is obvious that a strongly degenerate Fermi-dirac gas possesses energy and exerts a pressure even at 0K, quite unlike a Bose Einstien and classical gases where the energy and pressure at absolute zero are zero.

Case (b) At temperature above absolute zero :but A> >1or T<<Tf

In this case the Fermi –gas is strongly degenerate at low temperature and ϵ is still positive. From equation (17) the number of particles lying in the energy range between ϵ and ϵ+dϵ is given by

$$dn(\epsilon) = f(\epsilon)d(\epsilon) = 3/2\, n/[\epsilon_F(0)]^{3/2}.\ \epsilon^{1/2} d\epsilon / e^{(\epsilon-\epsilon F)/kT} + 1 \quad \text{-------(10)}$$

Therefore, the total number of particles is

$$n = \int_0^\infty dn(\epsilon) = 3/2\, n/[\epsilon_F(0)]^{3/2} \int_0^\infty \epsilon^{1/2} d\epsilon / e^{(\epsilon-\epsilon F)/kT} + 1 \quad \text{----------- (11)}$$

and the total integral energy is

$$E = \int_0^\infty \epsilon dn(\epsilon) = 3/2\, n/[\epsilon_F(0)]^{3/2} \int_0^\infty \epsilon^{1/2} d\epsilon / e^{(\epsilon-\epsilon F)/kT} + 1 \quad \text{------------ (12)}$$

To solve the integrals in equations (31) and (32), let us consider the general integral of the type

$$I = \int_0^\infty \emptyset \frac{(\epsilon)d\epsilon}{e^{\frac{\epsilon-\epsilon_F}{kT}}} + 1 \quad \text{----------- (13)}$$

Where Ø(ϵ) is a simple function of such that Ø( ) =0 when =0.

The integral of eqn. (33) can be expanded using the method of taylor's series expansion,

Where Ø', Ø''' etc. denote the first, third etc. differentials of the function Ø.

Now for $\Phi(\epsilon) = \epsilon^{1/2}$ --------- (15)

$$\epsilon_F / \epsilon_F(0) = [1+1/8(\pi kT/\epsilon F)^2 + 7/640\, (\pi kT/\epsilon_F)^4 +]^{-2/3} \quad \text{---------- (16)}$$

Remembering that kT < < f,we can take into account only the first two terms in the bracketed expression and write

$$\epsilon_F/\epsilon_F(0) = [1+1/8(\pi kT/\epsilon F)^2]^2 \approx 1-1/12\, (\pi kT/\epsilon F)^2 \quad \text{--------- (17)}$$

This gives

$$1/\epsilon_F^2 \approx 1/[\epsilon_F(0)]^2\, [1+1/6\, (\pi kT/\epsilon F)^2] \quad \text{------------ (18)}$$

Now make the crude approximation by putting f= f(0) in the second term of above expression

$$1/\epsilon_F^2 \approx 1/[\epsilon_F(0)]^2\, [1+1/6\, (\pi kT/\epsilon_F(0)^2] \quad \text{----------- (19)}$$

Now using equation (19), equation (17) gives

$$\epsilon_F \approx \epsilon_F (0) [1-1/12 (\pi kT/ \epsilon_F(0))^2] \qquad \text{------------ (20)}$$

$$E\approx n\, \epsilon_F (0) (\epsilon F /\epsilon_F (0)^{5/2} \quad [1+5/8 (\pi kT/ \epsilon_F)^2]$$

Now using equations (39) and (40),we get

$$E\approx 3/5\, n\, \epsilon_F (0) [1+5/12(\pi kT/ \epsilon_F (0)] \qquad \text{----------- (22)}$$

The corresponding pressure is

$$P = 2/3\, E/V \cong 2/5\, (n\, \epsilon_F (0)/V) [1+5/12 (\pi kT/ \epsilon_F (0)^2] \qquad \text{------------- (23)}$$

Equations (22) and (23) represent the approximate energy and pressure of a strongly degenerate gas.

Ising and Heisenberg Model

Transition of non-ferromagnetic state into ferromagnetic state is called phase transition, in this transition, the state of the body changes continuously.

Consider a ferromagnetic substance, like iron and nickel. Without any external field being applied, some of the spins of the atoms become spontaneously polarized in the same direction, below curie temperature Tc. Thiscreate a macroscopic magnetic field. The spontaneous magnetization, created vanishes if temperature is greater than Tc, because thermal energy makes some of the aligned spin to flip over. Thus spins get oriented at random no net magnetic field is produced. As the curie temperature approached both sides of the specific heat of the metal approaches infinity. The transition from non-ferromagnetic to the ferromagnetic state, called the phase transition, is associated with some kind of change in the symmetry of the lattice; For example the ferromagnetism symmetry of the spins is involved. In Ising model the system considered is the array of N fixed points called lattice sites that from an n-dimensional periodic lattice (n=1,2,3). Associated with each lattice site is a spin variable, s_i, i =1 to n, It is a number that either +1 or -1. There are no other variable. If $s_i = +1$ the ith state is said to have spin up and $s_i =-1$, it is said to have spin down. A given set of $\{s_i\}$ specifies a configuration of the whole system, whose energy is defined to be

$$E_1\{s_i\} = -\sum_{\langle i,j\rangle} \in_{ij\, s_i} si\, sj - \mu H \sum_{i=1}^{N} si \qquad \text{------------- (1)}$$

Where the subscript I stands for Ising and the symbol $\langle i,j\rangle$ denotes a nearest-neighbour pari of spins. There is no distinction between $\langle i,j\rangle$ and $\langle j,i\rangle$ is the interaction energy μH interaction is associated with the external magnetic field H. For spontaneous magnetization H= 0. $\in_{ij}$ and H are given constants. Applied the model to the case is isotopic interaction so that all $\in_{ij}$ have the same value ∈. For energy

$$E_1\{s_i\} = -\in \sum_{\langle i,j\rangle} si\, sj - \mu H \sum_{i} si \qquad \text{--------- (2)}$$

The case ∈ > 0 corresponds to ferromagnetism and the case ∈< 0 to antiferromagnetism. In the former case neighbor spins tend to be parallel while in the latter case they tend to be antiparallel. In eq. (2) the sum over $\langle i,j\rangle$ contains N/2 terms where is the number of nearest neighbors of any given site. In the Ising model eq. 2, geometry of the lattice enters through and interaction energy $\in_{ij}$

Consider only these case ∈ > o. The partition function is

$$Z = \sum_{S1} \sum_{S2} \sum_{SN} e^{-\beta E1\,\{Si\}}$$

POSSIBLE QUESTIONS

1. Define specific heat capacity at constant volume.
2. Explain Ising and Heisenberg model.
3. Discuss about specific heat of solids.
4. What are called photons?
5. State Dulong and Petit's law.
6. Give a note on liquid helium.
7. Define degeneracy.
8. Give a note on pauli paramagnetism.
9. What are the applications of quantum statistical mechanics?
10. State Kirchhoff's law.
11. Write a note on black body and Planck radiation law.

