KUNTHAVAI NAACHIYAAR GOVT. ARTS OLLEGE FOR WOMEN (AUTONOMOUS), THANJAVUR – 7.

DEPARTMENT OF PHYSICS

M. SC PHYSICS - STUDY MATERIAL

SUB. CODE: 18KP1P03

SUB. TITLE: STATISTICAL MECHANICS

UNIT I
THERMODYNAMICS

THERMODYNAMICS

Thermodynamics is the branch of physics that deals with the relationships between heat and other forms of energy. In particular, it describes how thermal energy is converted to and from other forms of energy and how it affects matter.

Thermal energy is the energy a substance or system has due to its temperature, i.e., the energy of moving or vibrating molecules.

Heat

Heat is another mode by which a system can exchange with the surroundings. Wherever a temperature difference exists between the system and surroundings heat either flows in or out of the system. It is not a state function because the quantity of heat involved in a process depends upon the path. Heat like work is an **extensive property**.

It is not a property of system or surroundings. Heat as such cannot be measured at all, but the effects which it produces are measured. It was formerly measured by the increase in temperature of water. The amount of heat required to raise the temperature of 1 g of water by 1°C becomes a unit of heat, the **Calorie**.

In modern practice, it is defined in terms of **Joule**. Because **Joule**, in 1850, showed that there is a definite relationship between mechanical work done (w) and heat produced (H). i.e.

$$w \propto H$$
$$w = JH$$

'J' is known as mechanical equivalent of heat. Its numerical value is taken as 4.185×10^{-7} ergs = 4.185 Joules.

Heat is an algebraic quantity and the convention used for heat is q. A + q shows that heat is added to the system and a – q means that the system has lost the heat.

Work

Mechanical work is done whenever there is a change (increase or decrease) in the volume of the system i.e. expansion or compression of a gas.
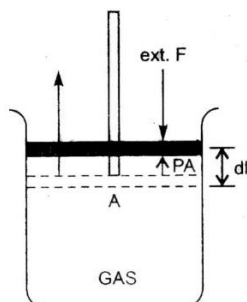
This is known as **Pressure volume work or PV work or Expansion work.**

Consider a gas enclosed in a cyclinder provided with a piston. If P is the pressure of the gas, it exerts a force F on the piston given by:

$$F = PA$$

where A is area of cross-section of the piston. This force can be balanced by an equal force, Fem acting on the piston, (fig). If there is an infinitesimally small movement of the piston (dl) outward, the small amount of work done (dw) by the gas (system) on the surroundings will be given by,

$$dw = F \times dl$$
$$= P \times A \times dl$$
$$P \times dV \,(\because dV = A \times dl)$$

where dV is the small increase in volume of gas that has taken place in the process. This process of expansion may be carried out in infinitesimally slowly (i.e. in a thermodynamic reversible) manner in a series of steps. The work done in each step will be given by PdV.

If, ultimately, the volume of the system changes by a finite quantity, say, from $V_1 to V_2$ then the total work (w) done by the system on the surroundings will be obtained by the integration of the factor PdV. i.e.

$$w = \int_{V_1}^{V_2} PdV$$

where P is a variable factor.

On the other hand, if there is infinitesimal contraction of the gas resulting from infinitesimal movement of the piston inward, then the small amount of work done by the surroundings on the system will be given by:

$$dw = PdV$$

where 'dV' is the decrease in volume of the gas that has taken place in the process. If the work of contraction is carried out in the above manner in a series of steps, the work done (w) by the surroundings on the system is given by integration of the factor PdV. i.e.

$$\int_{V_2}^{V_1} PdV$$

When the volume of the system decreases from $V_1 to V_2$.

Work done at constant pressure

If the-pressure P remains constant throughout the process, the above integration gives

$$w = P(V_2 - V_1)$$
$$\text{i.e. } w = P\Delta V$$

where V_1 is the volume of the system in the initial state,. Then ΔV, evidently, is the change in volume of the system. Thus,

If ΔV is positive i.e. the gas expands in the process, w will have a positive value. The work, in this case, is done by the system on the surroundings.

If ΔV is negative i.e. the gas undergoes contraction, w will have a negative value. The work, in this case, is done by the surroundings on the system.

Work done at constant volume

If the volume is constant, $dV = 0$, then $w = 0$

Maximum work

Suppose the pressure applied on the piston is negligibly small in comparison with the pressure of the gas inside the cylinder, the gas will then expand rapidly i.e. irreversibly. In this case, the work done by the system will be negligibly small since the opposing force has been negligibly small.

If the opposing pressure on the piston is zero, the work done by the system will be zero. $PdV = 0$

Hence, it follows that when a gas expands freely (free expansion) i.e. when it expands against vacuum such that $P = 0$, no work is done by the system.

It also follows from the above discussion that the magnitude of work done by a system on expansion depends upon the magnitude of the opposing (external) pressure. The close is the opposing pressure to the gaseous system in the cylinder, the greater will be the work performed by it on expansion.

In other words, maximum work is obtained when the two opposing pressures differ only by an infinitesimally small amount from one another.

This condition, evidently, is demanded for an ideal reversible process. Hence the condition for maximum work coincides with that for thermodynamic reversibility.

Temperature

The amount of heat transferred by a substance depends on the speed and number of atoms or molecules in motion. The faster the atoms or molecules move, the higher the temperature, and the more atoms or molecules that are in motion, the greater the quantity of heat they transfer.

Temperature is "a measure of the average kinetic energy of the particles in a sample of matter, expressed in terms of units or degrees designated on a standard scale," Scientists worldwide, however, use the Kelvin (K with no degree sign) scale, named after William Thomson, 1st Baron Kelvin.

Kelvin scale starts at absolute zero, the temperature at which there is a total absence of heat energy and all molecular motion stops. A temperature of 0 K is equal to minus 459.67 F or minus 273.15 C.

Specific heat

The amount of heat required to increase the temperature of a certain mass of a substance by a certain amount is called specific heat, or specific heat capacity. The conventional unit for this is calories per gram per kelvin. The calorie is defined as the amount of heat energy required to raise the temperature of 1 gram of water at 4 C by 1 degree. The specific heat of a metal depends almost entirely on the number of atoms in the sample, not its mass.

Heat Capacity of gases

Specific and molar heat capacity of gases

Specific heat (or heat capacity) of a substance may be defined as the quantity of heat required to raise the temperature of 1 g of that substance by 1^0C. it is expressed in calories or joules. Molar heat capacity may be defined as :

Molar heat capacity = Sp. Heat × Mol. Mass

Since the gases expand on heating, hence molar heat capacity of gases is termed as follows:

(i) **Molar heat capacity at constant pressure (Cp):** it is the amount of heat in calories required to raise the temperature of one mole of a gas through 1^0C at constant pressure, while the volume is allowed to increase.

(ii) **Molar heat capacity at constant volume (Cv):** it is the amount of heat in calories required to raise the temperature of one mole of a gas through 1^0C at constant volume, while the pressure is allowed to increase.

With the help of kinetic gas euation it is calculated that,

$$Cv = \frac{3}{2}R$$ (for mono atomic gas)

And Cp – Cv = R

or, $$Cp = R + Cv = R + \frac{3}{2}R$$

or, $$Cp = \frac{5}{2}R$$

C_P/C_V = (5/2) R / (3/2) R = 1.66

It means that ratio of Cp and Cv is equal to 1.66 for mono atomic gases.

Heat transfer

Heat can be transferred from one body to another or between a body and the environment by three different means: conduction, convection and radiation.

Conduction is the transfer of energy through a solid material. Conduction between bodies occurs when they are in direct contact, and molecules transfer their energy across the interface.

Convection is the transfer of heat to or from a fluid medium. Molecules in a gas or liquid in contact with a solid body transmit or absorb heat to or from that body and then move away, allowing other molecules to move into place and repeat the process.

Radiation is the emission of electromagnetic (EM) energy, particularly infrared photons that carry heat energy. All matter emits and absorbs some EM radiation, the net amount of which determines whether this causes a loss or gain in heat.

Zeroth law of Thermodynamics:

When a body 'A' is in thermal equilibrium with another body 'b', and also separately in thermal equilibrium with a body 'C', then body 'B' and 'C' will also be in thermal equilibrium with each other. This statement defines the zeroth law of thermodynamics. The law is based on temperature measurement. In simple terms, it can be said, "Systems that are in thermal equilibrium exist at the same temperature".

Concept of heat:

Heat is energy in transit. We cannot consider work or heat in a body. Work is done by or on the body. Heat can flow from or into a body. If a body is at constant temperature it has both mechanical and thermal energies. It is not possible to separate them. If flow of heat stops heat cannot be considered. It is only used when there is transfer of energy.

Heat Content or Enthalpy

When the change of state of a system is brought about at constant pressure, there will be a change in volume. The *heat* transferred such a process is known as *heat content* or enthalpy and is denoted by H.

It may be defined as:

H = E + PV

Where E is an internal energy. P and V are the pressure and volume of the system respectively.

Heat change at constant pressure may be expressed as:

$$\Delta H = \Delta E + P\Delta V$$

$$= \Delta E + \Delta nRT$$

Where, ΔH = Heat of reaction at constant pressure

ΔE = Change in internal energy

Δn = No. of moles of gaseous reactants

R = Gas constant

T = Absolute temperature

If $\Delta H_1 and \Delta H_2$ are the heat of reaction at the temperatures $T_1 and T_2$ respectively, then

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

Where $\Delta C_{P=}$ Molar heat capacity of products — molar heat capacity of reactants at constant pressure. Similarly, if $\Delta E_1 and \Delta E_2$ are the change in internal

$$\Delta C_v = \frac{\Delta E_2 - \Delta E_1}{T_2 - T_1}$$

Where ΔC_c is the difference in the heat capacities of the products and reactants at constant volume.

These relations of ΔC_P and are ΔC_V are known as Kirchhoff's equations.

Enthalpy [Heat content]

Let the change of state of a system be brought about at constant pressure. In such a case, there will be a change of volume. Let the volume increase from V_A to V_B at constant pressure 'P'.

Then the work done (w) by the system will be:

$$w = P(V_B - V_A)$$

Substituting the value of w from equation, we get:

$$dE = q - P(V_B - V_A)V$$

$$E_B - E_A = dE = q - P(V_B - V_A) \cdots (2)$$

$$\text{or} (E_B + PV_B) - (E_A + PV_A) = q \cdots (3)$$

This quantity E + PV is known as Heat content or Enthalpy of the system and is denoted by H.

Thus, H = E + PV

Since E, P and V are definite properties, it follows that 'H' is also a definite property depending upon the state of the system.

Using the value in equation (3), we get

$$H_B - H_A = \Delta H = q$$

So, that the increase of the heat content of a system is equal to the heat absorbed at constant pressure. Substituting the value of AH for q in equation (3), we get

$$E_B - V_A = \Delta H - P(V_B - V_A)$$

$$or \, \Delta H = (E_B - E_A) + P(V_B - V_A)$$

$$or \, \Delta H = \Delta E + P.\Delta V$$

i.e. The change in heat content or enthalpy at constant pressure is equal to the sum of the increase in internal energy and mechanical work of the expansion.

The equation (4) may also be written as :

$$\Delta H = \Delta E + \Delta n RT$$

Where Δn = Difference in no. of moles of gaseous products and reactants

R = gas constant and

T = Temperature in Kelvin.

It is clear that if $\Delta n = 0, \Delta H = \Delta E; \Delta n > O, \Delta H > \Delta E$ and $\Delta n 0, \Delta H \Delta E$

Heat change at constant pressure and constant volume

If the change of state is brought about at constant volume, then no mechanical work is done by the system i.e w = 0. Under such conditions,

$$dE = q$$

i.e. the whole of the heat absorbed by a system at constant volume is utilised to increase the internal energy.

If the change is brought about adiabatically so that system is neither in a position to gain nor to lose heat then q = 0. Under such conditions,

$$-dE = w$$

(Decrease in internal energy in an abiabatic system is equal to the work done by the system).

Internal Energy of a System

Each substance is associated with a certain amount of energy which depends on its chemical nature, temperature, volume, pressure etc. Thus **internal energy** of the system is simply the sum of all types of energies associated with the substance in the system. It is denoted by E or U.

$E = E_T + E_K + E_P$......

$E_T \rightarrow$ Transitional energy

$E_K \rightarrow$ Kinetic energy

$E_V \rightarrow$ irrational energy

$E_N \rightarrow$ Nuclear energy

$E_P \rightarrow$ Potential energy

The exact measurement of *internal energy* is not possible so it is measured in terms of Internal energy change. Only change in its value can be measured. i.e. ΔE or ΔU

It depends only upon Temperature (for Ideal gas) Internal energy E' is a state function hence ΔE does not depend upon path or way of process or it depends upon initial and final states only.

For path I: Internal energy change is ΔE_1

For path II: ΔE_2 i.e.
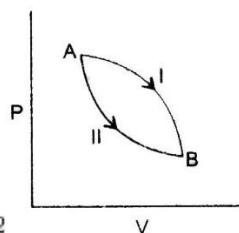
Here $\Delta E_1 = \Delta E_2$

Internal energy

- It is an extensive property.
- Δ is measured by using Bomb Calorimeter as follow

$$\Delta E = C \times \delta T \times \frac{M}{m}$$

M = molar mass; m = Mass of substance; C = Heat capacity of calorimeter; ΔT = Rise in temperature

If the state of the system is changed by supplying heat Q to the system and if W is the work done by the system during the change then increase in the internal energy of the system is

$$U2 - U1 = Q - W$$

First law of thermodynamics

When a certain amount of heat Q is supplied to a system which does external work W in passing from one state to other, the amount of heat is equal to sum of the increase in the internal energy of the system and the external work done by the system.

$$Q = (U2 - U1) + W$$

For a very small change $\delta Q = \delta U + \delta W$

This law establishes an exact relation between heat and work, which means that it is impossible to get work from any machine without giving it an equivalent amount of energy in any form.

The first law of thermodynamics states that the energy of the universe remains constant, though energy can be exchanged between system and surroundings, it can't be created or destroyed.

Here no information about how much heat is converted into work and whether the transformation itself can takes place or not. The law which specifies the condition of transformation is second law.

First law of thermodynamics (Law of conservation of energy)

The first law of thermodynamics is simply a statement of the principle of conservation of energy. This law was first enunciated by **J**ulius Robert Mayer (1842) and this great concept was first explained by Helmholtz in 1847. This law states that:

'The energy of an isolated system remains constant, although it may be changed from one form to the other'. Or Energy can neither be created nor destroyed but can be converted from one form to another form.

Thus the heat supplied to a system is never lost but is partly converted into internal energy and partly in doing work by the system.

In other words,

∴ Heat supplied = Work done by the system + Increase in internal energy

∴ Increase in internal energy = Heat supplied – Work done by the system

This statement can be mathematically represented as:

dE = q – w

Where dE is the increase in internal energy in the system, q is the heat supplied and w is the work done by system.

