Note further that if it is given that system is isolated then its total energy will be constant equal to $-\mu H$. Then postulate of equal a priori probabilities asserts that when the system is in equilibrium it is equally likely to be found in any of these three states.

1•1. PHASE SPACE : SPECIFICATION OF STATES OF A SYSTEM :

In classical mechanics, the position of a point particle is described in terms of three cartesian coordinates x, y, z and the particle is said to have three degrees of freedom. The state of the motion of particle is described in terms of velocity components $\dot{x}, \dot{y}, \dot{z}$ (where the dot indicates the differentiation with respect to time). Sometimes it is more convenient to use momentum coordinates $p_x, p_y, p_z\,(m\dot{x}, m\dot{y}, m\dot{z}$ where m is the mass of the particle) instead of velocity coordinates. Thus the position of a single particle can be specified in terms of cartesian coordinates x, y, z and its corresponding momentum components p_x, p_y, p_z. In order to apply laws of mechanics, it is convenient to devise a scheme which can be used to describe the state (position and momentum) of the particle at a particular instant. For this purpose, we imagine a six dimensional space in which the six coordinates x, y, z and p_x, p_y, p_z are marked along six mutually perpendicular axes in space. *The combined position and momentum space is then called as phase space or* Γ *space.* A point in the phase represents the position and momentum of the particle at some particular instant.

Division of phase space into cells : The meaning of a point in phase space can be understood with the help of uncertainty principle. The phase space is divided into six dimensional cells whose sides are $dx, dy, dz, dp_x, dp_y, dp_z$. Such cells are called phase cells. Further, we approach close to the limit of a point in phase space reducing the size of a cell. The volume of each cell is given by

$$d\tau = dx\ dy\ dz\ dp_x\ dp_y\ dp_z$$

But according to uncertainty principle,

$$dx\ dp_x \geq h, \qquad dy\ dp_y \geq h, \qquad dz\ dp_z \geq h,$$

Thus $$d\tau \geq h^3$$

A point in the phase space is actually considered to be a cell whose minimum volume is of the order of h^3. So the particle in the phase space can not be considered exactly located at point x, y, z, p_x, p_y, p_z but can only be found somewhere within a phase cell centred at that point.

Phase-space diagram of an oscillator :

Consider a three dimensional harmonic oscillator of mass m and spring constant k, having energy

$$E = \frac{p^2}{2m} + \frac{1}{2}kq^2,$$

where the first term on the right is kinetic energy while second term is potential energy; q and p are position coordinate and conjugate momentum respectively.

The above equation can be written as

$$\frac{p^2}{2mE} + \frac{kq^2}{2E} = 1$$

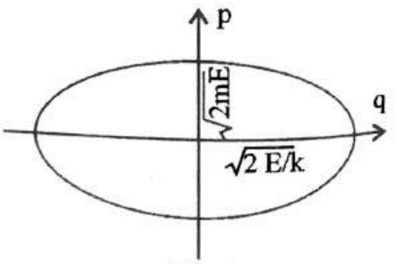


Fig. 1

or $$\frac{q^2}{(2E/k)}+\frac{p^2}{2mE}=1.$$

For constant energy E, equation (1) describes an ellipse in phase space *i.e.*, in the q-p plane. The phase points are those lying on the elliptical path, having a semi major axis of $\sqrt{\left(\frac{2E}{k}\right)}$ and a semi-minor axis of $\sqrt{(2mE)}$. At any particular instant, the phase of the oscillator is represented by some point on the ellipse.

The area of the ellipse in the space is given by πab where a is semi-major axis and b is semi-minor axis. Then

$$A=\pi ab=\pi\sqrt{\left(\frac{2E}{k}\right)}\sqrt{(2mE)}=2\pi E\sqrt{(m/k)}$$

It represents the phase space available to the oscillator having energy between 0 and E. The phase space available to the oscillator having energy between E and $E + dE$ is then given by

$$\delta A=2\pi\sqrt{\frac{m}{k}}\,\delta E$$

and represents the region of states *accessible* to the oscillator.

1•1–1. VOLUME IN PHASE SPACE :

We shall consider the volume of the momentum space lying between the values of total momentum p and $(p + dp)$. A small element of momentum space with coordinates in the range p to $(p + dp)$, θ to $(\theta+d\theta)$, and ϕ to $(\phi+d\phi)$ is shown in fig. 2. The element is considered in polar coordinates p, θ and ϕ like the polar coordinates of position r, θ and ϕ.