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE – 641 021					
DEPARTMENT OF PHYSICS					
I MSc PHYSICS (17PHP103)					
THERMODYNAMICS AND STATISTICAL MECHANICS					
UNIT-V					
Questions	**opt1**	**opt2**	**opt3**	**opt4**	**Answer**
In solid heat is transferred by _________	Conduction	convection	radiation	Irradiation	Conduction
In liquid heat is transferred by _________	Conduction	convection	radiation	Irradiation	convection
Conduction and convection cannot take place in __________	solid	liquid	inert gas	empty space	empty space
______________ does not require any material medium.	Conduction	convection	radiation	Irradiation	radiation
Radiant energy is also called as ____	latent heat	radiant heat	entropy	enthalpy	radiant heat
The wavelength of infrared ranges from ________	7500Å to 1000000Å	750Å to 100000Å	7500Å to 10000Å	750Å to 1000000Å	7500Å to 1000000Å
____________ travels with speed of light.	Conduction	convection	radiation	Irradiation	radiation
The nature of radiant energy is same as that of _______	sound	heat	light	electricity	light
The radiant energy emitted depends on _________	temperature	material	volume	height	temperature
For a black body the emissive power is denoted by __________	E	λ	λE	Eλ	E
Unit of emissive power is ________	1 W/m	1WmÅ	1WÅ	1W/m2Å	1W/m2Å
For a perfectly black body aλ = ________	0	∞	1	-∞	0
Absorptive power is represented by _____	a	λ	λa	aλ	aλ
Kirchoff's law of radiation =	eλ/aλ = Eλ	eλ/aλ = λ	aλ/eλ = Eλ	eλ/Eλ = aλ	eλ/aλ = Eλ
___________ black is nearest approach to a perfectly black body.	gold	platinum	diamond	silver	gold
Which is considered as a perfect absorber as well as a perfect emitter?	Gray body	Black body	Real body	White body	Black body
Which body that emits a constant emissivity regardless of the wavelength?	Gray body	Black body	Real body	White body	Gray body
At same temperatures, the radiation emitted by all real surfaces is ______ the radiation emitted by a black body.	Less than	Greater than	Equal to	Either less than or greater than	Less than
Which is NOT a characteristic of emissivity?	It is high with most nonmetals	It is directly proportional to temperature	It is independent with the surface condition of the material	It is low with highly polished metals	It is low with highly polished metals
What is the emissivity of a black body?	0	1	0.5	0.25	1
What is the absorptive of a black body?	0	1	0.5	0.25	0
Above Curie point	A ferromagnetic material becomes paramagnetic	a ferrite becomes an insulator	a insulating material becomes a ferrite	a diamagnetic material becomes a paramagnetic material	A ferromagnetic material becomes paramagnetic
Which of the following is a paramagnetic material?	Palladium	Lead	Pure Iron	Bismuth	Lead
Which of the following is a ferromagnetic material?	Palladium	Lead	Iron	Bismuth	Iron
All of the following materials are Ferromagnet except	Nickel	Bismuth	Silicon	Mild steel	Mild steel

By adding silicon to ferromagnetic , materials	electrical resistivity increases and also magnetic permeability increases	electrical resistivity decreases and also magnetic permeability decreases	electrical resistivity decreases and magnetic permeability increases	electrical resistivity increases and magnetic permeability decreases.	electrical resistivity decreases and magnetic permeability increases
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^{-1} °C^{-1}	670 J kg^{-1} °C^{-1}	705 J kg^{-1} °C^{-1}	740 J kg^{-1} °C^{-1}	670 J kg^{-1} °C^{-1}
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^{-1} °C^{-1}	140 J kg^{-1} °C^{-1}	160 J kg^{-1} °C^{-1}	180 J kg^{-1} °C^{-1}	140 J kg^{-1} °C^{-1}
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
The temperature at which liquid changes into vapour is called as	Melting point	boiling point	expansion point	phase transition	boiling point
In Conduction process the molecules of the solid pass the heat from one to another	without themselves moving from their positions		themselves move from one place to another	without themselves moving from one place to another	without themselves moving from their positions
The process of transfer of heat in liquids & gases is called as	Conduction	Radiation	Convection	absorption	Convection
Solids are not heated by convection because	solid are not free to move from one place to another	molecules only vibrate about fixed position	both A and B	they are loosely packed	both A and B
It is the process of heat transfer from a hot body to a colder body without heating the space between the two is called as	Conduction	Radiation	Convection	absorption	Radiation

The transfer of heat by radiation	does not require any medium.	require any medium	does not require any space	require any space	does not require any medium.
Heat of sun reach the earth by	Conduction	Radiation	Convection	absorption	Radiation
A cold steel spoon is dipped in a cup of hot milk. It transfers heat to its other end by the process of…………….	Conduction	Radiation	Convection	absorption	Conduction
Why conduction is only possible in solids	particles of solids are closely packed	heat is transferred from the hotter end to the colder end of an object	heat is transferred from the colder end to the hotter end of an object	both A and B	both A and B
The water is poor conductors of heat so do not heated by	Conduction	Radiation	Convection	absorption	Conduction
Which of the following are the examples of conductors?	plastic	iron	wood	silicon	iron
Which of the following are the examples of insulators ?	copper	iron	wood	silicon	wood
Radiation is the transfer of heat by means of	magnetic wave	electromagnetic waves	electrical wave	radio waves	electromagnetic waves
Materials which lack permanent magnetic dipoles are called	dia magnet	ferro magnet	semi-magnet	para magnet	dia magnet
Materials having a high dielectric constant, which is non-linear, are known as	elastomers	ferroelectric materials	super die-electrics	hard die-electrics	ferroelectric materials
In ferromagnetic materials	the atomic magnetic moments are antiparallel and unequal	the atomic magnetic moments are parallel	the constituents is iron only	one of the constituent is iron	the atomic magnetic moments are parallel
The temperature beyond which substances lose their ferroelectric properties, is known as	curie temperature	critical temperature	inversion temperature	conversion temperature	curie temperature
What is the degeneracy of the rotational energy level with $J = 4$ for a heteronuclear diatomic molecule?	1	2	3	9	9
Which type of statistics is used to describe the electron contribution to specific heat?	MB statistics	BE statistics	FD statistics	Classical statistics	FD statistics

Reg No…………….

[17PHP103]

KARPAGAM ACADEMY OF HIGHER EDUCATION, COIMBATORE-21

(Under Section3 of UGC Act 1956)

DEPARTMENT OF PHYSICS

I M. Sc PHYSICS

First Semester

I-Internal Examination

THERMODYNAMICS AND STATISTICAL MECHANICS

Date: 30.8.2017 Time:2 hours

Maximum:50 marks

PART-A(20x1=20Marks)