Explanation:

Consider a system represented by a state A in the figure. Suppose the conditions are now altered so that the system moves to B by the path I and then brought back to the state A by a different path II. As a consequence of **first law of thermodynamics** the total energy change at A is nil.
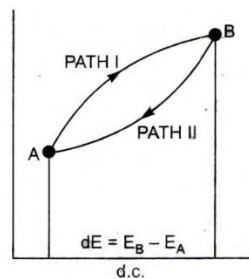
Internal energy as a function of state

If it is imagined that the energy involved in path I is greater than in the returning path II, then certain amount of energy would have increased in the system on its own accord. This is against the first law of thermodynamics and so it must be concluded that the net energy change of a system will depend on the initial and final states but not on the path followed. Let E A represents the energy in the state A and EB in the state B, the increase in energy on passing from A to B may be given by:

$$dE = \Delta E = E_B - E_A$$

which is independent of the path taken. The quantity is called the internal or intrinsic energy. When a system changes from one state to another it may lose or gain energy as heat and work. Suppose the heat absorbed by a system is Q. If in a change from A to B the energy constant of the system is increased by AE, the work done being W, then according to first law:

$$\Delta E = Q - W$$

The above equation is a form of *first law of thermodynamics.* Thus the difference between heat absorbed and the total work done by the system is equal to the increase in the energy content.

For infinitesimal change, the above equation may be put as:

dE = dQ – dW

or dE = q – w

where dE is the small increase in energy and q and w represent small quantities of heat absorbed and external work done by the system, respectively.

If as a result of a series of processes the system returns to its original state then its energy content remains unchanged so that ΔE must be zero. In such a case, it is evident that work done is equal to heat absorbed in the process. i.e.

$$q = w$$

This equation is an expression of the impossibility of perpetual motion of the first kind i.e. creation of energy out of nothing. This law has following limitations:

(i)   Why heat cannot be completely converted into work.

(ii)   It does not explain the spontaneity of the process.

(iii)   It puts no restriction about direction flow of heat.

Points to remember:

'q' is positive : If heat is absorbed by the system.

'q' is negative : If heat is evolved by the system.

'w' is positive: If work is done on the system.

'w' is negative: If work is done by the system.

For adiabatic process, q = 0, $\therefore w = -\Delta E$

For isothermal and cyclic processes, $\Delta E = 0, \therefore q = w$

For isochoric process, $qv = \Delta E$

Second law of thermodynamics

Kelvin statement: It is impossible to get a continuous supply of work by cooling a body to a temperature lower than its surroundings.

Clausius statement: it is impossible for a self acting machine unaided by any external agency to transfer heat from one body to another at a higher temperature.

Entropy and Second law of thermodynamics

Entropy is a definite 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

$$S_B - S_A = \int dQ/T \quad dQ\text{-heat absorbed/rejected at temp T}$$

It is noted that entropy remains constant during an adiabatic change, in all reversible processes and increases in all irreversible processes.

It is seen that entropy of the system in final state is greater than initial state. Though both the states are identical in energy point of view, entropy of the states is different.

Thus, entropy characterises the direction of a thermodynamical process. That is all the thermodynamical processes takes place in such a direction that the entropy of the system remains constant or increases.

Second law of thermodynamics also stands for same and therefore it can be stated that

A natural process that starts in one equilibrium state and ends in another will go in the direction that causes the entropy of the system plus environment to increase.

If the two states are very much closer then,

$$dS = dQ/T \text{ or } dQ = TdS$$

Entropy is a measure of disorder: solid, liquid and gas

Statistical definition of entropy:

The equilibrium state is the state of maximum entropy thermodynamically and most probable statistically.

The disorder of a system may be calculated by the theory of probability and expressed by a quantity ω known as thermodynamical probability.

The relation between entropy and probability is $S = k \log \omega$

Where k is Boltzmann constant

For entropy on the other hand, the fact that the heat capacity goes to zero as the temperature decreases has important consequences. Consider the change in the entropy of a pure substance whose heat capacity approaches some finite limiting value as its temperature decreases to absolute zero. For such a substance, C_P/T becomes arbitrarily large as the temperature decreases, and the entropy integral approaches minus infinity as the temperature approaches zero. For real substances, this does not occur. In the neighbourhood of absolute zero, heat capacities decrease more rapidly than temperature. The entropy change approaches zero as the temperature approaches zero.

The idea that the entropy change for a pure substance goes to zero as the temperature goes to zero finds expression as the third law of thermodynamics.

If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a positive finite entropy; but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.

Implicitly, the Lewis and Randall statement defines the entropy of any substance, at any temperature, T, to be the difference between the entropy of the constituent elements, at absolute zero, and the entropy of the substance at temperature T. Equivalently, we can say that it is the entropy change when the substance is formed at temperature T from its constituent elements at absolute zero. Arbitrarily, but very conveniently, the statement sets the entropy of an element to zero at absolute zero.

The distinction between perfect crystalline substances and less-than-perfect crystalline substances lies in the regularity of the arrangement of the molecules within the crystal lattice. In any lattice, each molecule of the substance is localized at a specific site in the lattice. In a perfect crystal, all of the molecules are in oriented the same way with respect to the lattice. Some substances form crystals in which the molecules are not all oriented the same way. This can happen when the molecule can fit into a lattice site of the same shape in more than one way.

One important consequence of Botlzmann's proposal is that a perfectly ordered crystal (i.e. one that has only one energetic arrangement in its lowest energy state) will have an entropy of 0. This makes entropy qualitatively different than other thermodynamic functions. For example, in the case of enthalpy, it is impossible have a zero to the scale without setting an arbitrary reference (which is that the enthalpy of formation of elements in their standard states is zero.) But entropy has a natural zero! It is the state at which a system has perfect order. This also has another important consequence, in that it suggests that there must also be a zero to the temperature scale. These consequences are summed up in the **Third Law of Thermodynamics**. The entropy of a perfectly ordered crystal at 0 K is zero. An entropy value determined in this manner is called a **Third Law Entropy**.

Naturally, the heat capacity will have some temperature dependence. It will also change abruptly if the substance undergoes a phase change. Unfortunately, it is exceedingly difficult to measure heat capacities very near zero K. Fortunately, many substances follow the **Debye Extrapolation** in that at very low temperatures, their heat capacities are proportional to T^3. Using this assumption, we have a temperature dependence model that allows us to extrapolate absolute zero based on the heat capacity measured at as low a temperature as can be found.

Physical significance of Entropy

The entropy of a substance is real physical quantity and is a definite function of the state of the body like pressure, temperature, volume of internal energy.

It is difficult to form a tangible conception of this quantity because it can not be felt like temperature or pressure. We can, however, readily infer it from the following aspects:

1. Entropy and unavailable energy

The second law of thermodynamics tells us that whole amount of internal energy of any substance is not convertible into useful work. A portion of this energy which is used for doing useful work is called **available energy**. The remaining part of the energy which cannot be converted into useful work is called **unavailable energy**. Entropy is a measure of this unavailable energy. In fact, the entropy may be regarded as the unavailable energy per unit temperature.

$$\text{Entropy} = \frac{\text{Unavailable energy}}{\text{Temperature}}$$

or, $$Unavailable \; energy \; = Entropy \times Temperature$$

The concept of entropy is of great -value and it provides the information regarding structural changes accompanying a given process.

2. **Entropy and disorder**

Entropy is a measure of the disorder or randomness in the system. When a gas expands into vacuum, water flows out of a reservoir, spontaneous chain reaction takes place, an increase in the disorder occurs and therefore entropy increases.
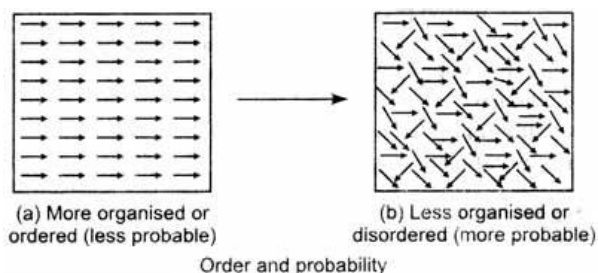
Similarly, when a substance is heated or cooled there is also a change in entropy. Thus increase in entropy implies a transition from on ordered to a less ordered state of affair.

3. Entropy and probability

Why is disorder favoured? This can be answered by considering an example, when a single coin is flipped, there is an equal chance that head or tail will show up. When two coins are flipped, there is a chance of two heads or two tails showing up but there are double chance of occurrence of one head and one tail. This shows that disorder is more frequent than order.

Changes in order are expressed quantitatively in terms of entropy change, ΔS. How are entropy and order in the system related? Since a disordered state is more probable for

systems than of order(see figure), the entropy and thermodynamic probabilities are closely related.

(a) More organised or ordered (less probable)   (b) Less organised or disordered (more probable)

Order and probability

Features of entropy:

(1) It is an extensive properly and a state function

(2) It's value depends upon mass of substance present in the system

(3) $\Delta S = S_{final} - S_{initial}$

(4) At equilibrium $\Delta S = zero$

(5) For a cyclic process $\Delta S = 0$

(6) For natural process $\Delta S > 0$ i.e Increasing.

(7) For a adiabatic process ΔS zero

Nernst's Heat Theorem

At the beginning of the twentieth century, Walther Nernst investigated heat capacities and heats of reaction at progressively lower temperatures. As a result of his studies, he enunciated an important principle that initially was restricted to the behaviour of reactions involving solids and liquids but which is now believed to apply to all processes and substances.

If any reaction takes place at constant pressure, the heat gained or lost is an increase or decrease in enthalpy H. The heat of reaction is usually given as ΔH, being positive for an endothermic reaction (in which the system gains heat) and negative for an exothermic reaction. It should be noted that spontaneous reactions are by no means always exothermic; some spontaneous reactions result in the absorption of heat from their surroundings and in a corresponding increase of enthalpy.

Nernst had noticed that, at progressively lower temperatures, the change in enthalpy and the change in the Gibbs function during a chemical reaction become more and more equal and the rate of change of the Gibbs function with temperature becomes less and less as the temperature is lowered. That this amounts to the same thing is evident from the Gibbs-Helmholtz relation.

$$\Delta H = \Delta G - T(\partial (\Delta G)/ \partial T)_P$$

Nernst proposed was that, in the limit, as the temperature approaches zero, the changes in the enthalpy and Gibbs function are equal – or, what amounts to the same thing, the temperature rate of change of the Gibbs function at constant pressure approaches zero at zero temperature. And since

$$(\partial (\Delta G)/ \partial T)_P = -\Delta S$$

this implies that chemical reactions at a temperature of absolute zero take place with no change of entropy. This is Nernst's Heat Theorem.

Planck later extended this to suppose that, not only does $\Delta G \rightarrow \Delta H$, but that, as , $T \rightarrow 0$ the enthalpy and the Gibbs function of the system approach each other asymptotically in such a manner that, in the limit, as $T \rightarrow 0$, $G \rightarrow H$ and $(\partial G / \partial T)_P \rightarrow 0$.

Thermodynamic Potentials (Chemical Potential)

It is a truth universally acknowledged that, if we add some heat reversibly to a closed thermodynamic system at constant volume, its internal energy will increase by $(\partial U/\partial S)_V$ dS or, if we allow it to expand without adding heat, its internal energy will increase by $(\partial U/\partial V)_S$ dV. (In most cases the derivative $(\partial U/\partial V)S$ is negative, so that an increase in volume results in a decrease of internal energy.) If we do both, the increase in internal energy will

$$dU = (\partial U/\partial S)_V \, dS + (\partial U/\partial V)S \, dV$$

By application of the first and second laws of thermodynamics, we find that this can be written

$$dU = TdS - PdV.$$

Likewise, it is a truism that, if we add some heat reversibly to a closed thermodynamic system at constant pressure, its enthalpy will increase by $(\partial H/\partial S)_P$ dS or, if we increase the pressure on it without adding heat, its enthalpy will increase by $(\partial H/\partial P)_S$ dP If we do both, the increase in internal energy will be

$$dH = (\partial H/\partial S)_P \, dS + (\partial H/\partial P)_S \, dP$$

By application of the first and second laws of thermodynamics, we find that this can be written

.$$dH = TdS + VdP$$

Likewise, it is a truism that, if we increase the temperature of a closed thermodynamic system at constant volume, its Helmholtz function will increase by $(\partial A/\partial T)_V \, dT$ or, if we allow it to expand at constant temperature, its Helmholtz function will increase by $(\partial A/\partial V)_T \, dV$ (In most cases both of the derivatives are negative, so that an increase in temperature at constant volume, or of volume at constant temperature, results in a decrease in the Helmholtz function.) If we do both, the increase in the Helmholtz function will be

$$dA = (\partial A/\partial T)_V \, dT + (\partial A/\partial V)_T \, dV$$

By application of the first and second laws of thermodynamics, we find that this can be written

.$$dA = - \, SdT - PdV$$

Likewise, it is a truism that, if we increase the temperature of a closed thermodynamic system at constant pressure, its Gibbs function will increase by $(\partial G/\partial T)_P \, dT$ (In most cases the derivative $(\partial G/\partial T)_P$ is negative, so that an increase in temperature at constant pressure results in a decrease in the Gibbs function.) If we increase the pressure on it at constant 8 temperature, its Gibbs function will increase by $(\partial G/\partial P)_T \, dP$ If we do both, the increase in Gibbs function will be

$$dG = (\partial G/\partial T)_P \, dT + (\partial G/\partial P)_T \, dP$$

By application of the first and second laws of thermodynamics, we find that this can be written

.$$dG = - \, SdT + VdP$$

However, we can increase any of these thermodynamical functions of a system without adding any heat to it or doing any work on it – merely by adding more matter. consider a system consisting of several components. Suppose that we add dN_i moles of component i to the system at constant temperature and pressure, by how much would the Gibbs function of the system increase? We might at first make the obvious reply: "dN_i times the molar Gibbs function of component i". This might be true if the component were entirely inert and did not interact in any way with the other components in the system. But it is possible that the added component might well interact with other components. It might, for example, shift the equilibrium position

of a reversible reaction $A + B \leftrightarrow C + D$. The best we can do, then, is to say merely that the increase in the (total) Gibbs function of the system would be $(\partial G/\partial N_i)_{T, P, N_j}\, dN_i$. Here, N_j refers to the number of moles of any component other than i.