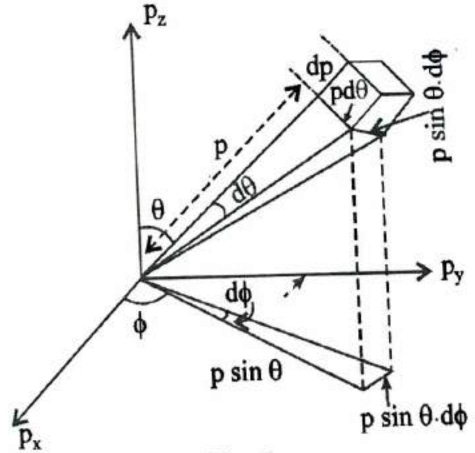


Fig. 2

The volume of the element is given by

$$d\tau_p=dp.\,pd\theta.\,p\,\sin\theta d\phi$$
$$=p^2\,dp\sin\theta\;d\theta d\phi \qquad \ldots(1)$$

Again, the volume of momentum space lying between p and $(p + dp)$, and independent of direction is given by

$$\Delta\tau_p=p^2\,dp.\int_0^{\pi}\sin\theta\,d\theta.\int_0^{2\pi}d\phi=\pi p^2\,dp. \qquad \ldots(2)$$

This volume is same as the volume of a spherical shell of thickness dp lying between p and $(p + dp)$.

Now we shall express the volume of phase space $\Delta\tau$ in terms of a volume $\Delta\tau_p$ of momentum space and the volume V of ordinary space. The relationship is given by

$$\Delta\tau=4\pi p^2\,dp\int_V dx\,dy\,dz$$

or $$\Delta\tau=4\pi p^2\,dp.V \qquad \ldots(3)$$

The element of phase space can also be expressed in terms of kinetic energy. We know that $\varepsilon = \frac{p^2}{2m}$, where m is the mass of the particle. Therefore

$$p = \sqrt{(2m\varepsilon)} \quad \text{and} \quad dp = \left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon$$

Substituting these values in equation (3), we get

$$d\tau = 4\pi(2m\varepsilon)\left(\frac{m}{2\varepsilon}\right)^{1/2} d\varepsilon . V$$

or

$$d\tau = 2\pi(2m)^{3/2}\varepsilon^{1/2} d\varepsilon . V \qquad \text{...(4)}$$

The equations (3) and (4) are of great importance in statistical mechanics as these are used in solving a number of problems.

1•1–2. NUMBER OF PHASE CELLS IN GIVEN ENERGY RANGE OF HARMONIC OSCILLATOR

For one dimensional oscillator, the area of a phase cell in phase space is given by

$$\delta x \, \delta p_x = h$$

as phase is two dimensional $(x - p_x)$.

The energy E of the oscillator with mass m is given by

$$E = \frac{p_x^2}{2m} + \frac{1}{2}kx^2$$

or

$$\frac{x^2}{(2E/k)} + \frac{p_x^2}{2mE} = 1 \qquad (1)$$

The equation represents an ellipse with semi major axis $a = \sqrt{\frac{2E}{k}}$ and semi-minor axis $b = \sqrt{(2mE)}$.

The phase space area of the oscillator having energy between 0 and E is

$$\pi ab = \pi\sqrt{\frac{2E}{k}}\sqrt{(2mE)} = 2\pi E\sqrt{\frac{m}{k}} \qquad \text{...(2)}$$

We know that the frequency ν of the oscillator is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \quad \text{or} \quad \sqrt{\frac{m}{k}} = \frac{1}{2\pi\nu} \qquad \text{...(3)}$$

From eqs. (2) and (3), area of phase space is

$$= 2\pi E \times \frac{1}{2\pi\nu} = \frac{E}{\nu}$$

so number of phase cells

$$= \frac{\text{area of phase space}}{\text{area of phase cell}}$$

$$= \frac{E/\nu}{h} = \frac{E}{h\nu}.$$

1•1–3. NUMBER OF PHASE CELLS IN THE GIVEN ENERGY RANGE FOR THREE DIMENSIONAL FREE PARTICLE

The microstate of a particle can be specified by three position coordinates x, y, z and three momentum coordinates p_x, p_y, p_z. The volume of phase cell in phase space is given by

$$\delta x\, \delta y \delta z\; \delta p_x\, \delta p_y\, \delta p_z = h^3 \qquad \ldots(1)$$

$$\text{Total volume of phase space } = \iiint\iiint dx\, dy\, dz\, dp_x\, dp_y\, dp_z$$

$$= V \iiint dp_x\, dp_y\, dp_z \qquad \ldots(2)$$

because $\iiint dx\, dy dz = V$

Consider that in the energy range 0 to E, the possible values of momentum are from 0 to p. Now

$$\iiint dp_x\, dp_y\, dp_z = \frac{4}{3}\pi\, p_{\max}^3$$

as the volume of momentum space is a sphere of radius p.