Answer all questions

1. The term “thermodynamics” comes from Greek. words “therme” and “dynamis” which means _______.
   A. Heat power
   B. Heat transfer
   C. Heat energy
   D. Heat motion
2. The macroscopic approach to the study of thermodynamics does not require a knowledge of the behavior of individual particles is called _____.
   A. Dynamic thermodynamics
   B. Static thermodynamics
   C. Statistical thermodynamics
   D. Classical thermodynamics
3. What law asserts that energy has quality as well as quantity?
   A. First law of Thermodynamics
   B. Second law of Thermodynamics
   C. Third law of Thermodynamics
   D. Zeroth law of Thermodynamics
4. Thermodynamics is applicable to
   A. microscopic systems only
   B. macroscopic systems only
   C. homogeneous systems only
   D. heterogeneous systems only.
5. A system that can transfer neither matter nor energy to and from its surroundings is called
   A. closed system
   B. an isolated system
   C. an open system
   D. a homogeneous system
6. The heat capacity at constant pressure is related to heat capacity at constant volume by the relation
   A. Cp-R =Cv
   B. Cv-R =Cp
   C. Cp-Cv =R
   D. R-Cp =Cv
7. If a system involves two phases, it is in ______ equilibrium when the mass of each phase reaches an equilibrium level and stays there.
   A. Chemical B. Thermal
   C. Mechanical D. phase
8. A system is said to be in thermodynamic equilibrium if it maintains ______ equilibrium.
   A. Mechanical and phase
   B. Thermal and chemical
   C. Thermal, mechanical and chemical
   D. Thermal, phase, mechanical and chemical
9. A system is in ______ equilibrium if there is no change in pressure at any point of the system with time.
   A. Pressure B. Thermal
   C. Mechanical D. Phase
10. What is a process during which the temperature remains constant?
    A. Isobaric process
    B. Isothermal process
    C. Isochoric process
    D. Isometric process
11. What is a process during which the specific volume remains constant?
    A. Isobaric process
    B. Isothermal process
    C. Isochoric or isometric process
    D. Isovolumetric process

12. Solid and liquids have

A. Only one value of specific heat

B. Two value of specific heat

C. Three value of specific heat

D. No value of specific heat

13. Volume of gas become four times if.

A. Temperature become four times at constant pressure

B. Temperature becomes two times at constant pressure

C. Temperature become one fourth at constant pressure

D. Temperature becomes half at constant pressure

14. Kinetic theory of gases provide a base for

A. Charle’s law B. Charle’s law and Boyle’s law C. Boyle’s law D. Stefan’s law

15. S.I. unit of universal gas constant is

A. cal/°C B. J/molK C. J/mol D. J/kg

16. At constant volume, temperature is increased. Then.

A. Collision on walls will be less

B. Collisions will be in straight lines

C. Number of collisions per unit time will increase

D. Collisions will not change

17. The specific heat of a gas

A. Has only two values Cp and Cv

B. Can have any value between 0 and ∞

C. Has a unique value at a given temperature

D. Depends upon the mass of the gas

18. Boltzmann's constant is

A. 1.38 x 10-23 j/k

B. 1.38 x 10-31 j/k

C. 1.38 x 10-32 j/k

D. 1.38 x 10-19 j/k

19. Which of the following statements is TRUE for an ideal gas, but not for a real gas?

A. PV = nRT

B. An increase in temperature causes an increase in the kinetic energy of the gas

C. The total volume of molecules on a gas is nearly the same as the volume of the gas as a whole

D. No attractive forces exists between the molecule of a gas

20. The unit of pressure in SI unit is

A. Kg/cm2 B. Mm of water column C. Pascal D. Bars

PART-B (3 × 2 = 6 Marks)

Answer all the questions

21. Write a short note on phase space.

22. Give a brief note on mean free path.

23. Describe about conservation of energy

PART-C (3 × 8 = 24 Marks)

Answer all the questions

24. a) Write a note on thermodynamic potentials, obtain Helmholtz and Gibbs functions

(OR)

b) Derive Clausius-Clapeyron equation and Van der Waals equation of state.

25. a) Describe about distribution function and Obtain Boltzmann Transport equation.

(OR)

b) Give a note on conservation of momentum and hydrodynamics.

26. a) Obtain the value of e^{α}.

(OR)

b) Discuss about Maxwell – Boltzmann energy distribution law

Reg No…………….

[17PHP103]

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C. **Mechanical** D. Phase

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20. The unit of pressure in SI unit is

A. Kg/cm2 B. Mm of water column C**. Pascal** D. Bars.

PART-B (3 × 2 = 6 Marks)

Answer all the questions

21. Write a short note on phase space.

Statistics involves the counting of states, and the state of a classical particle is completely specified by the measurement of its position and momentum. If we know the six quantities x,y,z,px,py,pz, then we know its state. It is often convenient in statistics to imagine a six-dimensional space composed of the six position and momentum coordinates. It is conventionally called "phase space". The counting tasks can then be visualized in a geometrical framework where each point in phase space corresponds to a particular position and momentum. That is, each point in phase space represents a unique state of the particle. The state of a system of particles corresponds to a certain distribution of points in phase space.

22. Give a brief note on mean free path.

The mean free path or average distance between collisions for a gas molecule may be estimated from kinetic theory. Serway's approach is a good visualization - if the molecules have diameter d, then the effective cross-section for collision can be modeled by using a circle of diameter 2d to represent a molecule's effective collision area while treating the "target" molecules as point masses. In time t, the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume.

23. Describe about conservation of energy.

If a system does not interact with its environment in any way, then certain mechanical properties of the system cannot change. They are sometimes called "constants of the motion". These quantities are said to be "conserved" and the conservation laws which result can be considered to be the most fundamental principles of mechanics. In mechanics, examples of conserved quantities are energy, momentum, and angular momentum.

PART-C (3 × 8 = 24 Marks)

Answer all the questions

24. a) Write a note on thermodynamic potentials, obtain Helmholtz and Gibbs functions.

The thermodynamics variables such as pressure P, Volume V, temperature T and entropy S, define the stole of thermo dynamical system. A relation b/n them exists because of the two thermodynamic laws.

$$dQ = dU + PdV$$

$$dQ = TdS$$

Combining

$$TdS = dU + PdV$$

$$dU = TdS - PdV$$

Any two of above variables are independent and with the help of above relation remaining variables be determined. These relations are termed as thermodynamic potentials of thermodynamic fn.

Enthalpy or Heat content H:

Thermodynamical phenomena at constant pressure are expressed in terms of another function called enthalpy or heat content of the system.

$$H = U + PV \qquad \text{---- (1)}$$

diff. $dH = dU + PdV + VdP$

$$= (TdS - PdV) + PdV + VdP$$

$$= TdS + VdP$$

$$dH = Tds \qquad \text{------ (2)}$$

because process is carried at constant pressure. Since Tds = dQ, we find dH=dQ enthalpy represents the quantity of heat given to the system from an external source & hence the name heat content.

Let H_i and H_f be the initial and final enthalpy,

$$H_f - H_i = Q$$

The change in enthalpy during an isobaric process equal too the heat transferred.

H has an important property in porous plug exp let P_i and V_i be the initial pressure & volume of a gas before passing through porous plug. Similarly pf and vf be the similar quantities of the gas after passing thro' the porous plug.

External work done by gas = $P_f V_f - P_i V_i$

This work done at the cost of internal energy of the because no heat exchanges b/n gas and surrounding, suppose Ui and Uf be the initial and final internal energy.

$$U_i - U_f = P_f V_f - P_i V_i$$

$$U_i + P_i V_i = P_f V_f + U_f$$

$$\text{(or)} \quad H_i = H_f$$

Thus in throttling process, the initial and final enthalpy remain same.