In a similar manner, if dN_i moles of component were added at constant volume without adding any heat, the increase in the internal energy of the system would be be $(\partial U/\partial N_i)_{V, S, N_j}\, dN_i$. Or if dN_i moles of component were added at constant pressure without adding any heat, the increase in the enthalpy of the system would be be $(\partial H/\partial N_i)_{P, S, N_j}\, dN_i$ Or if dN_i moles of component were added at constant temperature and volume, the increase in the Helmholtz function of the system would be $(\partial A/\partial N_i)_{T, V, N_j}\, dN_i$. If we added a little bit more of all components at constant temperature and volume, the increase in the Helmholtz function would be $\sum(\partial A/\partial N_i)_{T, V, N_j}\, dN_i$, where the sum is over all components. Thus, if the system is not closed, and we have the possibility of adding or subtracting portions of one or more of the components, the formulas for the increases in the thermodynamic functions become

$$dU = (\partial U/\partial S)_V\, dS + (\partial U/\partial V)_S\, dV + \sum(\partial U/\partial N_i)_{V, S, N_j}\, dN_i$$

$$dH = (\partial H/\partial S)_P\, dS + (\partial H/\partial P)_S\, dP + \sum(\partial H/\partial N_i)_{S, P, N_j}\, dN_i$$

$$dA = (\partial A/\partial T)_V\, dT + (\partial A/\partial V)_T\, dV + \sum(\partial A/\partial N_i)_{T, V, N_j}\, dN_i$$

$$dG = (\partial G/\partial T)_P\, dT + (\partial G/\partial P)_T\, dP + \sum(\partial G/\partial N_i)_{T, P, N_j}\, dN_i$$

The quantity $(\partial U/\partial N_i)_{V, S, N_j}$ is same as $(\partial H/\partial N_i)_{S, P, N_j}$ or as $(\partial A/\partial N_i)_{T, V, N_j}$ or as $(\partial G/\partial N_i)_{T, P, N_j}$ and it is called the chemical potential of species i, and is usually given the symbol μ_i. Its SI units are J kmole^{-1}. If we make use of the symbol μ_i, and the other things and from application of the first and second laws,

$$dU = TdS - PdV + \sum\mu_i dN_i$$

$$dH = TdS + VdP + \sum\mu_i dN_i$$

$$dA = -\,SdT - PdV + \sum\mu_i dN_i$$

and . $dG = -\,SdT + VdP + \sum\mu_i dN_i$

It will be clear that

$(\partial U/\partial S)_{V, N_i} = T;$ $\qquad$ $(\partial U/\partial V)_{S, N_i} = -P;$ $\qquad$ $(\partial U/\partial N_i)_{V, S, N_i} = \mu_i$

$(\partial H/\partial S)_{P, N_i} = T;$ $\qquad$ $(\partial H/\partial P)_{S, N_i} = V;$ $\qquad$ $(\partial H/\partial N_i)_{P, S, N_i} = \mu_i$

$(\partial A/\partial T)_{V, N i} = -S;$ $(\partial A/\partial V)_{T, Ni} = -P;$ $(\partial A/\partial N_i)_{V, T, Ni} = \mu_i$

$(\partial G/\partial T)_{P, Ni} = -S;$ $(\partial G/\partial P)_{T, Ni} = V;$ $(\partial G/\partial N_i)_{P, T, Ni} = \mu_i$

Since the four thermodynamical functions are functions of state, their differentials are exact and their mixed second partial derivatives are equal. Consequently we have the following Maxwell relations:

$$(\partial T/\partial V)_{S, Ni} = -(\partial P/\partial S)_{V, N i}$$

$$(\partial T/\partial P)_{S, Ni} = +(\partial V/\partial S)_{P, N i}$$

$$(\partial S/\partial V)_{T, Ni} = +(\partial P/\partial T)_{V, N i}$$

$$(\partial S/\partial P)_{T, Ni} = -(\partial V/\partial T)_{P, N i}$$

UNIT II

KINETIC THEORY

MAXWELL-BOLTZMANN DISTRIBUTION

The distribution of molecular velocities in a gas, established first by Maxwell and later proved rigorously by Boltzmann, is given by a function F and is today known as the Maxwell-Boltzmann velocity distribution function. Since this probability function depends upon the specified velocity u, F = F(u) and is defined such that F(u) dudvdw gives the probability that a molecule selected at random will, at any instant, have a velocity u with Cartesian components in the ranges u to u + du, v to v + dv, and w to w + dw.

The Maxwell-Boltzmann velocity distribution function refers specifically to a gas which is at rest (in the sense that no macroscopic flow exists) and in a state of thermodynamic equilibrium. Subject to these assumptions, the distribution law states that

$$F(u) = f(u)f(v)f(w)$$

$$= \left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-mc^2/2kT),$$

where m is the mass of one molecule, k is Boltzmann's constant, and c = |u| is the speed of the molecule. Note that F is given as the product f(u)f(v)f(w) and that the velocity components in different directions are therefore uncorrelated. In other words, the probability of the molecule possessing a specified velocity u in the x direction is not influenced by the values of v and w for that or any other molecule. The function f is thus a velocity distribution function for motion in a specified direction, and is given by

$$f(q) = \left(\frac{m}{2\pi kT}\right)^{1/2} \exp(-mq^2/2kT),$$

where q represents one of (u,v,w).

The distribution function Fc(c) for molecular speed, irrespective of direction, is easily found by:

$$F_c(c) = 4\pi c^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp(-mc^2/2kT).$$

Various 'average' molecular speeds may be obtained easily from the distribution function F_c as follows:

The most probable speed (maximum F_c): $\hat{c} = (2kT/m)^{1/2}$

The mean speed:
$$\langle c \rangle = \int_0^\infty F_c(c)c\,dc = (8kT/\pi m)^{1/2}$$

The root-mean-square speed:
$$\langle c^2 \rangle^{1/2} = \left(\int_0^\infty F_c(c)c^2\,dc\right)^{1/2} = (3kT/m)^{1/2}$$

The Maxwell-Boltzmann equation, which forms the basis of the kinetic theory of gases, defines the distribution of speeds for a gas at a certain temperature. From this distribution

function, the most probable speed, the average speed, and the root-mean-square speed can be derived.

The kinetic molecular theory is used to determine the motion of a molecule of an ideal gas under a certain set of conditions. However, when looking at a mole of ideal gas, it is impossible to measure the velocity of each molecule at every instant of time. Therefore, the Maxwell-Boltzmann distribution is used to determine how many molecules are moving between velocities v and $v + dv$. Assuming that the one-dimensional distributions are independent of one another, that the velocity in the y and z directions does not affect the x velocity, for example, the Maxwell-Boltzmann distribution is given by

$$dN/N=(m/2\pi kBT)^{1/2}e^{-mv2/2kBT}dv$$

where

- *dN/N* is the fraction of molecules moving at velocity v to $v + dv$,

- *m* is the mass of the molecule,

- k_b is the Boltzmann constant, and

- *T* is the absolute temperature.[1]

Additionally, the function can be written in terms of the scalar quantity speed c instead of the vector quantity velocity. This form of the function defines the distribution of the gas molecules moving at different speeds, between c1c1 and c2c2, thus

$$f(c)=4\pi c^2(m/2\pi kBT)^{3/2}e^{-mc2/2kBT}$$

Finally, the Maxwell-Boltzmann distribution can be used to determine the distribution of the kinetic energy of for a set of molecules. The distribution of the kinetic energy is identical to the distribution of the speeds for a certain gas at any temperature.[2]

BOLTZMANN'S TRANSPORT EQUATION

With ``Kinetic Theory of Gases'', Boltzmann undertook to explain the properties of dilute gases by analysing the elementary collision processes between pairs of molecules.

The evolution of the distribution density in mu space, $f(\vec{r},\vec{v};t)$, is described by **Boltzmann's transport equation**. A thorough treatment of this beautiful achievement is beyond the scope of our discussion. But we may sketch the basic ideas used in its derivation.

If there were no collisions at all, the swarm of particles in mu space would flow according to

$$f\left(\vec{r}+\vec{v}\,dt,\vec{v}+\frac{\vec{K}}{m}dt;t+dt\right) = f(\vec{r},\vec{v};t) \tag{1}$$

where $\vec{K}$ denotes an eventual external force acting on particles at point $(\vec{r},\vec{v})$. The time derivative of f is therefore, in the collisionless case,

$$\left(\frac{\partial}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} + \frac{\vec{K}}{m} \cdot \nabla_{\vec{v}}\right) f(\vec{r}, \vec{v}; t) = 0 \tag{2}$$

Where

$$\vec{v} \cdot \nabla_{\vec{r}} f \equiv v_x \frac{\partial f}{\partial x} + v_y \frac{\partial f}{\partial y} + v_z \frac{\partial f}{\partial z} \tag{3}$$

and

$$\frac{\vec{K}}{m} \cdot \nabla_{\vec{v}} f \equiv \frac{1}{m}\left(K_x \frac{\partial f}{\partial v_x} + K_y \frac{\partial f}{\partial v_y} + K_z \frac{\partial f}{\partial v_z}\right) \tag{4}$$

To gather the meaning of equation 2 for free flow, consider the collisionless, free flow of gas particles through a thin pipe: there is no force (i. e. no change of velocities), and mu-space has only two dimensions, x and v_x

At time t a differential ``volume element'' at $(x, v_{x)}$ contains, on the average, $f(x, v_x) dx\, dv_x$ particles. The temporal change of $f(x,v_x)$ is then given by

$$\frac{\partial f(x, v_x)}{\partial t} = -v_x \frac{\partial f(x, v_x)}{\partial x} \tag{5}$$

To see this, count the particles entering during the time span dt from the left (assuming $v_x > 0$, $n_{in} = f(x - v_x dt, v_x) dx\, dv_x$ and those leaving towards the right, $n_{out} = f(x, v_x) dx\, dv_x$. The local change per unit time is then

$$\frac{\partial f(x, v_x)}{\partial t} = \frac{n_{in} - n_{out}}{dt\, dx\, dv_x} \tag{6}$$

$$= \frac{f(x - v_x dt, v_x) - f(x, v_x)}{dt} \tag{7}$$

$$= \frac{f(x, v_x) - (v_x dt)(\partial f / \partial x) - f(x, v_x}{dt} \tag{8}$$

$$= -v_x \frac{\partial f(x, v_x)}{\partial x} \tag{9}$$

The relation $\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} = 0$ is then easily generalized to the case of a non-vanishing force,

$$\frac{\partial f}{\partial t} + v_x \frac{\partial f}{\partial x} + \frac{K_x}{m} \frac{\partial f}{\partial v_x} = 0 \tag{10}$$

All this is for collisionless flow only.

In order to account for collisions a term $(\partial f / \partial t)_{coll} dt$ is added on the right hand side:

$$\left(\frac{\partial}{\partial t} + \vec{v} \cdot \nabla_{\vec{r}} + \frac{\vec{K}}{m} \cdot \nabla_{\vec{v}} \right) f(\vec{r}, \vec{v}; t) = \left(\frac{\partial f}{\partial t} \right)_{coll} \tag{11}$$

The essential step then is to find an explicit expression for $(\partial f / \partial t)_{coll}$. Boltzmann solved this problem under the simplifying assumptions that

- only binary collisions need be considered (dilute gas);
- the influence of container walls may be neglected;
- the influence of the external force $\vec{K}$ (if any) on the rate of collisions is negligible;
- velocity and position of a molecule are uncorrelated (assumption of **molecular chaos**).

The effect of the binary collisions is expressed in terms of a ``differential scattering cross section'' $\sigma(\Omega)$ which describes the probability density for a certain change of velocities,

$$\{ \vec{v}_1, \vec{v}_2 \} \rightarrow \{ \vec{v}_1', \vec{v}_2' \} . \tag{12}$$

(Ω thus denotes the relative orientation of the vectors $(\vec{v}_2' - \vec{v}_1')$ and $(\vec{v}_2 - \vec{v}_1)$). The function $\sigma(\Omega)$ depends on the intermolecular potential and may be either calculated or measured.

Under all these assumptions, and by a linear expansion of the left hand side of equ. 2.1 with respect to time, the Boltzmann equation takes on the following form:

$$\left(\frac{\partial}{\partial t} + \vec{v}_1 \cdot \nabla_{\vec{r}} + \frac{\vec{K}}{m} \cdot \nabla_{\vec{v}_1} \right) f_1 = \int d\Omega \int d\vec{v}_2 \, \sigma(\Omega) |\vec{v}_1 - \vec{v}_2| \left(f_1' f_2' - f_1 f_2 \right) \tag{13}$$

where $f_1 \equiv f(\vec{r}, \vec{v}_1; t)$, $f_1' \equiv f(\vec{r}, \vec{v}_1'; t)$ etc. This integrodifferential equation describes, under the given assumptions, the spatio-temporal behaviour of a dilute gas. Given some initial density $f(\vec{r}, \vec{v}; t = 0)$ in mu-space the solution function $f(\vec{r}, \vec{v}; t)$ tells us how this density changes over time. Since f has up to six arguments it is difficult to visualize; but there are

certain moments of f which represent measurable averages such as the local particle density in 3D space, whose temporal change can thus be computed.

Chapman and Enskog developed a general procedure for the approximate solution of Boltzmann's equation. For certain simple model systems such as hard spheres their method produces predictions for $f(\vec{r},\vec{v};t)$ (or its moments) which may be tested in computer simulations. Another more modern approach to the numerical solution of the transport equation is the ``Lattice Boltzmann'' method in which the continuous variables $\vec{r}$ and $\vec{v}$ are restricted to a set of discrete values; the time change of these values is then described by a modified transport equation which lends itself to fast computation.

The initial distribution density $f(\vec{r},\vec{v};0)$ may be of arbitrary shape. To consider a simple example, we may have all molecules assembled in the left half of a container - think of a removable shutter - and at time $t = 0$ make the rest of the volume accessible to the gas particles:

$$f(\vec{r},\vec{v},0) = A\,\Theta(x_0 - x)\,f_0(\vec{v}) \tag{14}$$

where $f_0(\vec{v})$ is the (Maxwell-Boltzmann) distribution density of particle velocities, and $\Theta(x_0 - x)$ denotes the Heaviside function. The subsequent expansion of the gas into the entire accessible volume, and thus the approach to the stationary final state (= equilibrium state) in which the particles are evenly distributed over the volume may be seen in the solution $f(\vec{r},\vec{v};t)$ of Boltzmann's equation. Thus the greatest importance of this equation is its ability to describe also **non-equilibrium processes**.

The **Equilibrium distribution** $f_0(\vec{r},\vec{v})$ is that solution of Boltzmann's equation which is **stationary**, meaning that

$$\frac{\partial f(\vec{r},\vec{v};t)}{\partial t} = 0 \tag{15}$$

It is also the limiting distribution for long times, $t \to \infty$.

It may be shown that this equilibrium distribution is given by

$$f_0(\vec{r},\vec{v}) = \rho(\vec{r})\left[\frac{m}{2\pi k T(\vec{r})}\right]^{3/2} \exp\{-m[\vec{v}-\vec{u}_0(\vec{r})]^2 / 2kT(\vec{r})\} \tag{16}$$

where $\rho(\vec{r})$ and $T(\vec{r})$ are the local density and temperature, respectively.

Kinetic theory of gases

D. Bernaulli (1738) forwarded this theory which was developed by Clausius, Maxwell, Boltzmann, Kelvin etc.

The following are the main postulates of kinetic theory of gases:

(i)   Every gas consists of very large number of minute (tiny) particles called molecules. The actual volume of these molecules is negligible as compared to the total volume of the gas.