The energy E of a free particle is only kinetic, so

$$E = \frac{p^2}{2m} \quad \text{or} \quad p_{\max}^2 = p_x^2 + p_y^2 + p_z^2 = 2mE$$

$$\text{Therefore} \qquad \iiint dp_x\, dp_y\, dp_z = \frac{4}{3}\pi\,(2mE)^{3/2} \qquad \ldots(3)$$

From eqs. (2) and (3), the volume of phase space

$$= V\left\{\frac{4}{3}\pi\,(2mE)^{3/2}\right\}$$

so that number of cells in phase space

$$= V\left\{\frac{4\pi}{3}(2mE)^{3/2}\right\}\times\frac{1}{h^3}$$

$$= \frac{4\pi V}{3h^3}\times(2mE)^{3/2} \qquad \ldots(4)$$

as volume of a phase cell is h^3.

1•2 MORE ABOUT PHASE SPACE, ENSEMBLE AND ENSEMBLE AVERAGES:

We have already discussed about phase space. Now we shall introduce concept of an ensemble.

Let us take gas as a system (Fig. 3a). Each molecule can be specified in space, in cartesian set, by q_1, q_2, q_3 position coordinates and p_1, p_2, p_3 momentum coordinates. Such a space is referred to as μ-space (Fig. 3b), being six dimensional. It means for a system of N molecules there will be $6N$ dimensional space. We, infact, want to represent the whole system of N molecules as a *single point* called *phase point or representative point*. It is done by taking $[q]$ $[p]$ space where $[q]$ stands for $3N$ coordinate axes and $[p]$ for $3N$ momentum axes. It means if a system has f-degrees of freedom (*i.e.*, f for position coordinates and f for momentum coordinates) *elements*. It means all elements have same macroscopic state but different microscopic states (*i.e.*, they differ from one another in position and momenta coordinates of individual molecules). Through the concept of these elements we find ourself able to use the mathematical tool of the theory of probability in order to arrive at the parameters that characterise the whole system under observation.

Ensemble Average : It is the average at a *fixed time* over all the elements in an ensemble. This average closely agrees with time average provided :

(i) The system of interest is a macroscopic system consisting of a large number of molecules so that we can randomise in a true sense the microscopic variables.

(ii) The number of imagined elements that form the ensemble at one time is large so that they can truly represent the range of states accessible to the system over a long period of time.

We shall discuss more about ensemble in the next article.

1•3. ENSEMBLES :

If we have a collection of particles, we shall refer to a single particle as *a system* and to the collection of particles as a whole as *an assembly*. The collection of a large number of assemblies is called as *an ensemble*. All the members of *an ensemble*, which are identical in features like volume, energy and total number of particles are referred to as *elements*. These elements, though identical in structure (same macroscopic state) differ from one another in the coordinates and momenta of the individual molecules *i.e.*, they differ in their microscopic states. The elements, being imaginary, do not interact with each other and behave independently as discussed in art. 1.2.

Thus an ensemble is defined as a collection of a very large number of assemblies which are essentially independent (i.e., in calculating the possible eigenstate of an assembly we do not have to worry about any interaction between the assembly of interest and any of the other assemblies) of one another but which have been made macroscopically as identical as possible. By being macroscopically identical, we mean that each assembly is characterized by the same values of set of macroscopic parameters which uniquely determine the equilibrium state of the assembly.

In an ensemble, the system plays the same role as the non-interacting molecules do in a gas. The macroscopic identity of the systems constituting an assembly can be achieved by choosing the same values of some set of macroscopic parameters. These parameters uniquely determine the equilibrium state of the system. Accordingly three types of ensembles *i.e., microcanonical, canonical* and *grand canonical* are most widely used. Their description is as follows :

1•3–1. MICROCANONICAL ENSEMBLE :

The microcanonical ensemble is a collection of essentially independent assemblies having the same energy E, volume V, and number N of systems; all the systems are of the same type. The individual assemblies are separated by rigid, impermeable and well insulated walls (Fig. 4) such that the values of *E*, *V* and *N* are not affected by the presence of other systems. We can not actually specify the macroscopic energy of an assembly exactly.