Taking partial diff. of H w.r. to independent variables S and P,

$$\Longrightarrow \quad \left(\frac{\partial H}{\partial P}\right)_S = V \text{ and } \left(\frac{\partial H}{\partial S}\right)_P = T \qquad \text{------ (3)}$$

As dH is perfect diff.

$$\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)$$

Using (3), we get

$$\left(\frac{\partial V}{\partial P}\right)_V = \left(\frac{\partial T}{\partial P}\right)_S \qquad \text{------- (4)}$$

Which is third thermodynamical relation

Helmholtz Function F:

On combining I & II law of thermodynamics,

dU = Tds – dW

suppose the temp of the system remain constant, then

d(TS) = Tds

⇨ dU=d(TS)-dW

d(U-TS) = –dW

where the fn. F=U-TS

⇨ dF=-dW --------- (1)

is called Helmholtz fn. Or Helmholtz free energy, which represents that in revisable isotheral process, the work done by the system is equal to decrease in Helmholtz Fn. F is also called as work fn.

on diff. Eqn. (1), we pet

dF=dU-TdS-SdT

sub. dU=TdS-PdV

$$\Rightarrow \quad dF=TdS-PdV-TdS-SdT$$

$$= -PdV-SdT \qquad - (2)$$

On partial diff. Of F w.r.to independent variables T & V.

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \text{ and } \left(\frac{\partial F}{\partial V}\right)_T = -P \qquad \text{-------} (3)$$

As dF is a perfect diff,

$$\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial V}\right)$$

using eq. (3) we get

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

This eqn. given a relation b/n 4 thermo dynamical variable P,V,S and T. This is second thermodynamical relation

Gibbs potential (G):

If thermodynamic process is isothermal and isobaric (dp=0) then from qn.(2) we get

$$dH=T(ds)$$

$$= d\,(TS) \quad \text{[from Helmholtz fn.]}$$

$$d(H-TS) = 0$$

$$dG = 0$$

$$\text{Where } G = H - TS$$

$$G = U+PV-TS$$

is called gibb's fn. or free energy

on diff. (5), we get $dG = dU+PdV+VdP - TdS - SdT$

$$= (TdS - pdv) + pdV+VdP-TdS-SdT$$

$$dG = VdP-SdT \qquad \text{----- (6)}$$

Talking partial derivatives of a w.r. to independent variable P and T, we get

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S \qquad \text{------- (7)}$$

As dG is perfect diff ., $\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)$

This is called fourth thermodynamical relation.

b) Derive Clausius-Clapeyron equation and Van der Waals equation of state.

Consider the volume occupied by the gas molecules negligible compared with the total volume of gas and the molecules exert no appreciable forces on one another. It is evident that both these assumptions cannot be exactly true for actual gases particularly at high pressure. In driving van der waals eqn. Of state the effect both these factor is taken into account.

Due to the finite size of molecules, the free space available for their movement is less than the actual measured volume of the gas. Also the number of collisions with the walls of containing vessel, and the pressure will be greater than the calculated by simple theory. The actual volume can be brought about by subtracting a career term b from the measured volume and using (v-b) in place of V in ideal gas equation.

Let XY be the portion of boundary wall. Consider a molecule A in the interior far from the boundary wall. It is surrounded by other molecules equally distributed in all directions. Those molecules exert attractive force on molecule A, when averaged out, over a sufficient interval of time they cancel out and net cohesion force will be zero. On the other hand the molecule B is as rear the boundary as it can go. In this case the molecular distribution is only along one side. The adhesive force between the gas molecules and the boundary walls are always must smaller than the cohesive force, between the gas molecules. The force on B due to each adjacent molecule can be resolved into components to the boundary wall. The parallel components cancel out on the average but the perpendicular components will result a field of force acting inwards on the molecules near the boundary wall. Thus whenever a molecule will strike the walls of the containing vessel at B to contribute its share towards the total gas pressure, the measured pressure P is loss than the ideal pressure calculate on the assumption that the cohesive force is P, the add a correction term P, to the measured pressure P and use $(P+P_1)$ in place of P in ideal gas.

On using both corrections in ideal gas equation, we get for a gram molecule of a gas.

$$(P+P_1)(V-b) = RT \qquad (1)$$

The value of P_1 is to the number of molecules striking in area of the wall in unit time & to the intensity of the field of force. Both of these factors are proportional to the density of the gas.

$$p_1=a\rho^2$$

C->constant

$$\rho \propto 1/V$$

Hence $p_1=a/V^2$, where a is constant.

Sub. this value of p_1, in equation (1),

$$(p+a/V^2)(v-b)=RT \qquad \rightarrow(2)$$

This is van der waal's equation of state. This is the simplest and the most well known equation of stove for real gas.

Another useful form of the equation of state of a real gas is

$$PV=A+B/V+C/V^2+........ \quad \rightarrow(3)$$

A,B,C,... are from of temp and are called viral coeff.

For an ideal gas it is evident that A=RT and all other viral coeff. are zero.

Van der walls equation can be but in virial form as,

Equation (2) rewritten as,

$$1=RT/((P+a/V^2)(v-b))$$

(or) $$PV=RT(l-a/PV^2)^{-1}\ (l-b/v)^{-1} \qquad \rightarrow(4)$$

The correction terms a/PV^2 & b/V are both small composed with unity provided the gas is not too much compressed. Using binomial theorem & neglecting the terms of higher power a l/V, equation V1, becomes,

$$PV=RT(l-A/PV^2)\ (l+B/V)+b^2/v^2$$

$$=RT-RT/PV.a/v+RT.b/v+RTb^2/v^2$$

Since PV=RT approx,

$$PV=RT+(RTb-a)/v+RTb^2/v^2 \quad \rightarrow(5)$$

This is van der waal's equation in virial form having only three virial coeff., A,B,&C

$$A=RT,\ B=RTb-a,\ C=RTb^2$$

25. a) Describe about distribution function and Obtain Boltzmann Transport equation.

Consider a system of particles acted upon by external forces. For example the system may consists of electrons in a metal that is acted upon by electric and magnetic fields. In order to device the Boltyman transport equation consider a region of six dimensional space about the point (x,y,z,v_x,v_y,v_z)i.e.(r,v). An element of volume in this six dimensional space is written as $dxdydzdv_xdv_ydv_z$ or drdv. The number of particles having coordinates within ranges r to r+dr and v to v+dv can be represented as

$$dn=f(r,v,t)drdv \qquad \rightarrow(1)$$

Where f(r,v,t)is the distribution function.

At point (r,v) the variation of distribution function of with time may be caused by two independent ways:

(i) Drift-variation: The function f may vary because of the drift particles from one region of space to another. This variation pep time is represented by $(\partial f/\partial t)_{\text{drift}}$.

(ii) Collision or scattering Interactions: The function f may vary because of collision among the particles. The variation per time is represented by $(\partial f/\partial t)_{\text{collisions}}$.

Hence the rate of change of the function for may be expressed as

$$\partial f/\partial t=(\partial f/\partial t)_{\text{drift}}+(\partial f/\partial t)_{\text{collision}}$$

assumed that the number of particles in the system is conserved. If it is not so, then the term represent the generation and recombination of particles to the right hand side of equation(2).such additional terms are required in the theory of nuclear and function transistor.

To derive the Botlzman transport equation, let the particles in the differential phase space volume drdv around (r,v) move to a new position by virtue of their velocity in a short time interval dt. The velocity of the particles may change due to the external force acting upon them and the collision among themselves. Let the new position be represented by (r^1, v^1)such that

$$r' =r+vdt,\ v' =v+adt$$

Where a is the acceleration of the particle.