(ii)   The molecules of a gas are not stationary but are always in a state of rapid random motion in all possible directions with widely differing velocities. They travel in straight lines, but on collision with another molecule or with the sides of the containing vessel, direction of motion is changed.

(iii)   The molecules are spherical and perfectly elastic and therefore exert no appreciable attraction on each other. Hence there is no loss of kinetic energy on collision or mutual friction.

(iv)   The pressure exerted by a gas is due to the bombardment of the moving molecules on the walls of the containing vessel.

(v)   The motion imparted to the molecules by gravity is negligible in comparison to the effect of the continued collisions between them.

(vi)   The kinetic energy of a perfect gas depends on the temperature and not on the nature of the gas.

MEAN FREE PATH (How Far, How Fast, How Long)

The mean free path λ of a gas molecule is its average path length between collisions

Mathematically the mean free path can be represented as follows:

$$\lambda = \frac{1}{2\sqrt{\pi} d^2 \frac{N}{V}}$$

Let us look at the motion of a gas molecule inside an ideal gas, a typical molecule inside an ideal gas will abruptly change its direction and speed as it collides elastically with other molecules of the same gas. Though between the collisions the molecule will move in a straight line at some constant speed, this is applicable for all the molecules in the gas.

It is difficult to measure or describe this random motion of gas molecules thus we attempt to measure its mean free path λ.

As its name says λ is the average distance travelled by any molecule between collisions, we expect λ to vary inversely with N/V, which is the number of molecules per unit volume or the density of molecules because if there are more molecules more are the chances of them colliding with each other hence reducing the mean free path, and also λ would be inversely proportional to the diameter d of the molecules, because if the molecules were point masses then they would never collide with each other, thus larger the molecule smaller the mean free path, and it should be proportional to π Times Square of the diameter and not the diameter itself because we consider the circular cross-section and not the diameter itself.

Derivation of Mean Free Path

Let's assume that the molecule is spherical, and the collision occurs when one molecule hits the other, and only the molecule we are going to study will be in motion and rest molecules will be stationary.

Let's consider our single-molecule to have a diameter of d and all the other molecules to be points this does not change our criteria for collision, as our single-molecule moves through the gas, it sweeps out a short cylinder of cross-section area πd^2 between successive collisions, for a small-time t it will move a distance of vt where v is the velocity of the molecule, now if we sweep this cylinder we will get a volume of $\pi d^2 * vt$ so the number of point molecules inside this volume will give us the number of collisions the molecule might have,

Since N/V is the number of molecules per unit volume, the number of molecule in the cylinder will be N/V multiplied by the volume of cylinder i.e.$\pi d^2 vt$, the mean free path can be derived as follows,

λ = length of path during the time tnumber of collision in time r $\approx$ vtπd^2vtNV = 1πd^2NV

The equation is approximated the equation is because we have assumed that all the particles are stationary with respect to the particle we are studying, in fact, all the molecules are moving relative to each other, two velocities have been cancelled in the above equation but actually the v in the numerator is the average velocity and v In the denominator is relative velocity hence they both differ from each other with a factor $2-\sqrt{}$ therefore the final equation would be,

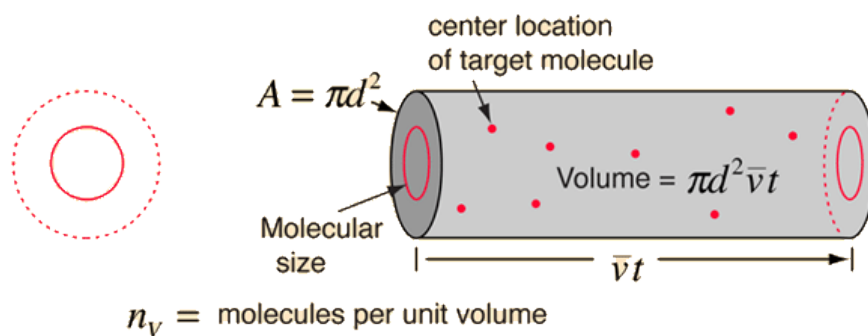λ = 12$\sqrt{}\pi d^2$NV

Following are the mean free path factors:

- Density

- Radius of molecule

- Number of molecules

- Temperature, pressure, etc.

The mean free path or average distance between collisions for a gas molecule may be estimated from kinetic theory. If the molecules have diameter d, then the effective cross-section for collision can be modeled by

d

The effective collision area is

$A = \pi d^2$
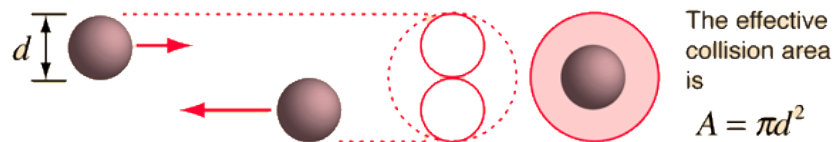
using a circle of diameter 2d to represent a molecule's effective collision area while treating the "target" molecules as point masses. In time t, the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume.

center location of target molecule

$A = \pi d^2$

Volume $= \pi d^2 \bar{v} t$

Molecular size

$\bar{v} t$

$n_V =$ molecules per unit volume

The mean free path could then be taken as the length of the path divided by the number of

Distance traveled

Mean distance per collision

Mean free path estimate $= \dfrac{\bar{v} t}{\pi d^2 \bar{v} t\, n_V} = \dfrac{1}{\pi d^2 n_V}$

Volume of interaction

Number of molecules per unit volume

collisions.

The problem with this expression is that the average molecular velocity is used, but the target molecules are also moving. The frequency of collisions depends upon the average relative velocity of the randomly moving molecules.

The intuitive development of the mean free path expression suffers from a significant flaw - it assumes that the "target" molecules are at rest when in fact they have a high average velocity. What is needed is the average relative velocity, and the calculation of that velocity from the molecular speed distribution yields the result

$$\text{Average relative velocity} \quad \overline{v_{rel}} = \sqrt{2}\ \overline{v}$$

which revises the expression for the effective volume swept out in time t

$$\text{Effective volume of targets swept} \quad \pi d^2 \sqrt{2}\ \overline{v} t \quad \text{The number of collisions is } \sqrt{2} \text{ times the number with stationary targets.}$$

The resulting mean free path is

$$\lambda = \frac{1}{\sqrt{2}\ \pi d^2 n_v}$$

The number of molecules per unit volume can be determined from Avogadro's number and the ideal gas law, leading to

$$n_v = \frac{nN_A}{V} = \frac{nN_A}{\frac{nRT}{P}} = \frac{N_A P}{RT}$$

$$\boxed{\text{Mean free path} \quad \lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P}}$$

It should be noted that this expression for the mean free path of molecules treats them as hard spheres, whereas real molecules are not. For noble gases, the collisions are probably close to being perfectly elastic, so the hard sphere approximation is probably a good one. But real molecules may have a dipole moment and have significant electrical interaction as they approach each other. This has been approached by using an electrical potential for the molecules to refine the calculation, and also by using the measured viscosity of the gas as a parameter to refine the estimate of the mean free path of molecules in real gases.

Transport phenomena

The molecule of a gas possesses momentum energy and mass which it carries as it moves about in the gas. The molecule of the gas also serve as carriers or transporters of momentum, energy or mass from one region to another through a series of successive collisions.

In a steady state or equilibriuin state of a gas, the transport of velocity, kinetic energy or molecular concentration in one direction is just balanced by an equal transport of the same quantity in the reverse direction and thus there is no net transport in any direction. But in non-equilibrium or disturbed state of a gas, there may be an excess of any one of these quantities in one region and a deficit in another. Molecules therefore may transport the quantity concerned from the former to the latter region to restore the equilibrium.

Viscosity

The different parts of the gas may have different velocities. This will result in the relative motion of the different layers of the gas with respect to one another. In such a case the layers moving faster will impart momentum to the layers moving slower to bring about an equilibrium state. This gives rise to the phenomenon of viscosity.

Conduction

The temperature of the gas may be different in different regions of the gas. In such cases the molecules of the gas will carry kinetic energy from regions of higher temperature to the regions of lower temperature to bring about equilibrium state. This gives rise to the phenomenon of conduction.

Diffusion

The different parts of the gas may have different molecular concentrations. That The moi is, the number of molecules per unit volume is different at different parts. In such case the molecule from higher concentration to regions of lower concentration to bring about equilibrium state. This will give rise to the phenomenon of diffusion.

In a gas the transport of momentum, thermal energy and mass from one region -to another region gives rise to the phenomenon of viscosity, thermal conduction and diffusion respectively which are known as transport phenomena.

Viscosity of gases-Transport of momentum

The different layers of gas in non-equilibrium condition may have different velocities. This will result in the relative motion of the different layers with respect to one another. In such a case the layer moving faster will impart momentum to the layer moving slower to bring about an equilibrium state. Thus the transport of momentum gives rise to the phenomenon of viscosity.

Let A, B and C be layers of a gas parallel to the plane OXPY at rest, A, be the distance between the layers and let there be a velocity gradient dv/dz in the Z-direction.
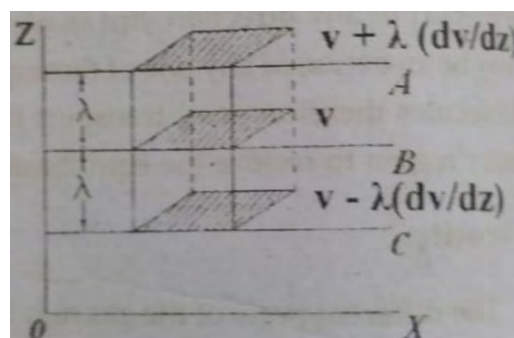
Let the drift velocity of B = v

The drift velocity of A = v + λ dv/dz

The dfift velocity of C = v – λ dv/dz

The momentum of a molecule in A due to the drift velocity = m (v + λ dv/dz)

The momentum of a molecule in B due to the drift velocity = m (v - λ dv/dz)

The molecules existing in B at any instant can be considered to have come from A or C where they have suffered a previous collision. Thus a change in momentum takes place in B due to the arrival of these molecules. The change in momentum in B due to a molecule arriving from A and another from C

m(v + λ dv/dz) -m(v + λ dv/dz) = 2mλ dv/dz

If 'n' be the number of molecules per unit volume of the gas with 'c' as mean velocity of each molecule, then out of 'nc' number of molecules, only nc/3 will on an average move along the Z-direction, half of them upward and half downward.

Thus the change in momentum on unit area of B in one second due to nc/6 molecules '

coming from A and nc/6 molecules from C = (nc/6) 2m λ dv/dz = (mnc/3) λ dv/dz

This is the viscous drag (F) on unit area of B when the velocity gradient is dv/dZ.

F = ηAdv/dz

Since A =1 m^2 and η is the coefficient of viscosity of the gas we can write,

ηAdv/dz = (mnc/3) λ dv/dz

The coefficient of viscosity η of the gas being the viscous drag on unit area per unit velocity gradient,

$$\eta = mnc\ \lambda/3 = \rho c\ \lambda/3$$

where mn = p the density of the gas.

The density p is directly proportional to the pressure and the mean free path λ is inversely proportional to the pressure of a gas. Thus $\rho\lambda$ is a constant for a gas at constant temperature. Moreover the average molecular speed 'c' is independent of pressure. Hence the coefficient of viscosity of a gas is independent of pressure.

The density ' p' of the gas decreases with increase in temperature but 'λ ' the mean free path increases in the same proportion so that ' pλ. ' remains constant. Since the average molecular speed 'c' is proportional to the square root of absolute temperature, the coefficient of viscosity must be directly proportional to the square root of the absolute temperature of the gas. This result was first predicted by Maxwell from theoretical consideration.

Thermal conductivity-Transport of thermal energy

The different layers of gas in non-equilibrium condition may have different temperatures. The molecules in these layers have different energies. The molecules will carry the kinetic energy (heat) from regions of higher temperature to the region of lower temperature to bring about an equilibrium state. Thus the transport of thermal energy gives rise to the phenomenon of thermal conductivity.

Let A, B and C be layers of a gas parallel to the plane OXPY, λ, be the distance between the layers and let there be a temperature gradient dΘ /dz in the Z-direction.
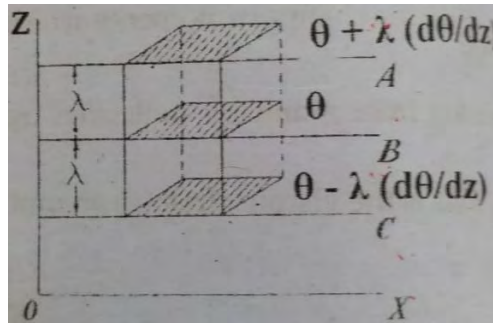
Let the temperatures of the layer B be Θ.

The temperature of the layer A which is at a distance of λ above layer B be Θ + λ(dΘ /dz)

The temperature of the layer C which is at a distance of A below layer B is Θ- λ(dΘ /dz)

Considering unit area of B, the number of molecules reaching this area in one second either from A or C = nc/6 where 'n' is the number of molecules per unit volume and 'c' is the average velocity of the molecule. If 'm' is the mass of each gas molecule, then the mass of gas crossing unit area of layer B above or below per second = mnc/6.

If C_V is the specific heat of the gas at constant volume then, heat energy carried by the molecules in crossing unit area of the layer B in the downward direction per second

= mass x specific heat x temperature = (mnc/6) C_V (Θ+λ(dΘ /dz)

Similarly, heat energy carried by the molecules crossing in unit area of the layer B in the upward direction per second is (mnc/6) C_V (Θ-λ(dΘ /dz)

Therefore the net transfer of energy per unit area of layer B per second

Q = (mnc/6) C_V (Θ+λ(dΘ /dz) - (mnc/6) C_V (Θ-λ(dΘ /dz)

= (mnc/6) C_V 2λ(dΘ /dz) = (mnc/3) C_V λ(dΘ /dz)

Since mn = p the density of the gas, we have Q = (ρc/3) C_V λ(dΘ /dz) ……(1)

The coefficient of thermal conductivity K of the gas is defined as the quantity of heat that flows per unit area per unit temperature gradient.

Q = K (dΘ /dz) ……(2)

Comparing the two equations (1) and (2) we have

K (dΘ /dz) = (ρc/3) C_V λ(dΘ /dz)

$K = (\rho c/3) \, C_V \, \lambda$

The density ρ of the gas decreases with increase in temperature but ' λ ' the mean free path increases in the same proportion so that ' pX, ! remains 6onstant. Since the average molecular speed 'c' is proportional to the square root of absolute temperature, the coefficient of thermal conductivity is directly proportional to the absolute temperature of the material. In other words, the coefficient of thermal conductivity increases with increase in the temperature.