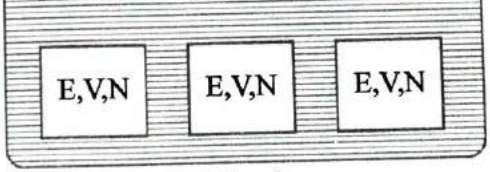


Fig. 4.

Consider a closed system for which the total energy $H(q\,p) = E$ remains constant, according to the equation

$$E(q_1, \ldots q_f, p_1 \ldots p_f) = \text{constant.}$$

The locus of all the phase points having equal energies in phase space is called *energy surface* or *ergodic surface*. We can now imagine a family of such energy surfaces constructed in phase space and let us consider two neighbouring surfaces with energies E and $E + \delta E$ (Fig. 5). Each surface divides the phase space into two parts, one of higher and the other of lower energy, hence they will never intersect each other. As they include some phase volume in between them, they will contain certain number of phase points. The number of phase points between them will be constant. A very useful ensemble can be obtained by taking the density as equal to zero for all values of the energy except in a selected narrow range E and $(E + \delta E)$. Using the terminology of Gibbs, such an ensemble, specified by

$$\rho = \text{constant} \quad (\text{in the range } E \text{ and } E + \delta E)$$
$$\rho = 0, \quad (\text{outside this range})$$

may be called a microcanonical ensemble.

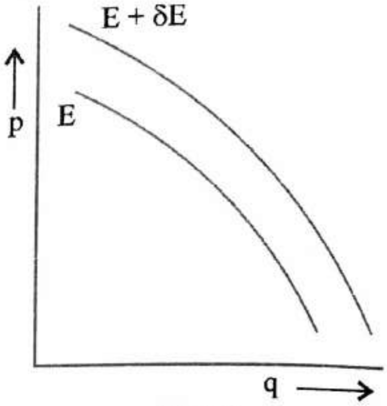


Fig. 5.
Energy shell in phase space.

We observe the following properties :

(i) As ρ is a function of energy, this ensemble is in statistical equilibrium.

(ii) The average properties predicted by such ensemble will not vary in time being in statistical equilibrium.

(iii) As ρ is constant within the energy shell, the distribution of phase points is uniform (by Liouville's theorem).

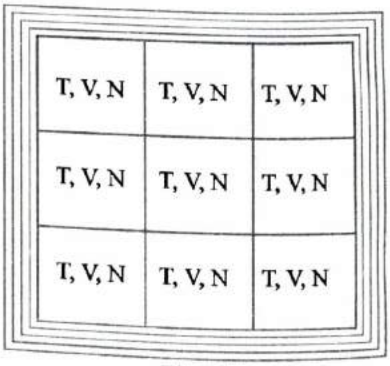
An ensemble of this kind can be regarded as obtained from an originally uniform ensemble by discarding all systems having phase points with positions that do not fall within the limits in the phase space and correspond the energy range E and $(E + \delta E)$.

1•3–2. CANONICAL ENSEMBLE :

The *canonical ensemble is a collection of essentially independent assemblies having the same temperature T, volume V, and number of identical particles N.*

To assure ourselves that all the assemblies have the same temperature, we could bring each in thermal contact with a large heat reservoir at temperature T or we could simply bring *all of the assemblies in thermal contact with each other.*

Fig. 6 represents symbolically a canonical ensemble. The individual assemblies are separated by rigid, impermeable, but diathermic walls. Since energy can be exchanged between the assemblies, they will reach a common temperature.



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

Fig. 6.

Thus in *canonical ensemble, system can exchange energy but not particles.*

1•3–3. GRAND CANONICAL ENSEMBLE :

The microcanonical ensemble is a collection of independent assemblies having the same energy E, volume V and number N of systems. The canonical ensemble is a collection of independent assemblies having the same temperature T, volume V and number of identical systems N. Thus in going from microcanonical ensemble to canonical ensemble, the condition of constant energy has been relaxed. This simplifies the calculations in thermodynamics where the exchange of energy takes place. Now the next logical step is to abandon the condition of total number of particles. Actually in chemical process this number varies and in various physical problems, *e.g.*, radioactive decay, it is difficult to keep the number of particles constant. Such an ensemble in which *exchange of energy as well as of particles takes place with the heat reservoir is known as grand canonical ensemble.*

The grand canonical ensemble is a collection of essentially independent assemblies having same temperature T, volume V and chemical potential μ. We will discuss the chemical potential in a later article.