Consider that no collision oceans diving the time Interval dt, then all of particles will move to the new volume dr’dv’ and write as

$$f(r+v\,dt, v+a\,dt, t+dt)dr'dv'=f(r,v,t)drdv \quad \rightarrow(3)$$

According to Lioville’s theorem,

$$dr'dv'=drdv \quad \rightarrow(4)$$

then equation (3)gives

$$f(r+vdt, v+adt, t+dt)=f(r,v,t) \quad \rightarrow(5)$$

Using Taylor series expansion on L.H.S and retaining terms linear in dt the time dt→0, above equation

$$f(r,v,t)+v\,dt.\ \text{grand}_r\, f + a\ dt.\ \text{grad}_v\, f+\partial f/\partial i\ dt=f(r,v,t)$$

$$v.\text{grad}_r\, f + a.\text{grad}_v\, f+ \partial f/\partial t=0 \quad \rightarrow 6$$

This is Botlzman's transport equation when no collision.

In this equation $\text{grad}_r=\Delta_r$ is the usual del operator and $\text{grad}_v= \Delta_v$ is the del operator in velocity space.

$$\Delta_r = i\frac{\partial}{\partial x}+j\frac{\partial}{\partial y}+ k\frac{\partial}{\partial z}$$

$$\Delta_v = i\frac{\partial}{\partial v_x}+j\frac{\partial}{\partial v_y}+ k\frac{\partial}{\partial v_z} \qquad \text{------- (7)}$$

$$v.\ \text{grad}_r\ f = v_x\frac{\partial}{\partial x}+v_y\frac{\partial}{\partial y}+ v_z\frac{\partial}{\partial z}$$

$$\text{and } a.\ \text{grad}_r\ f = a_x\frac{\partial}{\partial x}+a_y\frac{\partial}{\partial y}+ a_z\frac{\partial}{\partial z} \qquad \text{----------- (8)}$$

However, collisions are taken into account, then due to collisions among the particles some particles leave the volume element drdv and some ways from dr, dv, to drdv. This is equivalent to a loss or gain in the number of particles in volume element drdv. Now the change in number of particles in volume element drdv during the time interval from t to t+dt, using Liouvelle's theorem,

$$f(r+v\,dt,\ v+a\,dt,\ t+dt)drdv - f(r,v,t)drdv=(\partial f/ \partial t)_{collision}\ dtdrdv \quad \rightarrow (9)$$

$$\text{i.e. } \partial f/ \partial t+v\,\text{grad}_r f+a.\text{grad}_v f=(\partial f/ \partial t)_{collision}$$

This is Botlzman transport equation.

Comparing equation (2) &(9),

$$(\partial f/\partial t)_{drift} = -v.grad_r f - a.grad_v f \quad \rightarrow(10)$$

If J_{gain} & J_{loss} represents the number of particles gained and lost per unit volume element per unit time as a consequence collisions, then Botlzman's transport equation (9) may be written as

$$\partial f/\partial t + v.grad_r f + a.grad_v f = J_{gain} - J_{loss} \quad \rightarrow(11)$$

The collision term $\{f/t\}_{collision}$ in equation (9) or (J_{gain}-J_{loss}) in equation (11) may require special treatment. But the problem is possible to justify approximately the introduction of a parameter v_c called the relax time him or mean free time defined by the equation

$$\{\partial f/\partial t\}_{collision} = -f - f_0/\tau_c \quad \rightarrow(12)$$

Where f_0 is the distribution function in thermal equilibrium.

By definition $\partial f_0/\partial f=0$,equation(12) may be

$$(\partial f - f_0)/\partial t = f - f_0/\tau_c \quad \rightarrow(13)$$

This equation represents the rate at which distribution function approaches the equilibrium condition as being proportional to the deviation from equilibrium condition at a given time.

Eqn. (13) soln. Is

$$(f-fe)f = (f-f)_{i=o} \qquad \text{------ (14)}$$

Which indicates that $(f-f_o)_i$ proportional to the distribution towards equilibrium decays exponentially .

Using eqn (12) the Boltzmann's transport eqn (9) in reaction time approximately is written as

In the steady state $\frac{\partial f}{\partial t} = 3$

b) Give a note on conservation of momentum and hydrodynamics.

Hydrodynamics is the study of fluid flow, which was also developed prior to the conclusion of the atom vs. continuum debate. It is sufficient to treat a fluid as a continuous substance. Let fluids are made of particles, can explain some fluid phenomena in terms of more fundamental physics, for instance can predict the viscosity of a gas (a macroscopic quantity) by consideration of particles, mean-free paths and so on. The state of a fluid can be described in terms of a number of 'functions of state', which in a simple fluid is two, for instance pressure and temperature; all other variables, for instance density or entropy, can be found from the equation of state. To include more complex fluids in terms of the mean molecular weight is not fixed, or the salinity in an ocean or water vapour concentration in the atmosphere, for example. These quantities are called intensive variables as they can be defined and measured at any particular point in space, as opposed to extensive variables such as volume or mass which are properties of a whole system. The velocity and the thermodynamic variables are functions of position r and time t.

26. a) Obtain the value of e^{α}.

The total number N of the particles in the system is given by

$$N = \Sigma_r n_r = \sum_r e^{-\alpha} g_r e^{-Er/kT}$$

$$= e^{-\alpha} \Sigma_r \, g_r e^{-Er/kT}$$

$$= A \, \Sigma_r \, g_r e^{-Er/kT} \qquad \text{-------- (1)}$$

Where A$=e^{-\alpha}$

From eq. (1) $A = \frac{N}{\sum_r g_r\, e^{\frac{-Er}{kT}}}$

For continuous variation of energy of free particles of an ideal gas, g_r is replaced by g(E) dE, E_r is replaced by E and the sign of summation is replaced by the sign of integration.

$$A = \int_0^\infty \frac{N}{g(E)dE\, e^{\frac{-Er}{kT}}} \qquad \text{----------- (2)}$$

The limits of integration are taken from 0 to ∞ because energy of the particles of an ideal gas is entirely kinetic and so they can have any K.E. The value of g(E) dE for particles with no spin is given by

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

The integral in eq. (2) is evaluated as follows:

$$I = \int_0^\infty g(E)\, e^{-E/kT} dE$$

$$= 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty E^{1/2}\, e^{-E/kT} dE$$

Let E/kT = x, then E=kTx

Therefore dE = kTdx

$$I = 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (kTx)^{\frac{1}{2}}\, e^{-\frac{x}{kT}} (kT) dx$$

$$= 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (x)^{\frac{1}{2}}\, e^{-x} dx$$

$$= 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \int_0^\infty (x)^{\frac{3}{2}-1} e^{-x} dx$$

The integral on the R.H.S of this equation is a gamma-function defined as

$$\int_0^\infty (x)^{n-1} e^{-x} dx = \Gamma(n)$$

Therefore $\int_0^\infty (x)^{\frac{3}{2}-1} e^{-x} dx = \Gamma(3/2) = \frac{1}{2}\sqrt{\pi}$

$I = 2\pi V \left(\frac{2mkT}{h^2}\right)^{\frac{3}{2}} \times \frac{1}{2}\sqrt{\pi} = V \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}$

Sub. the value of this integral in eq. (2),

$$A = e^{-\alpha} = \frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2} \qquad \text{-------- (3)}$$

The constant A i.e., $e^{-\alpha}$ is called degeneracy parameter

$$\text{Taking log on both sides, } -\alpha = \log\left[\frac{N}{V}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}\right] \qquad \text{------------ (4)}$$

b) Discuss about Maxwell – Boltzmann energy distribution law.