Diffusion-Transport of mass

The phenomenon of diffusion is due to the transport of mass from a region of higher concentration to the region of lower concentration to bring about equilibrium. Let A, Band C be layers of a gas parallel to the plane OXPY, λ be the distance between the layers and let there be a concentration gradient dn/dz in the Z-direction.
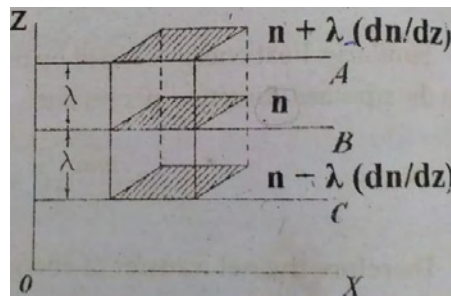
Let the concentration of the layer B be n. The concentration of the layer A which is at a distance of λ above layer B be n + λ dn/dz. The concentration of the layer C which is at a distance of 2, below layer B is n- λ dn/dz. The number of molecules coming from layer A and crossing B downward per unit area per second

= (1/6) c (n+(λ dn/dz.))

The number of molecules coming from layer C and crossing B upward per unit area per second

= (1/6) c (n-(λ dn/dz.))

Therefore the net number of molecules crossing per unit area per second of layer B

= (1/6) c (n+(λ dn/dz.)) - = (1/6) c (n-(λ dn/dz.)) = (1/3) c(λ dn/dz)

The coefficient of diffusion is defined as the ratio of the number of molecules crossing per unit area in one second per unit concentration gradient.

Coefficient of diffusion D = (1/3) c(λ dn/dz) /(dnldz) = (1/3) cλ

UNIT III
CLASSICAL STATISTICAL MECHANICS

STATISTICAL PHYSICS

It is impossible to solve the problem of a macroscopic body which consists of a very large number of individual particles by the use of ordinary laws of mechanics. Such problems have been successfully solved by the method of statistical mechanics. Statistical mechanics is the branch of science which establishes the interpretation of the macroscopic behaviour of a system in terms of its microscopics properties. The quantities, temperature and pressure refer to the macroscopic or bulk state of a gas and can be measured by ordinary apparatus. On the other hand, the position and velocity of individual molecules in the gas belong to the microscopic state and a complete knowledge of the continually changing motion of the molecules is not known. Statistical mechanics correlates these two states and thereby conclusions are drawn.

The statistical methods applied by Maxwell, Boltzmann, Gibbs, etc., are known as classical statistics or Maxwell - Boltzmann statistics. The classical statistics explained successfully many observed physical phenomena like temperature, pressure, energy, etc. But, it could not explain several other experimentally observed phenomena like black - body radiation, specific heat at low temperature etc. For explaining such phenomena Bose, Einstein, Fermi and Dirac made a new approach using new quantum idea of discrete exchange of energy between the systems. The new statistics, known as quantum statistics, is subdivided into two types.

(i) Bose - Einstein statistics (ii) Fermi - Dirac statistics

The first one holds good for photons while the other for elementary particles such as electrons. The classical statistics is only the limiting case of quantum statistics.

PRINCIPLE OF STATISTICAL MECHANICS

Statistical mechanics combines the laws of probability and dynamic principle to predict the properties of physical systems that are macroscopic in nature, i.e., the distribution of velocities among the molecules of an ideal gas, distribution of energy with wavelength in the case of electromagnetic radiation of energy among the free electrons of a conducting material. Many other thermodyamic properties and functions have been evaluated.

PHASE SPACE

In the theory of mechanics, the motion of a dynamical system is specified by three space coordinates x, y, z and three momentum coordinates P_x, P_y, P_z. There are now six dimensional space in which the co-ordinates are x, y, z, Px., Py, Pz.. This six dimensional space for a single molecule is called phase space or mu-space. The instantaneous state of a particle in the phase space is represented by a point known as phase point or representative point. The concept of phase space is very useful while dealing with dynamical systems. The volume element dx dy dz dPxdPydPz, in six dimensional space is called a cell. The phase space can be divided into a large number of cells.

In classical physics, the volume of the cell can be made as small as possible and it can even approach zero. However, in quantum statistics the volume of the phase cell is determined using Heisenberg's uncertainty principle, $\Delta x \ \Delta P \geq h$

Volume of the phase cell = $\Delta x \ \Delta y \ \Delta z \ \Delta Px \ \Delta Py \ \Delta Pz; = h^3$ where h is Planck's constant. It is now possible to study the distribution of particles of a dynamical system among the compartments and 'cells in the phase space.

ENSEMBLES

An ensemble is defined as collection of large number of identical but essentially independent systems. For example, a gas containing a large number of molecules may be assumed to be an ensemble with each of its gas molecules forming a system. The temperature, energy, etc., are considered as the average property of the constitutent molecules. Statistical mechanics is used to discuss this type of a average property of the ensemble.

The ensemble is divided into three types:

(1) Microcanoical ensemble (2) Canonical ensemble (3) Grand - canonical ensemble

The ensemble in which system has the same fixed energy and also the same number of particles is called a microcanonical ensemble. The ensemble which describes those system which are not isolated but are in thermal contact with a heat reservoir is called a canonical ensemble.

The ensemble which allows the sub system to exchange energy as well as the number of particles with the reservior is called a grand - canonical ensemble.

Microcanonical ensemble

The microcanonical ensemble is collection of essentially independent systems having the same energy E, volume V and number of particles N. For simplicity, it is assumed that all

the particles are identical. The individual systems of a microcanonical ensemble are separated by rigid, impermeable and well insulated walls such that the values of E, V and N for a particular system are not affected at all by the presence of other system.
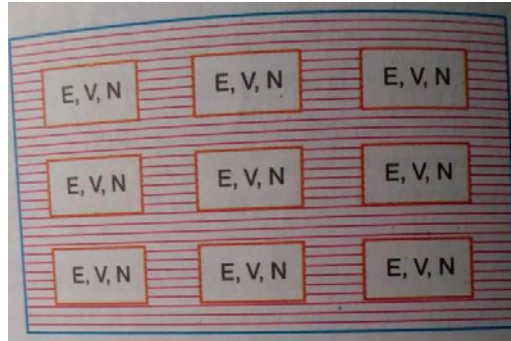
Consider a closed system for which the total energy remains constant. The locus of all such phase points having equal energies in phase space is called an Energy Surface or ergodic surface. A family of such energy spaces surfaces can be drawn in phase space. Consider any two such energy surfaces with energies very close to each other. Each energy Surface divides the phase space into two parts one on higher and other of lower energy and hence they will never intersect with each other. As they enclose same phase volume in between them, a certain number of phase points are included. The number of phase points between them will be a constant. According to Gibbs, a very useful and ensemble can be obtained by taking energy density constant in a narrow selected energy ranges and vanishes outside.

Canonical ensemble

The Canonical ensemble is a collection of essentially independent systems having the same temperature T, volume V and number of identical particles N. This is achieved by bringing all the systems in thermal contact with the large heat reservoir at constant temperature T or by simply bringing all of the systems in thermal contact with each other.


Figure represents symbolically a Canonical ensemble. The individual systems of the Canonical ensemble are separated by rigid, impermeable but diathermic walls. As the

separating walls are conducting, heat can be exchanged between the systems till they reach a common temperature. Thus, in Canonical ensemble, systems can exchange energy but not the matter.

Grand Canonical ensemble

In going from microcanonical ensemble to Canonical ensemble, the condition of constant energy has been relaxed. This simplifies the calculation in thermodynamics, where the exchange of energy takes place. Now the next logical step is to abandon the condition of same number of particles. Actually, in chemical process, this number N varies in various physical phenomena problems. Thus, the Grand Canonical ensemble is collection of large number of essentially independent systems having same temperature T, volume V and chemical potential μ. The individual systems of the Grand Canonical ensemble are separated by rigid permeable and conducting walls as shown.
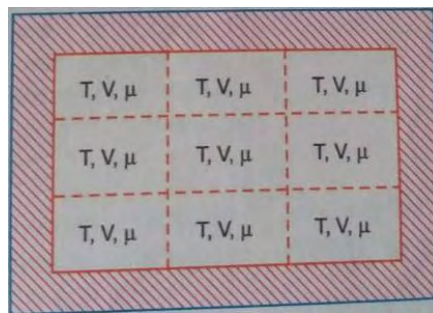
As the separating walls are conducting and permeable, the exchange of heat energy as well as that of particles between the systems takes place in such a way that all the systems arrive at common temperature and the chemical potential. Thus an ensemble in which the systems exchange energy but not matter is called them Canonical ensemble, that is which both energy and matter are exchanged between the systems is called a Grand canonical ensemble and that in which neither energy nor matter is exchanged is called microcanonical ensemble.

Specific choice of ensemble maybe thought of as corresponding to a particular physical situation. The microcanonical ensemble is fundamental and refers to the simple situation in which constituent systems are isolated and not influenced in any way by external disturbances.

Therefore it is the best suited for isolated systems. However, there is always some energy exchange with the surroundings. Hence, Canonical ensemble have been found to be more appropriate for dealing such systems. Besides, Canonical approach gives results applicable even when the constituents interact strongly.

POSTULATES OF STATISTICAL MECHANICS

1. Any gas may be considered to be composed of molecules which are in motion and behave like very small elastic spheres.

2. All the cells in the phase space are of equal size.

3. All accessible microstates corresponding possible macrostates are equally probable. This is called the postulate of equal a prior probability.

4. According to Boltzmann, entropy (S) = k log W where k is Boltzmann constant and W is the probability.

5. The equilibrium state of a system corresponds to the maximum probability and entropy.

6. The total number of molecules is constant.

LIOUVILLE'S THEOREM

Local Gas Density Is Constant along a Phase Space Path

The falling bodies phase space square has one more lesson for us: visualize now a uniformly dense gas of points inside the initial square. Not only does the gas stay within the distorting square, the area it covers in phase space remains constant, as discussed above, so the local gas density stays constant as the gas flows through phase space. Liouville's theorem is that this constancy of local density is true for general dynamical systems.

Landau's Proof Using the Jacobian

Landau gives a very elegant proof of elemental volume invariance under a general canonical transformation, proving the Jacobian multiplicative factor is always unity, by clever use of the generating function of the canonical transformation. Jacobians have wide applicability in different areas of physics, so this is a good time to review their basic properties, which we do below, as a preliminary to giving the proof.

Jacobian for Time Evolution

It have been established that time development is equivalent to a canonical coordinate transformation,

$$(p_t,q_t) \rightarrow (p_{t+\tau},q_{t+\tau}) \equiv (P,Q).$$

Since we already know that the number of points inside a closed volume is constant in time, Liouville's theorem is proved if we can show that the volume enclosed by the closed surface is constant, that is, with V' denoting the volume V evolves to become, we must prove

$$\int_{V'} dQ_1 \ldots dQ_s dP_1 \ldots dP_s = \int_V dq_1 \ldots dq_s dp_1 \ldots dp_s$$

If you're familiar with Jacobians, you know that (by definition)

$$\int dQ_1 \ldots dQ_s dP_1 \ldots dP_s = \int D dq_1 \ldots dq_s dp_1 \ldots dp_s$$

where the Jacobian

$$D = \partial(Q_1,\ldots,Q_s,P_1,\ldots,P_s) \partial(q_1,\ldots,q_s,p_1,\ldots,p_s).$$

Jacobians

Suppose we are integrating a function over some region of ordinary three-dimensional space,

$$I = \int_V f(x_1,x_2,x_3) dx_1 dx_2 dx_3$$

Let there is a change of variables of integration to a different set of coordinates (q_1,q_2,q_3) such as, for example, (r,θ,ϕ). The new coordinates are of course functions of the original ones $q_1(x_1,x_2,x_3)$, etc., and we assume that in the region of integration they are smooth, well-behaved functions. We can't simply re-express f in terms of the new variables, and replace the volume differential $dx_1 dx_2 dx_3$ by $dq_1 dq_2 dq_3$, that gives the wrong answer—in a plane, you can't replace $dxdy$ with $drd\theta$, you have to use $rdrd\theta$. That extra factor r is called the Jacobian, it's clear that in the plane a small element with sides of fixed lengths $(\delta r,\delta\theta)$ is bigger the further it is from the origin, not all $\delta r\delta\theta$ elements are equal, so to speak. The task is to construct the Jacobian for a general change of coordinates.

The volumes in the three-dimensional space represented by $dx_1 dx_2 dx_3$ and by $dq_1 dq_2 dq_3$. Of course, the x_i's are just ordinary perpendicular Cartesian axes so the volume

is just the product of the three sides of the little box, $dx_1 dx_2 dx_3$. Imagine this little box, its corner closest to the origin at (x_1, x_2, x_3) and its furthest point at the other end of the body diagonal at $(x_1+dx_1, x_2+dx_2, x_3+dx_3)$ Let's take these two points in the q_i coordinates to be at (q_1, q_2, q_3) and $(q_1+dq_1, q_2+dq_2, q_3+dq_3)$. In visualizing this, bear in mind that the q axes need not be perpendicular to each other (but they cannot all lie in a plane, that would not be well-behaved).

For the x coordinate integration, we imagine filling the space with little cubical boxes. For the q integration, we have a system of space filling infinitesimal parallelepipeds, in general pointing different ways in different regions (think (r, θ)). What we need to find is the volume of the incremental parallelepiped with sides we'll write as vectors in x - coordinates, $\vec{dq}_1, \vec{dq}_2, \vec{dq}_3$. These three incremental vectors are along the corresponding q coordinate axes, and the three added together are the displacement from (x_1, x_2, x_3) to $(x_1+dx_1, x_2+dx_2, x_3+dx_3) \equiv (q_1+dq_1, q_2+dq_2, q_3+dq_3)$.

Hence, in components,

$$\vec{dq}_1 = \left(\frac{\partial q_1}{\partial x_1} dx_1,\ \frac{\partial q_1}{\partial x_2} dx_2,\ \frac{\partial q_1}{\partial x_3} dx_3 \right).$$

Now the volume of the parallelepiped with sides the three vectors from the origin $\vec{a}, \vec{b}, \vec{c}$ is $\vec{a} \cdot \vec{b} \times \vec{c}$ (recall $|\vec{b} \times \vec{c}|$ is the area of the parallelogram, then the dot product singles out the component of $\vec{a}$ perpendicular to the plane of $\vec{b}, \vec{c}$).

So, the volume corresponding to the increments dq_1, dq_2, dq_3 in q space is

$$\vec{dq}_1 \cdot \vec{dq}_2 \times \vec{dq}_3 = \begin{vmatrix} \frac{\partial q_1}{\partial x_1} & \frac{\partial q_2}{\partial x_1} & \frac{\partial q_3}{\partial x_1} \\ \frac{\partial q_1}{\partial x_2} & \frac{\partial q_2}{\partial x_2} & \frac{\partial q_3}{\partial x_2} \\ \frac{\partial q_1}{\partial x_3} & \frac{\partial q_2}{\partial x_3} & \frac{\partial q_3}{\partial x_3} \end{vmatrix} dx_1 dx_2 dx_3 = D dx_1 dx_2 dx_3,$$

writing D (Landau's notation) for the *determinant*, which is in fact the *Jacobian*, often denoted by J.