In the grand canonical ensemble we then effectively have collection of assemblies, each occupying a separate volume V, but which can exchange energy and as well as molecules with each other. Fig. 7 represents a grand canonical ensemble. The individual assembly systems are separated by rigid, permeable, diathermic walls.

The grand canonical ensemble will thus correspond to the situation when we know both the average energy and the average number of particles in an assembly, but are otherwise completely ignorant about the state of the system.

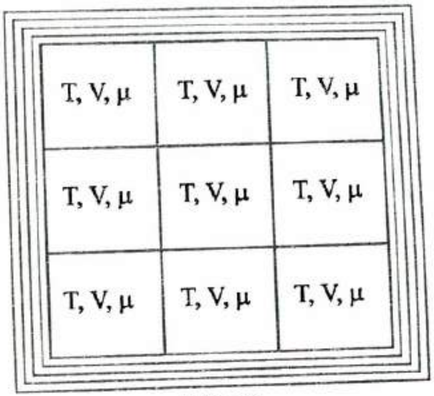


Fig. 7.

1•4. USES OF THE ENSEMBLE :

In article 1.3, we have classified ensembles into three main types. Each type corresponds to a different experimental situation. In fact, the three ensembles which we have introduced are only examples of the infinite number of ensembles that can be considered. These three are particularly useful for two main reasons :

Firstly, they correspond approximately to the types of thermodynamic measurements most frequently made in practice.

Secondly, in large assemblies, it is useful to find that the values of thermodynamic quantities are not very sensitive to the method of measurement. For example, in the measurment of specific heat of a liquid of known mass and thus known particle number, at temperatures far below the boiling point, it matters very little whether the liquid is isolated at constant temperature so that the number of systems is fixed as in a microcanonical ensemble or in equilibrium with its vapour the number of systems is fixed as in a microcanonical ensemble.
so that the number of systems can fluctuate as in grand canonical ensemble.

Example. Let us derive the relation $\rho = \exp.\left(\dfrac{C_1 - E}{K}\right)$, on using the idea of ensemble.

The probability that the phase points of the system S_1 lie in the element of volume dV_1 is $\rho_1(E_1)dV_1$. Similarly, the probability that the phase points of the system S_n lie in the element of volume dV_n is $\rho_n(E_n)dV_n$. Thus the probability that the ensemble lies in the element of volume dV is

$$\rho(E)dV = \rho_1(E_1)dV_1 . \rho_2(E_2)dV_2 ......\rho_n(E_n)dV_n \quad ...(1)$$

where

$$dV = dV_1 dV_2 dV_3 ... dV_n$$

and

$$\rho(E) = \rho_1(E_1)\rho_2(E_2)...\rho_n(E_n).$$

Equation (1) can be written as

$$\log \rho(E) = \sum_n \log \rho_\eta(E_n) \qquad \ldots(2)$$

$$\therefore \qquad \frac{1}{\rho}\left[\frac{\partial \rho}{\partial E_1} dE_1 + \frac{\partial \rho}{\partial E_2} dE_2 + \ldots\right] = \frac{1}{\rho_1}\frac{\partial \rho_1}{\partial E_1} dE_1 + \frac{1}{\rho_2}\frac{\partial \rho_2}{\partial E_2} dE_2 + \ldots.. \qquad \ldots(3)$$

Since ρ depends only on E, quantities like $\frac{1}{\rho_n}\frac{\partial \rho_1}{\partial E_n}$ for different values of n are equal *i.e.*,

$$\frac{1}{\rho_1}\frac{\partial \rho_1}{\partial E_1} = \frac{1}{\rho_2}\frac{\partial \rho_2}{\partial E_2} = \ldots.. = \text{constant} = -\frac{1}{K}(\text{say}). \qquad \ldots(4)$$

Integrating the equations, we get

$$\rho_1 = \exp.\left(\frac{C_1 - E}{K}\right) \qquad \ldots(5)$$

where C_1 and K are constants.

Using equation (1), we arrive at

$$\rho = \exp.\left[\frac{(C_1 + \ldots + C_n) - (E_1 + \ldots + E_n)}{K}\right]$$

or

$$\rho = \exp.\left(\frac{C_1 - E}{K}\right). \qquad \ldots(6)$$

1•5. DENSITY OF DISTRIBUTION IN PHASE SPACE :

The use of ensembles in statistical mechanics is guided by the following factors :

(1) There is no need to maintain distinction between individual systems as we are interested only in number of systems at any time which would be found in different states that correspond to different regions in the phase space.