The Maxwell –Boltzmann equation for distribution of energy among the molecules of an ideal gas is

$$n(E)dE = \frac{2\pi N}{(\pi KT)^{3/2}} E^{1/2} e^{-E/KT} dE \qquad \text{----------------------(1)}$$

A classical ideal gas is defined as an assembly of non-interacting molecules, each distinguishable from the other. Therefore, the molecules have no internal degrees of freedom, all the energy of the gas in the form of kinetic Energy of the molecules.

$$E=\frac{1}{2}mv^2=\frac{1}{2}m(v^2{}_x+v^2{}_y+v_z{}^2) \qquad \text{--------------------------(2)}$$

$$dE=mvdV \qquad \text{--------------------------(3)}$$

Substitute the expression for E and dE in eq(1), the number of molecules n(v)dv whose speeds lie in between v and v + dv is given by

$$n(v)dv=\frac{2\pi N}{(\pi KT)^{3/2}}\left(\frac{1}{2}mv^2\right)^{1/2}e^{-mv2/2KT}mv\ dv$$

$$=4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2} v^2e^{-mv2/2KT}dv \qquad \text{--------------------(4)}$$

This eq. is known as the Maxwell of Maxwell –Boltsmann law of distribution speeds among the molecules of a gas .In this equation n(v) is the number of molecules per unit speed range .Therefore , the unit of n(v) is molecules /(m/sec).

Discussion of the law:

The curves for n(v) plotted against v at three different temperatures T_1,T_2,T_3 where $T_1<T_2<T_3$

From the distribution curves we get the following conclusions.

(1)At any temperature there is no molecules having zero speed.

(2) As the speed increases the no of molecules in a given speed interval $\Delta\nu$ increases upto a certain maximum value.

(3) As the speed further increases beyond v_p , n(p) decreases exponentially towards zero. It means according to classical physical a molecules can have a infinite speed.

(4) As the temperature increases, v_p increases, and the range of speed is greater .Hence the curve become broad.

(5) At the given temperature the area under the distribution curves is equal to the total number of molecules in the gas .Thus

$$N=\int_0^\infty n(v)dv$$

Since the area must be same at all the temperature, the distributive curve must flatten as the temperature rises.

Reg No…………….

[16PHP103]

KARPAGAM ACADEMY OF HIGHER EDUCATION
COIMBATORE-21
(Under Section3 of UGC Act 1956)
DEPARTMENT OF PHYSICS
I M.Sc PHYSICS
First Semester
II-Internal Examination
THERMODYNAMICS AND STATISTICAL MECHANICS

Date: Time:2 hours
Maximum:50 marks

PART-A(20×1=20Marks)
Answer all questions

1. In solid heat is transferred by _________ A. Conduction B. convection C. radiation D. Irradiation
2. In liquid heat is transferred by _________ A. Conduction B. convection C. radiation D. Irradiation
3. Conduction and convection cannot take place in __________ A. solid B. liquid C. inert gas D. empty space
4. B.E distribution law is used to derive ___________of radiation
   A. Planck's law B. Weiss law
   C. Widemann Franz law
   D. Rayleigh's law
5. Wave function of the system of identical Bosons is A. asymmetric B. linear C.non-linearD. symmetric
6. The variable W in an equilibrium stands for
   A. minimum probability distribution
   B. probability distribution
   C. maximum probability distribution
   D.constant probability distribution
7. vp = ___A. v (2kT/m) B. 1.414vkT
   C. 1.732v(kT/m) D. 3.414vkT
8. Root mean square = ________
   A. v (2kT/m) B. 1.414v Kt
   C. 1.732v(kT/m) D. 3.414vkT
9. The equation for total internal energy of one mole of an ideal gas is
   A. U/N = 3/2 Kt B.U/N = 3/2
   C.U/N = kT D. U/N = 2/3 kT
10. ________ is the energy distribution function. A. f(E) B. g(E) C. n(E) D. f(V)
11. ____________ is the number of quantum states A. f(E)
    B. g(E) C.n(E) D. f(V)
12. In B.E. energy distribution, if ea =1, for E=0, then n(0) dE =
    A. postive B. infinity
    C. negative D. infinitive
13. The free electron gas in copper is _______ A. highly degenerate B. degenerate C. weekly degenerate D. non-degenerate
14. Surface potential barrier energy of the metal is denoted by ______ A. EP B. ES C. S D. SE
15. Richardson explain his theory in the year ______ A. 1801 B. 1701 C. 1901 D. 1921
16. S. Dushmann explained his theory in the year __ A. 1801 B. 1701 C. 1923 D. 1921
17. The value of b is given by
    A. 3 KT B. KT
    C. 1/KT D.4KT
18. What is the emissivity of a black body?
    A. 0 B. 1 C. 0.5 D.0.25
19. What is the absorptive of a black body?
    A. 0 B. 1 C. 0.5 D. 0.25
20. Above Curie point
    A. A ferromagnetic material becomes paramagnetic **B**. A ferrite becomes an insulator **C.** A insulating material becomes a ferrite **D**. A diamagnetic material becomes a paramagnetic material

PART-B (3×2=6 Marks)

Answer all the questions

21. Write a note on liquid helium.
22. Give a note on black body radiation.
23. Discuss about the electron gas in metals

PART-C (3×8=24 Marks)

Answer all the questions

24. A) Derive an expression for Bose Einstein distribution law of energies in the range E to E+dE.

(OR)

B) Give a note on specific heat of solids

25. A) Obtain Planck's law from B.E. distribution law

(OR)

B) Explain the limiting case of Bose-Einstein statistics

26. A) At what temperature will the average speed of H_2 molecules be the same as that of N_2 molecules at 35^oC? Given: molar mass of H_2 molecules = 2 x 10^{-3} kg/ mol, molar mass of N_2 molecules = 28 x 10^{-3} kg/mol.

(OR)

B) Find the Fermi level at absolute zero for copper. Given that: molar mass of copper M = 63.55 X 10^{-3} kg/mol, its density = 8.93 X 10^3 kg/m^3, avogadro's number = 6.023 X 10^{23} /mol, h = 6.63 X 10^{-34}Js.

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    C. **1901** D. 1921
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17. The value of b is given by
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    A. **A ferromagnetic material becomes paramagnetic** **B**. A ferrite becomes an insulator **C.** A insulating material becomes a ferrite **D**. A diamagnetic material becomes a paramagnetic material

PART-B (3×2=6 Marks)

Answer all the questions

21. Write a note on liquid helium.
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 $_2He^4$. 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 gm / 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 at least 23 atm.

(iii) For He^1 in liquid phase there is another phase transition called λ 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 λ and this peculiar transition is called λ transition and the discontinuity temp. 2.186 K is called λ point. Kesson concluded that transition He I → He II at T_λ is second order transition. The transition temp. decreases as the pressure is increased.

22. Give a note on black body radiation.

Black Body Radiation:

A body which completely absorbs radiation of all wavelength incident on 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.

23. Discuss about the electron gas in metals.

Electron Gas

A metal can be considered to be composed of a system of fixed positive nuclei and a no. of mobile electrons referred to us the electron gas.