The standard notation for this determinantal Jacobian is

$$D = \frac{\partial(q_1, q_2, q_3)}{\partial(x_1, x_2, x_3)},$$

So the appropriate replacement for the three dimensional incremental volume element represented in the integral by $dq_1 dq_2 dq_3$ is

$dq1 dq2 dq3 \rightarrow \partial(q1,q2,q3)\partial(x1,x2,x3)dx1dx2dx3.$

The *inverse*

$D{-}1=\partial(x1,x2,x3)\partial(q1,q2,q3),$

this is easily established using the chain rule for differentiation.

Thus the change of variables in an integral is accomplished by rewriting the integrand in the new variables, and replacing

$I=\int Vf(x1,x2,x3)dx1dx2dx3=\int Vf(q1,q2,q3)\partial(x1,x2,x3)\partial(q1,q2,q3)dq1dq2dq3.$

The argument in higher dimensions is just the same: on going to dimension n+1, the hypervolume element is equal to that of the n dimensional element multiplied by the component of the new vector perpendicular to the n dimensional element. The determinantal form does this automatically, since a determinant with two identical rows is zero, so in adding a new vector only the component perpendicular to all the earlier vectors contributes.

It have been seen that the chain rule for differentiation gives the inverse as just the Jacobian with numerator and denominator reversed, it also readily yields

$\partial(x1,x2,x3)\partial(q1,q2,q3)\cdot\partial(q1,q2,q3)\partial(r1,r2,r3)=\partial(x1,x2,x3)\partial(r1,r2,r3),$

and this extends trivially to n dimensions.

It's also evident form the determinantal form of the Jacobian that

$\partial(x1,x2,x3)\partial(q1,q2,x3)=\partial(x1,x2)\partial(q1,q2)$

identical variables in numerator and denominator can be canceled. Again, this extends easily to n dimensions.

Jacobian proof of Liouville's Theorem

After this rather long detour into Jacobian theory, recall we are trying to establish that the volume of a region in phase space is unaffected by a canonical transformation, we need to prove that

$\int dQ_1 \dots dQ_s dP_1 \dots dP_s = \int dq_1 \dots dq_s dp_1 \dots dp_s$,

and that means we need to show that the Jacobian

$$D = \frac{\partial(Q_1,\dots,Q_s,P_1,\dots,P_s)}{\partial(q_1,\dots,q_s,p_1,\dots,p_s)} = 1.$$

Using the theorems above about the inverse of a Jacobian and the chain rule product,

$$D = \frac{\partial(Q_1,\dots,Q_s,P_1,\dots,P_s)}{\partial(q_1,\dots,q_s,P_1,\dots,P_s)} \Big/ \frac{\partial(q_1,\dots,q_s,p_1,\dots,p_s)}{\partial(q_1,\dots,q_s,P_1,\dots,P_s)}.$$

Now invoking the rule that if the same variables appear in both numerator and denominator, they can be cancelled,

$$D = \left\{ \frac{\partial(Q_1,\dots,Q_s)}{\partial(q_1,\dots,q_s)} \right\}_{P=\text{constant}} \Big/ \left\{ \frac{\partial(p_1,\dots,p_s)}{\partial(P_1,\dots,P_s)} \right\}_{q=\text{constant}}.$$

Up to this point, the equations are valid for any nonsingular transformation—but to prove the numerator and denominator are equal in this expression requires that the equation be canonical, that is, be given by a generating function, as explained earlier.

Recall now the properties of the generating function $\Phi(q,P,t)$,

$$d\Phi(q,P,t) = d(F + \sum P_i Q_i) = \sum p_i dq_i + \sum Q_i dP_i + (H'-H)dt,$$

from which

$$p_i = \partial\Phi(q,P,t)/\partial q_i, \quad Q_i = \partial\Phi(q,P,t)/\partial P_i, \quad H' = H + \partial\Phi(q,P,t)/\partial t.$$

In the expression for the Jacobian D, the i,k element of the numerator is $\partial Q_i/\partial q_k$.

In terms of the generating function $\Phi(q,P)$ this element is $\partial^2\Phi/\partial q_k\partial P_i$.

Exactly the same procedure for the denominator gives the i,k element to be $\partial P_i/\partial p_k = \partial^2\Phi/\partial q_i\partial P_k$. In other words, the two determinants are the same (rows and columns are switched, but that doesn't affect the value of a determinant). This means D=1, and Liouville's theorem is proved.

Simpler Proof of Liouville's Theorem

Landau's proof given above is extremely elegant: since phase space paths cannot intersect, point inside a volume stay inside, no matter how the volume contorts, and since time development is a canonical transformation, the total volume, given by integrating over volume elements dqdp, stays the same, since it's an integral over the corresponding volume elements dQdP and we've just shown that dQdP=dqdp.

The points in the volume represent a "gas" of many systems in the two dimensional (q,p) phase space, and with a small square area $\Delta q, \Delta p$, tagged by having all the systems on its boundary represented by dots of a different color. What is the incremental change in area of this initially square piece of phase space in time dt?

Begin with the top edge: the particles are all moving with velocities $(\dot{q}, \dot{p})$, but of course the only change in *area* comes from the $\dot{p}$ term, that's the outward movement of the boundary, so the area change in dt from the movement of this boundary will be $\dot{p}\Delta q dt$. Meanwhile, there will be a similar term from the bottom edge, and the *net* contribution, top plus bottom edges, will depend on the change in $\dot{p}$ from bottom to top, that is, a net area change from movement of these edges $(\partial \dot{p}/\partial p)\Delta p \Delta q dt$.

Adding in the other two edges (the sides), with an exactly similar argument, the total area change is

$(\partial \dot{p}/\partial p + \partial \dot{q}/\partial q)\Delta p \Delta q dt$.

But from Hamilton's equations $\dot{p}=\partial H/\partial q, \quad \dot{q}=-\partial H/\partial p$, so

$\partial \dot{p}/\partial p = \partial 2H/\partial p \partial q, \quad \partial \dot{q}/\partial q = -\partial 2H/\partial p \partial q$

and therefore

$\partial \dot{p}/\partial p + \partial \dot{q}/\partial q = 0$,

establishing that the total incremental area change as the square distorts is zero. The conclusion is that the flow of the gas of systems in phase space is like an incompressible fluid, *but* with one important qualification: the density may vary with position! It just doesn't vary along a dynamical path.

MAXWELL - BOLTZMANN DISTREBUTION LAW (CLASSICAL STATISTICS)

Maxwell - Boltzmann statistics is also known as classical statistics. This is applicable to the identical distinguishable particles of any spin. The molecules of a gas are the particles.

Let us consider a system of N distinguishable molecules of a gas. Suppose n1, of them have energy E1, n2 have energy E2 and so on. Let each energy level (compartment) be divided into equal sized cells and g1, g2,…. cells corresponding to the energy intervals E1, E2,……

The total number of particles N is a constant. Then,

$N = n1 + n2 + n3 + = $ a constant ...(1)

or $dN = \Sigma dni = 0$ ...(2)

The total energy of the gas molecules is also a constant. Then

$E = n1E + n2E2 + = $ a constant ...(3)

$dE = E1dn1 + E2dn2 + …… = 0$ ...(4)

or $\Sigma Ei \, dni = 0$ ……. (5)

The number of ways for arranging n1 particles from N particles = $N! / n! (N—n1)!$

The number of ways for arranging n2 particles from the remaining (N — n1) particles =

$(N-n1)! / n2! (N—n1-n2)!$

and so on. Hence the number of ways in which n1,n2,n3 particles can be choosen from N particles is given by

$W1 = (N! / n1! (N—n1)!)((N-n1)! / n2! (N—n1-n2)!)$ ………

$W1 = N! / n1! n2! n3!...$ ...... (6)

The total number of ways in which ni molecules can be distributed in gi cells is given by

$W2 = (g1)^{n1} (g2)^{n2}…..$ …….(7)

Applying classical statistics, the thermodynamic probability for the most probable macrostate is given by

$W = W1W2 = (N! / n1! n2! n3! ......)(= (g1)^{n1} (g2)^{n2}……)$ …………(8)

Taking natural logarithms on both sides,

$\log W = \log N! + \Sigma ni \log gi – \Sigma \log ni!$ …………….(9)

By Stirling's Theorem, $\log_e N! = N \log_e N - N$

$\log W = N \log N - N + \Sigma n_i \log g_i - \Sigma n_i \log n_i - \Sigma n_i$

$= N \log N + \Sigma n_i \log g_i - \Sigma n_i \log n_i$

For the most probable state, $d (\log W) = 0$

$0 = 0 + \Sigma dn_i \log g_i - \Sigma dn_i \log n_i - \Sigma n_i (1/n_i) dn_i$

$0 = \Sigma dn_i \log g_i - \Sigma dn_i \log n_i - \Sigma dn_i$

$\Sigma(\log g_i - \log n_i)dn_i = 0 \qquad …………..(10)$

Multiplying equation (2) by $-\alpha$ and equation (5) by $-\beta$ and adding to equation (10)

$\Sigma(\log g_i - \log n_i - \alpha - \beta E_i)dn_i = 0$

As the various dn_i are independent of one another, the expression within the bracket should be zero for each value of i.

$\log g_i - \log n_i - \alpha - \beta E_i = 0$

$\log (n_i/g_i) = -\alpha - \beta E_i$

Taking exponentials,

$(n_i/g_i) = e^{-\alpha - \beta E_i}$

$n_i = g_i e^{-\alpha - \beta E_i} \qquad …(11)$

Since n_i is the number of molecules having energy E_i , the right hand side should be dimensionless. Since E_i is expressed in energy unit, β should be the reciprocal of the energy unit. The product β and E_i should be a dimensionless quantity. For this $1/\beta$ should be equal to $1/kT$ where k is the Boltzmann constant and T is the temperature in kelvin (kT = joules).

$n_i = g_i e^{-\alpha - E_i/kT} \quad$ or $\quad n_i/g_i = e^{-\alpha - \beta E_i} \quad ………(12)$

This result is called Maxwell - Boltzmann distribution law.

APPLICATION OF MAXWELL - BOLTZMANN STATISTICS TO AN IDEAL GAS

According to the Maxwell - Boltzmann distribution law,

$n_i = g_i e^{-\alpha - E_i/kT}$

Suppose an ideal gas contains N molecules with continuous distribution of molecular energies. Then the number of molecules having energies between E and E + dE is

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

where g(E) dE represents the number of states that have energies between E and E + dE.

$E = \frac{1}{2} mv^2 = \frac{1}{2} \, m^2v^2 /m \; = p^2/ 2m$

$p = \sqrt{2mE} \; = \sqrt{p_x^2 + p_y^2 + p_z^2}$

Let us consider a momentum space with co-ordinate axis Px, Py, Pz. The number of momentum states g(p) dp available to a particle that have momentum between p and p + dp is proportional to the volume of a spherical shell in momentum space of radius p and thickness dp. Volume of this spherical shell is $4\pi p^2 dp$. Hence

$g(p)dp = \beta p^2 dp$

where β is a constant. Since each momentum magnitude p corresponds to a single energy,

$g(E)dE = \beta p^2 dp$

$p^2 = 2mE$.

$dp = mdE/p = mdE / \sqrt{2mE}$

$g(E)dE = \sqrt{2}\beta m^{3/2} \sqrt{E} \, dE$

$n(E)dE = \sqrt{2}\beta m^{3/2} e^{-\alpha} \, \sqrt{E} \, e^{-Ei/kT} \, dE$

Let $\sqrt{2}\beta m^{3/2} e^{-\alpha} \; $ = a constant, C

Hence, $n(E)dE = C\sqrt{E} \, e^{-Ei/kT} \, dE$

Using normalization condition, the constant C is evaluated. $C = 2\pi N/(\pi kT)^{3/2}$

Therefore $\qquad\qquad n(E) = 2\pi N/(\pi kT)^{3/2}\sqrt{E} \, e^{-Ei/kT}$

This equation is known as Maxwell's law of distribution of energy. The total energy of the system is

$E = \int E \, n(E)dE$

$\quad = \quad 2\pi N/(\pi kT)^{3/2} \int E \, e^{-Ei/kT} \, dE$

$\quad = \quad 3/2 \, NkT$

The average energy of an ideal gas molecule is given by E/N = 3/2 kT. Then the number of molecules with speeds between v and v+dv in an assembly of gas containing N molecules at T K is given by

$n(v)dv = (\sqrt{2}\pi N(m^{3/2})\ v^2)\ /\ e^{-mv2/2kT}dv$

This eqution is known as Maxwell's law of distribution of velocity.

LAW OF EQUIPARTITION ENERGY

This law is related to the distribution of thermal energy throughout an ensemble like the molecules of a gas. Maxwell first stated that for a molecule in translatory motion, the energy is equally distributed between the degrees of freedom. Boltzmann extended the equal energy distribution for a the translatory, rotatory and vibratory motions of a rigid body. The law of equipartition energy may therefore be stated as the total mean kinetic energy of a molecule distributed between the total numbers of degrees of freedom.

The principle of equipartition energy applies only for those degrees of freedom which involves energy in terms of velocity co-ordinates. Thus, if the molecules are considered to be rigid bodies we have three degrees of freedom for the translatory motion.

Let u^2, v^2 and w^2 represent the mean square velocities of the molecules moving in X, Y, and Z directions.

c^2 represents the mean square velocity of the molecules

$c^2 = u^2 + v^2 + w^2$

Since the molecules are alike,

$u^2 = v^2 = w^2$. Therefore $c^2 = 3u^2 = 3v^2 = 3w^2$

The average kinetic energy of a molecule per degree of freedom

$\frac{1}{2}\ mu^2 = \frac{1}{2}\ mv^2 = \frac{1}{2}\ mw^2$

$= \frac{1}{2}\ m\ (1/3\ c^2) = 1/3\ (\frac{1}{2}\ mc^2)$

But, $PV = (1/3)\ Mc^2 = RT$

$M = Nm$

$(1/3)Nmc^2 = RT$

$mc^2 = 3(R/N)\ T = 3Kt$

Since $R/N = k$

$\frac{1}{2}\ mc^2 = (3/2)\ kT$

Hence, the average kinetic energy of a molecule per degree of freedom

$= (1/3)(3/2) kT = \frac{1}{2} kT$

Therefore, the average kinetic energy associated with each degree of freedom is $\frac{1}{2}$ kT whether it is translatory or rotatory or vibratory motion. This is known as the Boltzmann law of equipartition energy. Hence, this law is stated as the total energy of a dynamical system in thermal equilibrium shared equally by all its degree of freedom and the energy associated per molecule per degree of freedom is equal to $(3/2) kT$ where k is the Boltzmann constant and T is the absolute temperature of the gas.