(2) The number of elements in an ensemble is so large that there is a continuous change in their number in passing from one region of phase to another.

The condition of an ensemble at any time can be specified by the density ρ with which the phase points are distributed over the phase space. It is called the *probability density* or *distribution function*. The density of distribution ρ of the phase points is a function of f position coordinates and f momentum coordinates *i.e.*, $q_1, q_2, \ldots\ldots. q_f$ and $p_1, p_2 \ldots\ldots. p_f$ corresponding to the $2f$ axes in phase space. The density of distribution is also a function of time because, at any time, the density will change due to the motion of phase points in phase space. Hence

$$\rho = \rho(q_1, q_2, \ldots\ldots. q_f, p_1, p_2, \ldots\ldots. p_f, t) \qquad \ldots(1)$$

or simply as

$$\rho = \rho(q, p, t) \qquad \ldots(2)$$

The physical significance of the density of distribution is that it denotes the number of systems δN which are found at any given time in a given small volume of the phase space. The so called *hyper-volume* $\delta\Gamma$ of the phase points is

$$\delta\Gamma = \delta q_1, \delta q_2 \ldots \delta q_f, \delta p_1, \delta p_2 \ldots \delta p_f. \qquad \ldots(3)$$

The number of systems δN lying in the specified region can be obtained by multiplying the density of distribution and the hyper-volume in the phase space *i.e.,*

$$\delta N = \rho(q, p, t)\, \delta q_1 \ldots\ldots\ldots \delta q_f . \delta p_1 \ldots\ldots\ldots \delta p_f , \qquad \ldots(4)$$

or simply,

$$\delta N = \rho\, \delta q_1 , \ldots\ldots\ldots \delta q_f . \delta p_1 \ldots\ldots \delta p_f .$$

In brief

$$\delta N = \prod_{i=1}^{f} \rho \delta q_i . \delta p_i \qquad \ldots(5)$$

It can be seen that the density of distribution will be analogous to the probability that a number of systems or ensemble is found in a given state. By integrating over the whole of the phase space, we can write

$$N = \int \rho\, dq_1 \ldots\ldots\ldots dq_f . dp_1 \ldots\ldots\ldots dp_f . \qquad \ldots(6)$$

Equation (6) gives

$$\frac{\rho(q, p, t)}{N} = \frac{\rho(q, p, t)}{\int \ldots \int \rho(q, p, t)\, dq_1 \ldots dp_f} \qquad \ldots(7)$$

as *the probability per unit extension in the phase space* that the phase point for a system, chosen at random from the ensemble, would be found, at time t, to have the specified values of q's and p's. It is sometimes convenient to regard ρ as normalized to unity inaccordance with the equation

$$1 = \int \ldots \int \rho(q, p, t)\, dq_1 \ldots dp_f . \qquad \ldots(8)$$

The quantity ρ itself then gives directly the probability per unit volume for finding the phase point for system picked up at random from the ensemble in different regions of the phase space.

1•6. GENERAL DISCUSSION OF MEAN VALUES (ENSEMBLE AVERAGES)

The average value of a variable u in an ensemble is calculated by multiplying each possible value u_r by the number n_r of the system in the ensemble (which exhibits this value), and adding the resultant product for all possible values of the variable u and then finally dividing this sum by the total number of systems in the ensemble as shown in equation (1) below.

Let u be the variable which can assume any of the M discrete values represented by

$$u_1 , u_2 \ldots\ldots u_M$$

with respective probabilities $\omega(u_1), \omega(u_2) \ldots \omega(u_M)$.

Then mean (or average) value of u, denoted by $\bar{u}$, is defined by

$$\bar{u} = \frac{\omega(u_1)\, u_1 + \omega(u_2)\, u_2 + \ldots\ldots + \omega(u_M) u_M}{\omega(u_1) + \omega(u_2) + \ldots\ldots + \omega(u_M)} \qquad \ldots(1)$$

$$= \frac{\sum_{i=1}^{M} \omega(u_i)\, u_i}{\sum^{M} \omega(u_i)} \qquad \ldots(2)$$

$$\int \rho \, d\Gamma = 1. \qquad \ldots(3)$$

When the distribution functions are given, the average value [eq. (1)] can be obtained by multiplying all the possible values of $x(P)$ by their respective probabilities and then integrating over all states *i.e.,*

$$x = \int_M x(P)\, \rho(P)\, d\Gamma \qquad \ldots(3)$$

1•7. LIOUVILLES THEOREM :

We know that every possible dynamical state of a system is represented by a unique point in its phase space. The state of the system at any *given* time determines uniquely its state at any other time. The point in phase space moves along a path, called trajectory. One and only one trajectory passes through each point in phase space as Hamilton's equations of motion fix the local gradients uniquely. So trajectory is determined from Hamilton's equations of motion :

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \quad \text{and} \quad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

where $H = H\,(q_i \ldots q_f, \ldots p_1 \ldots p_f)$ is the Hamiltonian of the system.