To study the properties of an electron gas at low temperature in the region. For electrons

s=1/2 so $g_z = 2s+1 = 2$.

$$\varepsilon_f = h^2/2m \left(\frac{3n}{4\pi . V . 2}\right)^{2/3}$$

$$= h^2/8m \left(\frac{3n}{\pi . 2}\right)^{2/3} \qquad \text{----- (1)}$$

$$E_a = 3/5\ n\ \varepsilon_f \qquad \text{----------- (2)}$$

In the limit T → 0

Which means that in the limit every one of the states is occupied fully up to the energy level ε_f whereas all the states above this energy level are empty. For electrons m = 9.1 x 10^{-28}gm, and g =2.

$$\frac{1}{D} = \frac{h^2}{2\ x\ 9.1\ x\ 10^{-28}\ kT}\left(\frac{3n}{8\pi V}\right)^{2/3}$$

A typical metal atomic weight 100 and density 10 so that the volume of gm. atom of 10cc. and the number of electrons assuming one free electron from atom is 6.02 x 10^{23}. Then

$$\frac{1}{D} = \frac{(6.62\ x\ 10^{-27})^2}{2\ x\ 9.1\ x\ 10^{-28}\ x\ 1.38\ x\ 10^{-18}\ x\ T}\left(\frac{3x\ 6.02\ x\ 10^{23}}{8\ x\ 3.14\ x\ 10}\right)^{2/3}$$

$$= 10^5 / 1.5T$$

Which means degeneracy is sufficiently high. It shows clearly that for electron gas, a classical statistics is not valid and can be applied only at temperature of the order of 10 ^{5}K. Therefore at low and other ordinary working temperatures, it is necessary to use Fermi- Dirac statistics to study the electron gas in the metals. At low temperature electronic contribution to the specific heat of metals is given by the equ.

$$C_v = \frac{1}{2}\, nk\, \pi^2 \,(kT/\, \varepsilon_f)$$

$$D = (kT/\, \varepsilon_f)$$

$$C_v = \frac{1}{2}\, nk\, \pi^2\, D$$

Using this value find the value of 1/D,

$$C_v = \frac{1}{2}\, nk\, \pi^2 \text{ x } 1.5 \text{ x } 10^{-5} \text{ x } T$$

$$\text{Sub. } nk = R$$

$$= 1.987 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$= 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$$

$$\pi^2 = 10$$

$$C_v = \frac{1}{2} \text{ x } 1.5 \text{ x } 10^{-5} \text{ x } 2 \text{ x } 10 \text{ x } T$$

$$= 1.5 \text{ x } 10^{-4} \text{ x } T \text{ cal/gm. atom}$$

Pressure of the electron gas can be obtained by,

$$P_o = \frac{2}{5}\,\frac{n\varepsilon_f}{V}$$

$$= \frac{2}{5V}\,\frac{h^2}{2m}\left(\frac{3n}{4\pi V g_s}\right)^{2/3}$$

$$= \frac{nh^2}{20mV}\left(\frac{3n}{\pi V}\right)^{2/3} \text{ using } g_s = 2$$

For a metal of atomic weight 100 and density 10

$$P_o \sim 10^5 \text{ atoms}$$

Which means at normal temperature the pressure of gas is sufficiently high.

PART-C (3×8=24 Marks)

Answer all the questions

24. A) Derive an expression for Bose Einstein distribution law of 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

$$n(E)\,dE = f(E)\,g(E)\,dE \qquad \text{---------------}\ (1)$$

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

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

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

Substituting this equ. in (2)

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

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

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

(i) if e^{α} is <1, then for E = 0

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

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

$$\text{which is impossible.}$$

(ii) if e^{α} = 1, then for E = 0

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

Which is also impossible. Therefore e^{α} must be greater than 1.

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

The B-E distribution is given by

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

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

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

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

$$= \frac{2\pi N}{(\pi kT)3/2} E^{1/2}\,e^{-E/kT}\,dE$$

The condition for this is that

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

$$\text{i.e. } \frac{A}{eE/kT}\,e^{E/kT} << 1$$

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

$$A<<1.$$

B) Give a note on 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 specific heat 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 equipartition of energy 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.

$$\text{Energy per mole} = 3kTN_A$$

k= Boltzmann's constant
T= Temperature in Kelvins
N_A= Avogadro's number

The Law of Dulong & Petit

$$C_V = \frac{\partial}{\partial T}(3kTN_A) = 3kN_A / mole = 24.94 J / mole\ K$$

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 hν where h is the Planck's constant and ν 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 ν giving god fit for a particular solid is represented by ν_E and is called **Einstein's Frequency for that solid.** θ corresponding to ν_E is represented as θ_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:

(i) 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, hν/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.

(ii) When the value of temperature tends to zero, hν/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 ν. At corresponding temperatures, such that the value of the ratio ν/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

$$E_{oscillators} = \frac{3h\upsilon N_A}{e^{h\upsilon/kT} - 1} mole^{-1}$$

In the Einstein treatment, the appropriate frequency in the expression had to be determined empirically by comparison with experiment for each element. The quantity hν/k is sometimes called the Einstein temperature. Although the general match with experiment was reasonable, it was not exact.

$$C_V = \frac{\partial E}{\partial T} = \frac{3N_A k \left(\frac{h\upsilon}{kT}\right)^2 e^{h\upsilon/kT}}{\left(e^{h\upsilon/kT} - 1\right)^2} mole^{-1}$$

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 quantum behavior showed why the specific heat became temperature dependent at low temperatures, and it had a high temperature limit which agreed with the Law of Dulong and Petit. To show this, note that for high temperatures, a series expansion of the exponential gives

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

The Einstein specific heat expression then becomes

$$C_V = \frac{\partial E}{\partial T} = \frac{3N_A k \left(\frac{h\upsilon}{kT}\right)^2 \left(1 + \frac{h\upsilon}{kT}\right)}{\left(\frac{h\upsilon}{kT}\right)^2} mole^{-1}$$

This reduces to the Law of Dulong and Petit.

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

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, ν and hν/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 ν and ν +dν.

25. A) Obtain Planck's law from B.E. distribution law

According to planck's radiation law the energy of radiation of wavelength in the range between λ and λ+dλ emitted per unit volume by a perfectly black body at absolute temperature T is given by U

$$(\lambda)d\,\lambda = \frac{8\pi hc}{\lambda^5}\,\frac{d\lambda}{e^{\frac{hc}{kT}} - 1}$$

Derivation of law

According to the Bose- Einstein distribution law the number of Bosons having energies between E and E+dE is

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

where g(E) dE is the number of quantum stage of energies E and E +dE.

Let T be the absolute temp. of a black body chamber of volume v. The chamber is supposed to be filled with photons each having energy hν .They move in all possible directions with the speed of light C. Each photon has unit spin angular momentum equal to h(h/2π).Hence photons are bosons and use B.E distribution law to derive Planck's law of radiation.

1. *Constant α*:

Photons of different energies are absorbed and re-emitted by the walls of the chamber at constant temp.

In this process a higher energy photon is converted into a number of low energy photons and vice-versa. Though the total energy of the photons remain constant, the total no of photons present in enclosure is not constant. Therefore the condition $\sum_r n_r$ = N or $\sum_r dn_r$ = 0 is not applicable for the distribution and hence the multiplier α is zero, i.e $e^{-\alpha}$ is equal to 1.

2. *Expression for g(E)dE:*

The number of quantum states corresponding to the momenta in the range between p and p+dp for particles with no spin is given by

$$g(p)\, dp = \frac{4\pi V p^2 dp}{h^3}$$

each photon has unit spin angular momentum, there are two allowed quantum states for each photon. Hence photons of the same energy can have the two different directions of polarization circularly clockwise and circularly anti-clockwise. Taking the spin in two account for photonswe have

$$g(p)\, dp = \frac{2 x\, 4\pi V p^2 dp}{h^3}$$

$$= \frac{8\pi V p^2 dp}{h^3} \quad \text{---------} (2)$$

For photons of frequency ν.