PARTITION FUNCTION

Let us consider an assembly of ideal gas molecule obeying classical statistics i.e Maxwell – Boltzmann distribution law. Using this distribution law, let n_i molecules occupy ith state with energy between E_i and E_i+dE_i and degeneracy g_i, then

$n_i = g_i \; n_i = g_i \; e^{-\alpha} \; e^{-E_i/kT}$

$= g_i \; A \; e^{-\beta E_i}$ where $A = e^{-\alpha}$ and $\beta = 1/kT$

So the total number of molecules in the system

$N = \Sigma n_i \;\; = \;\; A \; \Sigma g_i \; e^{-\beta E_i} \;\; ; \; N/A = \;\; \Sigma g_i \; e^{-\beta E_i}$

$= \;\; Z$ where Z is called the Boltzmann's partition function or simply the partition function.

The term $\Sigma g_i \; e^{-\beta E_i}$ represents the sum of all the $\Sigma g_i \; e^{-\beta E_i}$ terms for every energy state of the given molecule. Consequently, the quantity Z indicates that how the gas molecules of a system are distributed or partitioned among the various energy levels and hence is called partition function.

UNIT IV
QUANTUM STATISTICAL MECHANICS

QUANTUM STATISTICS – BASIC CONCEPTS

Postulatory Foundations Of Quantum Mechanics :

Postulate I : In classical mechanics, the state of a system is specified by its generalized coordinates q and generalized momenta p at a particular time t. In quantum mechanics; the complete knowledge of a dynamical state (values of p and q at a time t) cannot be determined. The state of the system is completely determined by the state function or wavefunction $\psi(q, t)$.

The wavefunction, in general, is complex, finite, single valued and continuous. $\psi \psi^*$ denotes the probability of finding the system in a volume dq at time t, where ψ^* is the complex conjugate of ψ. All the possible information about the system can be derived from this wavefunction.

In general the state of a system cannot be measured directly. We measure certain physical quantities such as energies, momenta etc which are called observables.

Postulate II : Any observable or dynamical variable can be represented by an operator say A (p, q, t). An operator A is a mathematical operation which may be applied to a function f(x) whieh changes the function to another function g(x). This can be represented as

Af(x) = g(x)

Moreover, the operators must be so chosen that for any pair of operators A and B

(AB - BA) = (h/2лi) [A,B]

...(2)

where (AB - BA) is known as commutator of the two operators and [A,B] is an operator associated with the classical poisson bracket

Postulate III : For an assembly of N identical system, with N->α, all in the state ψ (q, t) at the time t, and if a measurement of a (p, q) is made at t on all these systems, then the average value a of a (p, q) is found from the following equation

a(t) = ∫ψ*(q, t) A (p, q) ψ (q, t) dq / ψ * (q, t) ψ (q, t) dq

where ψ^* stands for the complex conjugate of ψ.

Postulate IV : The time variation of a quantum mechanical state is determined by the equation

H ψ(q.t) = (ih/2л) ψ(q,t)/t

$\Psi(q,t) = \psi(q)e^{-(2\pi i/h)}E_n t$

Where H is the Hamiltonian operator.

TRANSITION FROM CLASSICAL STATISTICAL MECHANICS TO QUANTUM STATISTICAL MECHANICS :

The two important concepts of quantum mechanics which have greatly influenced the transition from classical statistical mechanics to quantum mechanics are

(1) Physical quantities, in quantum mechanics, in general are assumed to have discrete spectra. This fact requires that finite sums or infinite series be used in place of the usual integrals of classical mechanics.

(2) Physical quantities, in addition to depending on the usual Hamiltonian variables of classical mechanics, depend on 'spin' variables which are essential to quantum physics and have no analogue in classical mechanics. Assemblies of particles with integral spins and zero spin are found to obey Bose-Einstein statis-tics, and assemblies of particles with half spins are found to obey Fermi-Dirac statistics. In classical mechanics the state of the system is uniquely determined if all the physical quantities associated with the system are known, whereas in quantum mechanics, the state of a system defines the physical quantities only a random variables i.e., it determines the laws of distribution obeyed by the physical quantities and not their values.

DISTRIBUTION LAWS

A study of statistical mechanics can be classified mainly into two divisions :

(a) classical statistics or Maxwell-Boltzmann statistics,

(b) quantum statistics.

The quantum statistics was developed by Bose, Einstein, Fermi and Dirac. This can again be put in two categories :

(i)   Bose-Einstein (B—E) statistics.
(ii)   (ii) Fermi-Dirac (F—D) statistics.

The classical statistics is based on the classical results of Maxwell-Boltzmarin velocity distribution of particles of an assembly in equilibrium. This successfully explains the observed phenomenon such as pressure, temperature, energy etc. This fails to account several observed

phenomenon like black body radiation, specific heat at low temperature, photoelectric effect etc.

In order to deduce the Planck's radiation law, Bose in 1924, formulated certain fundamental assumptions which were different from classical statistics. On the basis of these assumptions he derived the radiation law. On the same year, Einstein utilised practically the same principles and explained the kinetic theory of gases. The new statistics developed by Bose and Einstein is known as Bose Einstein statistics.

In 1926, Fermi and Dirac modified Bose-Einstein statistics using some additional principles suggested by Pauli in connection with -electromagnetic structure of atoms. According to Pauli principle no two electrons having all the quantum numbers same, may be in the same state. In statistical form two or more phase points cannot possibly occupy the same phase cell. In this way the new quantum statistics developed by Fermi and Dirac is known as Fermi-Dirac statistics. Now we consider the following three kinds of identical particles :

(a) Identical particles of any spin which are separated in the assembly and can be distinguished from one another. The molecules of the gas are particles of this kind.

(b) Identical particles of zero or integral spin which cannot be distinguished from one another. These particles are known as Bose particles or Bosons. The do not obey Pauli's exclusion principle. Photons, a-particles, etc. are the particles of this kind.

(c) Identical particles of half integral spin and which cannot be distinguished from one another. These particles obey Pauli's exclusion principle. Electrons, protons, neutrons are particles of this kind.

The first kind of these particles are classical particles while the second and third kinds of particles are quantum particles. The essential distinction between classical statistics and quantum statistics is that in classical statistics the particles of a system are distinguishable among themselves and are individually recognisable, while in quantum statistics the particles are not distinguishable.

To understand the distinction between Bose-Einstein (B—E) statistics and Fermi Dirac (F—D) statistics, let us divide a volume accessible to a system into number of cells, then according to Bose-Einstein statistics more than one particle can occupy the same cell, while according to Fermi-Dirac statistics, only one particle, or none can occupy the same cell.

BOSE-EINSTEIN STATISTICS

The conditions of Bose-Einstein statistics are :

1) The particles are indistinguishable from each other so that there is no distinction between the different ways in which ni par-ticles can be chosen.
2) Each cell or sublevel of ilk quantum state may contain 0, 1, 2...,n; identical particles.
3) The sum of energies of all the particles in the different quantum groups taken together constitutes the total energy of the system.

For this distribution, let us imagine a box divided into gi sections and the particles are distributed among these sections. The choice that which of the compartment will have the sequence, can be made in gi ways. Once this has been done, the remaining (gi-1) compartments and ni particles i.e. total particles can be arranged in any order i.e. number of ways doing this will be equal to

$$(ni+gi—l)! \quad ....(1)$$

Thus the total number of ways realising the distribution will be gi (ni+ gi-1) ! ….(2)

The particles are indistinguishable and therefore rearrangement of particles will not give rise to any distinguishable arrangement. There are ni ! permutations which correspond to the same configuration, hence equation 1 should be divided by ni ! Secondly, the distributions which can be derived from one another by mere permutation of the cells among themselves, do not produce different states, the equation 1 should also be divided by gi ! We thus obtain the required number of ways as

$$gi \ (ni+gi-1)! \ /gi \ ! \ ni \ ! \ ....(3)$$

$$or \ (ni+gi-1)! \ / \ ni! \ (gi-1)! \quad ....(4)$$

Similar expressions will be for the various other quantum states. Therefore, the total number of ways in which n1 particles can be assigned to the level with energy E1, n2 to E2 …. and so on is given by the product of such expressions as given below

$$W = \prod (\ (ni+gi-1)! \ / \ ni! \ (gi-1)! \ ) \ x \ constant \quad (5)$$

So to obtain the condition of maximum probability take log on both the sides we have

$$log \ W = \Sigma \ (log \ (ni +gi-1) \ ! \ – log \ ni! \ - log \ (gi-1) \ ! \ ) + constant \qquad ....(6)$$

By Stirling's Theorem, $\log_e N! = N \log_e N - N$

$\log W = \Sigma(ni+gi) \log (ni+gi) - (ni+gi) - ni \log ni + ni - gi \log gi + gi$ ......(7)

$= \Sigma(ni+gi) \log (ni+gi) - ni \log ni - gi \log gi$ ...(8)

For the most probable state, $d (\log W) = 0$ ....(9)

$0 = \Sigma(\log (ni+gi) - \log ni) dni$ ......(10)

Multiplying Σdni by $-\alpha$ and $\Sigma Ei \, dni$ by $-\beta$ and adding to equation (10)

$\Sigma(\log (ni+gi) - \log ni) - \alpha - \beta Ei)dni = 0$

As the various dni are independent of one another, the expression within the bracket should be zero for each value of i.

$\log (ni + gi) - \log ni - \alpha - \beta Ei = 0$

$\log (ni+gi/gi) = \alpha + \beta Ei$

Taking exponentials,

$(ni+gi/gi) = e^{-\alpha - \beta Ei}$

$ni = gi / e^{-\alpha - \beta Ei} - 1$ ...(11)

Since ni is the number of molecules having energy Ei , the right hand side should be dimensionless. Since Ei is expressed in energy unit, β should be the reciprocal of the energy unit. The product β and Ei should be a dimensionless quantity. For this $1/\beta$ should be equal to $1/kT$ where k is the Boltzmann constant and T is the temperature in kelvin (kT = joules).

$ni = gi / e^{-(\alpha - Ei/kT)} - 1$ .....(12)

This equation is known as   Bose-Einstein distribution law.

FERMI-DIRAC STATISTICS

In the case of Fermi-Dirac statistics, the problem is assigning ni indistinguishable particle to gi distinguishable levels under the restriction that only one particle will be occupied by a single level ; obviously, gi, must be greater than or equal to ni, because there must be atleast one elementary wave function available for every element in the group.

Thus in Fermi-Dirac statistics, the conditions are

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

(2) Each sublevel or cell may contain 0 or one particle. Obviously g, must be greater than or equal to ni.

(3) The sum of energies of all the particles in the different quantum groups taken together constitute the total energy of the system.

Now the distribution of ni particles among the g, states can be done in the following way: It is easily find that the first particle can be put in any one of the ith level in gi ways. Now according to Pauli exclusion principle no more particles can be assigned to that filled state. Thus we are left with (gi - 1) states in (gi —1) ways, and so on.

Thus the number of ways in which ni, particles can be assigned to gi states is

gi (gi-1) (gi-2) (gi—ni+1) gi!

gi! /(gi-ni) !   ……(1)

The permutations among identical particles do not give dis-tinct distribution, and hence such permutations must be excluded from equation (1), which can be done on dividing it by ni!. Thus we have the required number as

 gi !/ (gi—ni)!

The total number of eigen states for which whole system is given

by

W = gi / ni!(gi - ni)!

The probability of the specific state is

W = ∏ (gi! / ni! (gi-1)!) x constant   (5)

So to obtain the condition of maximum probability take log on both the sides we have

log W = Σ (log gi ! – log ni! - log (gi-ni) !) + constant   …………….(6)

By Stirling's Theorem, $\log_e N! = N \log_e N - N$

log W = Σgi log gi – gi - ni log ni +ni – (gi+ni) log (gi -ni) + (gi-ni)   ……(7)

$= \Sigma g_i \log g_i - n_i \log n_i - (g_i + n_i) \log (g_i - n_i) \ldots (8)$

For the most probable state, $d (\log W) = 0 \ldots (9)$

$0 = \Sigma (\log (g_i - n_i) - \log n_i) dn_i \ldots (10)$

Multiplying Σdn_i by $-\alpha$ and $\Sigma E_i dn_i$ by $-\beta$ and adding to equation (10)

$\Sigma (\log (g_i + n_i) - \log n_i) - \alpha - \beta E_i) dn_i = 0$

As the various dn_i are independent of one another, the expression within the bracket should be zero for each value of i.

$\log (g_i + n_i) - \log n_i - \alpha - \beta E_i = 0$

$\log (g_i - n_i)/n_i) = \alpha + \beta E_i$

Taking exponentials,

$(g_i - n_i /n_i) = e^{\alpha + \beta E_i}$

$n_i = g_i / e^{\alpha + \beta E_i} + 1 \quad \ldots (11)$

Since n_i is the number of molecules having energy E_i, the right hand side should be dimensionless. Since E_i is expressed in energy unit, β should be the reciprocal of the energy unit. The product β and E_i should be a dimensionless quantity. For this $1/\beta$ should be equal to $1/kT$ where k is the Boltzmann constant and T is the temperature in kelvin (kT = joules).

$n_i = g_i / e^{(\alpha + E_i/kT)} + 1 \quad \ldots (12)$

This equation is known as Fermi - Dirac distribution law.

Bose-Einstein Condensation

A state of matter in which atoms or particles are chilled to such low energies that they 'condense' into a single quantum state. The atoms are bosonic in nature; that is, their total spin must possess an integral value, such as 0, 1, 2. Particles, like everything, have wave properties, such as wavelength. The trick is getting into a regime where the wave properties emerge. The wavelength (called Debroglie wavelength) of an atom is related to its temperature - the colder the atom, the longer the wavelength. At room temperature, atoms can be treated like billiard balls bouncing around. At low temperatures, the wavelengths become longer, and so the wave

properties become relevant. For sufficiently low temperature, a few millionths of a degree above zero temperature, the bosonic atoms effectively become overlapping waves that share the same phase. The atoms become a BEC, which has quantum mechanical behavior.

The BEC phenomenon was first predicted by Satyendra Bose and Albert Einstein in the 1920s, hence the name. BEC was first noted to exist in liquid helium.