As a result of this motion, the density ρ of the system in phase space changes with time. We are interested in finding rate of change of density, $\frac{\partial \rho}{\partial t}$, at a given point in phase space, using Liouville's theorem.

Liouvilles theorem is primarily concerned with defining a fundamental property of the phase space, in which the system, represented uniquely by a point, moves in time. The theorem consists of two parts :

(1) The principle of conservation of density in phase space : This part states the conservation of density in phase space, *i.e.,* the rate of change of density of phase point in phase space is zero or $\frac{d\rho}{dt} = 0$.

(2) The principle of conservation of extension in phase space : This part gives the conservation of extension in phase space *i.e.,* $\frac{d}{dt}(\delta\Gamma) = 0$ or the volume at the disposal of a particular number of phase points is conserved throughout the phase space.

First Part : *Principle of conservation of density in phase space :*

Consider any arbitrary hyper volume

$$d\Gamma = \delta q_1\, \delta q_2 \ldots \delta q_f, \delta p_1\, \delta p_2 \ldots\ldots. \delta p_f$$

in the phase space located between q_1 and $(q_1 + \delta q_1)$ ...., q_f and $(q_f + \delta q_f), p_1$ and $(p_1 + \delta p_1), \ldots, p_f$ and $(p_f + \delta p_f)$. The number of systems (phase points) in this volume element $(\delta q_1 \ldots \delta q_f, \delta p_1 \ldots \delta p_f)$ changes as the coordinates and momenta of the system vary with time. If ρ be the density of phase points, the number of phase points in this volume element, at any instant, t, is given by

$$\delta N = \rho\, \delta\Gamma = \rho\, \delta q_1 \ldots \delta q_f, \delta p_1 \ldots \delta p_f.$$

The change in number in phase points in the volume element per unit time is given by

$$\frac{d}{dt}(\delta N) = \frac{d}{dt}(\rho\,\delta\Gamma) = \dot{\rho}\,\delta\Gamma$$

$$= \dot{\rho}\delta q_1 \ldots \delta q_f, \delta p_1 \ldots \delta p_f.$$

In a time dt, the change in number of phase points within the volume of phase space is given by

$$= \dot{\rho}\,dt\ \delta q_1 \ldots \delta q_f, \delta p_1 \ldots \delta p_f$$

This change is due to the number of systems entering and leaving this volume in time dt. Consider two faces of hyper volume normal to q-axis with coordinates q_1 and $q_1 + \delta q_1$ as shown in fig. (8). In this figure only two axes are shown.

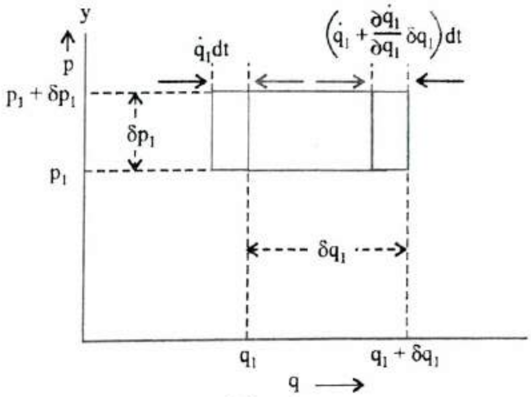


Fig. 8

If $\dot{q}_1$ is the component of velocity of phase point at $q_1 \ldots q_f, p_1 \ldots p_f$, then the number of phase points entering the first face in time dt will be

$$\rho \dot{q}_1\, dt\, \delta q_2 \ldots \delta q_f\, \delta p_1 \ldots \delta p_f. \qquad \ldots(1)$$

Again the phase points leaving the face $(q_1 + \delta q_1)$ in time dt will be

$$\left(\rho + \frac{\partial \rho}{\partial q_1}\delta q_1\right)\left(\dot{q}_1 + \frac{\partial \dot{q}_1}{\partial q_1}\delta q_1\right)dt\,.\,\delta q_2 \ldots \delta q_f\, \delta p_1 \ldots \delta p_f, \qquad \ldots(2)$$

because density ρ changes with change in position and momentum coordinates. At opposite face as coordinate q_1 changes to $q_1 + \delta q_1$, density ρ also changes to $\{\rho + (\partial\rho/\partial q_1)\delta q_1\}$. Similarly, the velocity $\dot{q}_1$ changes to $\{\dot{q}_1 + (\partial \dot{q}_1/\partial q_1)\delta q_1\}$.