Energy, $E = mc^2 = h\nu$ and momentum $p = mc = mc^2/2 = h\nu/c$

By sub these values in equ. (2), $g(\nu)\, d\nu = \frac{8\pi V \nu^2 d\nu}{C^3}$ -------- (3)

Sub. the values of α and g(E) dE in eq. (1)

$$n(\nu)\, d\nu = n\,(E)dE$$

$$= \frac{8\pi V}{c^3}\ \nu^2\, d\nu / e^{h\nu/kT} - 1 \qquad \text{--------}\ (4)$$

This equ. Gives the number of photons of frequencies between ν and ν + dν in the enclosure of volume v at temp T.

Now the energy per unit volume of the enclosure,of the photons of frequencies between ν and ν + dν is

$$U(\nu)d\,\nu = \frac{h\nu n(\nu)d\nu}{\nu}$$

$$== \frac{8\pi h}{c^3}\nu^3\ \ d\nu/e^{h\nu/kT} - 1 \qquad \text{------------------}(5)$$

This is this the plancks law of radiation in terms of frequency ν

*Eq*n(5) can be transformed in terms of the wavelength λ by using the relations

$$\nu = \frac{c}{\lambda},\ d\nu = -\frac{c}{\lambda^2}d\lambda$$

The energy u(ν)d ν contained in a frequency interval between ν and ν + dν is equal to the contained in a corresponding wavelength interval b/n λ and λ+ d λ.

$$U(\lambda)d\,\lambda = u(\nu)d\nu$$

$$= \frac{8\pi h}{c^3}\,\frac{\left(\frac{c}{\lambda}\right)3\left(-\frac{c}{\lambda^2}d\lambda\right)}{eh\nu/kT - 1}$$

Omitting the negative sign we get,

$$U(\lambda)d\,\lambda = \frac{8\pi hc}{\lambda^5}\,d\lambda\ /\ e^{h\nu/kT} - 1 \quad \text{--------------------------------}\ (6)$$

This is the planck’s law of radiation in terms of wavelength λ

B) Explain the limiting case of Bose-Einstein statistics

Limiting Case of Bose-Einstein Statistics:

For an ideal Bose-Einstein distribution the degeneracy parameter A(=e^{α})cannot be greater than 1;its maximum value can be 1.If the temperature of the gas is decreased, the value of A increases from a low value towards 1.At a certain temperature T_B, the value of A becomes just less than 1,and then there is no change in the value below T_B .At T_B some proportion of the molecules start reaching the zero-energy state. This critical temperature is called the Bose temperature.

Expression for the Bose Temperature:

In the ideal Bose-Einstein gas of spinless molecules in the thermal equilibrium at the temperature T, the tot al number of N molecules is given by

$$N= 2\pi V\left(\frac{2mkT}{h^2}\right)^{3/2}\int_0^{2} \frac{x^{1/2}}{e^{\alpha}e^{x}-1}\,dx$$

Where

x=E/kT

The value of integral

$$N= 2\pi V\left(\frac{2mkT}{h^2}\right)^{3/2}\frac{\sqrt{\pi}}{2}\left[\frac{1}{e^{\alpha}}+\frac{1}{2^{\frac{3}{2}}e^{2\alpha}}+\frac{1}{3^{\frac{3}{2}}e^{3\alpha}}+\ \dots\dots\right]$$

Substituting the value $e^{1/A} = e^{-\alpha} = A$

$$N= V\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\left[\frac{A}{1}+\frac{A^2}{2^{\frac{3}{2}}}+\frac{A^3}{3^{\frac{3}{2}}}+\ \dots\dots\right]$$

At Bose Temperature $T=T_B$,

$$N=V\left(\frac{2\pi mkTB}{h^2}\right)^{3/2}\left[1+\frac{1}{2^{\frac{3}{2}}}+\frac{1}{3^{\frac{3}{2}}}+\ \dots\dots\right]$$

The series in the square bracket is the Riemann Zeta function whose value is 2.612.

$$N=V\left(\frac{2\pi mkTB}{h^2}\right)^{3/2}\ \text{x}\ 2.612$$

$$=2.612\ V(\frac{2\pi m\ kTB}{h^2})^{3/2} \qquad \text{--------(1)}$$

Where

$$T_B=(\frac{h^2}{2\pi mk})\ (N / 2.612\ V)^{3/2} \qquad \text{---------(2)}$$

For all known Bose-Einstein gas, the Bose temperature T_B is very low. For ex, for helium $({}_2He^4)T_B= 3.15$ K

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

$$N_e=N- n_0 \qquad \text{-------------------- (3)}$$

The zero –energy state occupation number is given by

$$n_0=\frac{g0}{\frac{1}{A}-1} \qquad \text{-------------------- (4)}$$

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

N_e is given by,$N_e=2.612V(\frac{2\pi mKT}{h2})^{3/2}$ -------------------- (5)

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

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

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

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

where $T<T_B$

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

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

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 at T_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 $_2He^4$-I to superfluid liquid $_2He^4$-II at the observed temperature 2.18K can be expanded by Bose- Einstein condensation process.

25. A) At what temperature will the average speed of H_2 molecules be the same as that of N_2 molecules at 35°C? Given: molar mass of H_2 molecules = 2 x 10^{-3} kg/ mol, molar mass of N_2 molecules = 28 x 10^{-3} kg/mol.

$$V_P = \sqrt{\frac{2KT}{m}}$$

$$= \sqrt{\frac{2*8.314*300T}{28}}$$

= 4.26x10^2 m/sec

$$V = \sqrt{\frac{8KT}{3.14*m}}$$

$$= \sqrt{\frac{8*8.314*300}{3.14*28}}$$

= 4.766 x 10^2 m/s

$$V_{rms} = \sqrt{\frac{3KT}{m}}$$

$$= \sqrt{\frac{3*8.314*300}{28}}$$

= 5.67 x 10^2 m/sec

temperature

$$V_T = \sqrt{\frac{8KT}{3.14*m}}$$

T= 273+35

= 308

$$V_{308} = \sqrt{\frac{3*8.314*308}{3.14*28}}$$

= 22 K

B) Find the Fermi level at absolute zero for copper. Given that: molar mass of copper M = 63.55 X 10^{-3} kg/mol, its density = 8.93 X 10^{3} kg/m^{3}, avogadro's number = 6.023 X 10^{23} /mol, h = 6.63 X 10^{-34}Js.

$$u = (3k\,N\,T / M)^{1/2}$$

$$= (3\,R\,T / M)^{1/2}$$

$$= (3*8.3145*310 / 0.002)^{1/2}$$

$$= 1966 \text{ m/s}$$

Note that the molecular mass of hydrogen is 0.002 kg/mol. These units are used because the constant *R* has been calculated using the SI units. The calculation for other gases is accomplished using their molar mass in kg.

$$u = (3k\,N\,T / M)^{1/2}$$

$$= (3\,R\,T / M)^{1/2}$$

$$= (3*8.3145*310)^{1/2}/M^{1/2}$$

$$= 87.9345/M^{1/2} \text{ m/s}$$