Consider a gas of weakly-interacting bosons. It is helpful to define the gas's *chemical potential*,

$$\mu = k T \alpha, \tag{1}$$

whose value is determined by the equation

$$N = \sum_r \bar{n}_r = \sum_r \frac{1}{e^{\beta(\epsilon_r - \mu)} - 1}. \tag{2}$$

Here, N is the total number of particles, and ϵ_r the energy of the single-particle quantum state r. Because, in general, the energies of the quantum states are very closely spaced, the sum in the previous expression can approximated as an integral. Now, the number of quantum states per unit volume with wavenumbers in the range k to k+dk is

$$\rho_k(k)\, dk = \frac{k^2}{2\pi^2}\, dk. \tag{3}$$

However, the energy of a state with wavenumber k is

$$\epsilon = \frac{\hbar^2 k^2}{2 m}, \tag{4}$$

where m is the boson mass. Let $\rho(\epsilon)\, d\epsilon$ be the number of bosons whose energies lies in the range ϵ to $\epsilon + d\epsilon$. It follows that

$$\rho(\epsilon)\, d\epsilon = V\, \rho_k(k)\, \frac{dk}{d\epsilon}\, d\epsilon, \tag{5}$$

where V is the volume of the gas. Here, we are assuming that the bosons are spinless, so that there is only one particle state per translational state. Hence,

$$\rho(\epsilon) = \frac{V}{4\pi^2} \frac{(2\,m)^{3/2}}{\hbar^3} \epsilon^{1/2},$$

(6)

and Equation (2) becomes

$$N = \int_0^\infty \frac{\rho(\epsilon)}{e^{\beta\,(\epsilon-\mu)} - 1} \, d\epsilon = \frac{V}{4\pi^2} \frac{(2\,m)^{3/2}}{\hbar^3} \int_0^\infty \frac{\epsilon^{1/2}}{e^{\beta\,(\epsilon-\mu)} - 1} \, d\epsilon.$$

(7)

However, there is a significant flaw in this formulation. In using the integral approximation, rather than performing the sum, the ground-state, $\epsilon = 0$, has been left out. Under ordinary circumstances, this omission does not matter. However, at very low temperatures, bosons tend to condense into the ground-state, and the occupation number of this state becomes very much larger than that of any other state. Under these circumstances, the ground-state must be included in the calculation.

We can overcome the previous difficulty in the following manner. Let there be N_0 bosons in the ground-state, and N_{ex} in the various excited states, so that

$$N = N_0 + N_{ex}.$$

(8)

Because the ground-state is excluded from expression (7), the integral only gives the number of bosons in excited states. In other words,

$$N_{ex} = \frac{V}{4\pi^2} \frac{(2m)^{3/2}}{\hbar^3} \int_0^\infty \frac{\epsilon^{1/2}}{e^{\beta\,(\epsilon-\mu)} - 1} \, d\epsilon.$$

(9)

Now, because the ground-state has zero energy, its mean occupancy number is

$$N_0 = \frac{1}{e^{-\mu/kT} - 1}.$$

(10)

Moreover, at temperatures very close to absolute zero, we expect $N_0 \simeq N$, which implies that

$$N \simeq \frac{1}{e^{-\mu/kT} - 1}. \tag{11}$$

We conclude that

$$-\frac{\mu}{kT} \simeq \ln\left(1 + \frac{1}{N}\right) \simeq \frac{1}{N}, \tag{12}$$

for large N. Hence, at very low temperatures, we can safely set $\exp(-\mu/kT)$ equal to unity in Equation (9). Thus, we obtain

$$N_{ex} = \frac{2}{\sqrt{\pi}}\left(\frac{2\pi m kT}{h^2}\right)^{3/2} V \int_0^\infty \frac{x^{1/2}}{e^x - 1}\,dx, \tag{13}$$

Furthermore, $\Gamma(3/2) = \sqrt{\pi}/2$, and $\zeta(3/2) = 2.612$. Hence,

$$N_{ex} = \zeta(3/2)\, V \left(\frac{2\pi m kT}{h^2}\right)^{3/2}. \tag{14}$$

The so-called *Bose temperature*, T_B, is defined as the temperature above which all the bosons are in excited states. Setting $N_{ex} = N$ and $T = T_B$ in the previous expression, we obtain

$$T_B = \frac{h^2}{2\pi m k}\left[\frac{N}{\zeta(3/2)\, V}\right]^{2/3}. \tag{15}$$

Moreover,

$$\frac{N_{ex}}{N} = \left(\frac{T}{T_B}\right)^{3/2}. \tag{16}$$

Thus, the fractional number of bosons in the ground-state is

$$\frac{N_0}{N} = 1 - \left(\frac{T}{T_B}\right)^{3/2}. \tag{17}$$

combining Equations (9) (with $N_{ex} = N$) and (15) yields

$$\Gamma(3/2)\,\zeta(3/2) = \left(\frac{T}{T_B}\right)^{3/2} \int_0^\infty \frac{x^{1/2}}{e^{x-\alpha}-1}\,dx, \tag{18}$$

where $x = \epsilon/(kT)$ and $\alpha = \mu/(kT)$. Expanding in powers of $e^{-(x-\alpha)}$, we obtain

$$\Gamma(3/2)\,\zeta(3/2) = \left(\frac{T}{T_B}\right)^{3/2} \Gamma(3/2) \sum_{n=1,\infty} \frac{e^{n\alpha}}{n^{3/2}}, \tag{19}$$

where y = nx , which reduces to

$$\zeta(3/2) = \left(\frac{T}{T_B}\right)^{3/2} \sum_{n=1,\infty} \frac{e^{-n\alpha}}{n^{3/2}}. \tag{20}$$

The previous equation can be solved numerically to give $\alpha = \mu/(kT_B)$ as a function of T/T$_B$.

UNIT V
APPLICATIONS OF Q.M.S

APPLICATION OF BOSE - EINSTEIN STATISTICS

Planck radiation law (or Photon gas)

The Planck's radiation formula for photons can be derived using Bose-Einstein distribution. Consider a hollow enclosure containing radiations at a constant temperature T. These radiations carry energy in discrete units or bundles or quanta. According to quantum theory, radiation frequency υ has a quantum of energy $h\upsilon$ where h is Planck's constant and momentum $h\upsilon/c$ where c is the velocity of light.

These quanta are known as photons and can be treated as particles. The radiation inside the hollow enclosure consists of a very large number of photons of different energies as these have different wavelengths (or frequencies) and be supposed to form a photon gas. There is an important difference between the photons and the other particles, namely, the photon number is not constant. That means, $\alpha = 0$

Hence, Bose - Einstein distribution law is

$$n_i = g_i / e^{-(E_i/kT)} - 1 \quad \dots(1)$$

The number of photons in the frequency range υ and $\upsilon + d\upsilon$ is given by

$$n(\upsilon)d\upsilon = g(\upsilon)d\upsilon / e^{-(h\upsilon/kT)} - 1 \quad \text{since } E_i = h\upsilon \quad \dots(2)$$

The number of cells in the phase space for photons with left handed and right handed polarisation is given by

g(p)dp = 2 x (volume in the phase space / h3)

The factor 2 comes for the two types of photons.,

$$g(p)dp = 2x(\int dv \, dy \, dz \, dp_x \, dp_y \, dp_z)h^3$$

$$= 2 \times h3$$

Jdx dy dz f dpxdpydpz

$= 2 (V/h^3)$ x volume of the sphere in the momentum space of radius p and thickness dp.

$$= 2 (V/h^3) 4\pi p^2 dp$$

$$g(p)dp = 8\pi(V/h^3) \, p^2 \, dp \quad \dots(3)$$

$p = h/\lambda$ and $\lambda = c/\upsilon$

therefore $p = h\upsilon/c$ and $dp = hd\upsilon/c$,

Substituting the values of p^2 and dp in equation (3).

$g(\upsilon)d\upsilon = (8\pi V/c^3)\upsilon^2\, d\upsilon$ ...... (4)

Substituting equation (4) in equation (2),

$n(\upsilon)d\upsilon = (8\pi V/c^3)\ (\upsilon^2\, d\upsilon\ /\ e^{-(h\upsilon/kT)} - 1\ )$ ...... (5)

      The energy density $E(\upsilon)d\upsilon$ is defined as the amount of energy per unit volume due to radiations lying between the frequencies u and u + do is given by

$E(\upsilon)d\upsilon = h\upsilon n(\upsilon)d\upsilon / V$

Substituting the value of n (u)d u from equation (5)

$= h\upsilon 8\pi V\upsilon^2 d\upsilon\ /\ Vc^3\ (e^{-(h\upsilon/kT)} - 1\ )$

$E(\upsilon)d\upsilon = 8\pi h\ /\ c^3\ ((\upsilon^2\, d\upsilon\ /\ e^{-(h\upsilon/kT)} - 1\ )$

This is Planck's formula in terms of frequency.

Since $c/\lambda = \upsilon$ and $d\upsilon = (c/\lambda^2)d\lambda$

$E(\lambda)d\lambda = (8\pi h/\lambda^5)\ (d\lambda\ /\ e^{-(hc/\lambda kT)} - 1\ )$

This is known as Planck's formula for black body radiations.

APPLICATION OF FERMI - DIRAC STATISTICS – ELECTRON GAS

      The behaviour of free electrons inside a metallic conductor can be studied on the basis of Fermi - Dirac statistics. The free electrons continuously collide with the fixed ions and they thus behave like an electron gas.

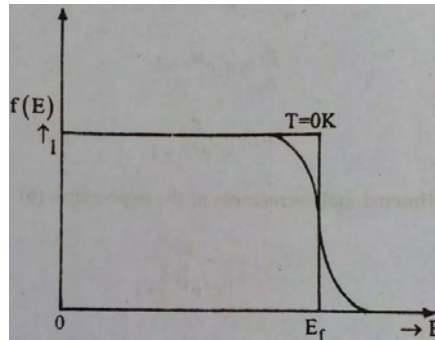The distribution function for electrons is given by f(E)

$= n_i /g_i = 1/e^{(E - Ef / kT)} + 1$

From equation $n_i = g_i /e^{(\alpha - Ei/kT)} + 1$, Ei is replaced by E and α by $- Ef / kT$. The energy Ef is called Fermi energy.

At 0 K, the distribution function has the form

f (E) = 1 when E< E f and f (E) = 0 when E> Ef

That means, all energy levels below Ei f are completely filled and all levels above Ei are completely empty as shown.

When the temperature increases, f(E) changes from 1 to 0 more and more gradually.

When E = Ef, f (E) = ½ at all temperatures.

The probability of finding an electron with energy equal to the Fermi - energy in 1 a metal is thus ½ at any temperature.

The number of electrons in terms of momentum is given by

g(p)dp = 2 x V/h^3 x volume of the cell in momentum space

The factor 2 is for the two types of electron with spin + ½ and – ½

g(p)dp = 2V4лp2dp/h^3 ...(2)

But E = 1/2 mv^2 and p = mv

Substituting p and p.dp in equation (2), the number of quantum states available to electrons with energies between E and E + dE is given by

g (E)dE = (8лV/h^3) (2mE)$^{1/2}$ mdE ....(3)

where 'm' is the mass of the electron and V is the volume of the electron gas.

The energy value up to which all the energy states are full at 0 l< and above which all the energy states are empty is known as Fermi energy denoted by Ef At 0 K, the number of electrons (N) is equal to the number of energy states occupied by the electron from 0 to Ef, since each state has only one electron. E

N = ∫g(E)dE

Substituting the value for g (E) dE

N = 16√2лVm$^{3/2}$ Ef $^{3/2}$/ h^3

Ef $^{3/2}$ = 3Nh^3/(16√2лVm$^{3/2}$)

Therefore $E_f = (h^2/2m)(3N/8\pi V)^{2/3}$

The quantity N/V is the density of free electron. It is the number of free electrons per unit volume of the metal.

Fermi Energy and Fermi Temperature

The maximum kinetic energy of free electron in the metal at 0 Kelvin is called Fermi energy. The Fermi temperature is given by $\Theta_f = E_f/k$

DEGENERACY

The position of a particle in Quantum statistics cannot be measured accurately according to Heisenberg Uncertainty Principle. That means we cannot say that in the ith energy state all ni particles have energy exactly equal to Ei. However, it can be safely expressed that energy of each of particles is very close to Ei. It means that that can be a number of energy levels around Ei in which particles are distributed. let the number of such energy levels be gi which is called the degeneracy of the energy state.
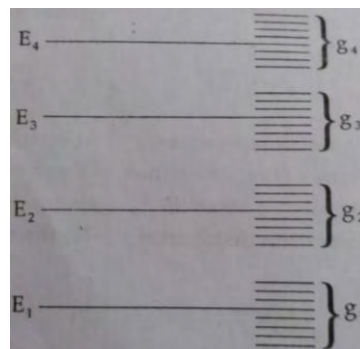

Figure shows the degeneracy of all energy states. For the energy state Ei, there are ni particles having energies around Ei. There are sub energy levels in which ni bosons are distributed. Each of gi levels can have any number of particles present in it. Each energy level Ei consists of gi states.

It is therefore concluded that a system with Quantum particles obeying either Bose - Einstein or Fermi - Dirac statistics maybe called degenerate gas.

PAULI PARAMAGNETISM

In a non-magnetic system, there are equal number of spin up and spin down electrons ($n\uparrow = n\downarrow = n$). In presence of magnetic field, the Zeeman energy term shifts the bands which means that there is an imbalance of up and down spins creating a magnetization.

Let us consider a simple model with on-site repulsion (i.e. an energy cost U when two electrons occupy the same site). As per the Pauli exclusion principle, it is required that if two electrons were to occupy the same site, they need to have opposite spins.

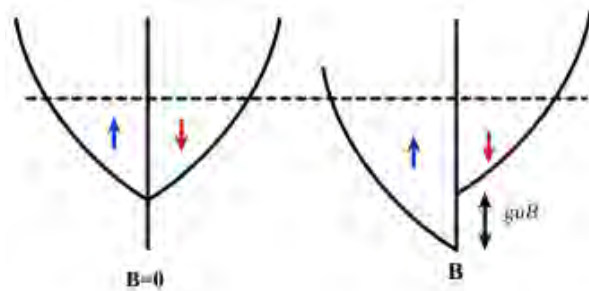The Zeeman term in the Hamiltonian is

$H_z = -g\mu \cdot B$ ....(1)

where μ is the spin magnetic moment of the electron.

Considering the magnetic field applied in the z-direction

$H_z = -g\mu \cdot B = -g\mu_z B$ ......(2)

where $\mu_z = \pm\mu_B/2$ is the spin magnetic moment for up/down spins (Bohr magneton μ_B).

The electrons can lower their energies by aligning parallel to the magnetic field. There is an imbalance in the number of up and down spins $n\uparrow/\downarrow = n \pm \delta n$. The change in number of spin can be related to the change in energy by means of the density of states.

The density of states is defined as the number of states in the energy interval [E, E + dE] is $D(E) = dn\ dE$ ......(3)

Since the occupation change happens close to the Fermi level, we can relate the variation in number density δn and the change in energy dE through the density of states at the Fermi level.

$\delta n = D_F\ dE = D_F\ g\ \mu_B\ B$ ......(4)

Thus the change in magnetization is $\delta m = (g\ \mu_B/\ 2)\ 2\delta n = D_F\ (g\ \mu_B)^2\ B$ ....(5)

Therefore the Pauli paramagnetic susceptibility is

$\chi Pauli = \delta m\ /B = D_F\ (g\mu_B)^2$ ....(6)

BOOKS FOR STUDY AND REFERENCE

1. Elementary Statistical Mechanics by GUPTA KUMAR
2. Thermal Physics and Statistical Mechanics by Dr. D. JAYARAMAN, Dr. K. ILANGOVAN
3. Statistical Mechanics by SATHYA PRAKASH
4. Heat, Thermodynamics and statistical Physics by BRIJLAL, Dr. N. SUBRAMANIYAM and P. S. HEMNE