Neglecting higher order terms, we have

$$\left[\rho \dot{q}_1 + \left(\rho \frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\right)\delta q_1\right] dt\, \delta q_2 \ldots \delta q_f;\ \delta p_1 \ldots \delta p_f \qquad \ldots(3)$$

Subtracting equation (3) from equation (1), we have

$$-\left(\rho \frac{\partial \dot{q}_1}{\partial q_1} + \dot{q}_1 \frac{\partial \rho}{\partial q_1}\right) dt\, \delta q\ \ldots \delta q_f; \delta p_1 \ldots \delta p_f \qquad \ldots(4)$$

Similarly, for p_1 coordinate, we have

$$-\left(\rho \frac{\partial \dot{p}_1}{\partial p_1} + \dot{p}_1 \frac{\partial \rho}{\partial p_1}\right) dt\ \delta q_1 \ldots \delta q_f;\ \delta p_1 \ldots \delta p_f \qquad \ldots(5)$$

The net increase of number of systems in time dt in this volume of phase space is then obtained by summing the net number of systems entering the volume through all the faces labelled by $q_1 \ldots q_f$ and $p_1 \ldots p_f$. Hence

$$\frac{d}{dt}(\delta N) = -\sum_{i=1}^{f}\left\{\rho\left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i}\right) + \left(\frac{\partial \rho}{\partial q_i}\dot{q}_i + \frac{\partial \rho}{\partial p_i}\dot{p}_i\right)\right\} dt\, \delta q_1 \ldots \delta q_f \delta p_1 \ldots \delta p_f \qquad \ldots(6)$$

As $$\frac{d}{dt}(\delta N) = \frac{\partial \rho}{\partial t} dt\, \delta q_1 \ldots \delta q_f \delta p_1 \ldots \delta p_f.$$

therefore

$$\frac{\partial \rho}{\partial t} dt\, \delta q_1 \ldots \delta q_f \delta p_1 \ldots \delta p_f = -\sum_{i=1}^{f} \left\{ \rho \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) + \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \right\} dt\, \delta q_1 \ldots \delta q_f ; \delta p_1 \ldots \delta p_f$$

or

$$\frac{\partial \rho}{\partial t} = -\sum_{i=1}^{f} \left\{ \rho \left(\frac{\partial \dot{p}_i}{\partial p_i} + \frac{\partial \dot{q}_i}{\partial q_i} \right) + \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \right\} \qquad \ldots(7)$$

The above equation can be simplified as follows :

The equations of motion in canonical form are

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \text{ and } \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

Now

$$\frac{\partial \dot{q}_i}{\partial q_i} = -\frac{\partial \dot{p}_i}{\partial p_i} = \frac{\partial^2 H}{\partial q_i\, \partial p_i} .$$

since the order of differentiation is immaterial. We can put

$$\therefore \qquad \sum_{i=i}^{f} \left(\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right) = 0. \qquad \ldots(8)$$

Substituting equation (8) in equation (7), we get

$$\left(\frac{\partial \rho}{\partial t} \right)_{q.p} = -\sum_{i=1}^{f} \left(\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right) \qquad \ldots(9)$$

This result is known as Liouville's theorem.

Equation (9) can be written as

$$\left(\frac{\partial \rho}{\partial t} \right)_{q.p} + \sum \frac{\partial \rho}{\partial q_i} \frac{dq_i}{dt} + \sum_i \frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} = 0 \qquad \ldots(10)$$

and is identical with the equation of continuity in hydro-dynamics. If ρ is a function of q, p and t, and q, p are functions of t, then total differential coefficient of ρ with respect to t is given by

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \frac{\partial \rho}{\partial q} \cdot \frac{dq}{dt} + \frac{\partial \rho}{\partial p} \cdot \frac{dp}{dt}$$

Generalising this for all f p's and f q's, we get

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_i \frac{\partial \rho}{\partial q_i} \frac{dq_i}{dt} + \sum_i \frac{\partial \rho}{\partial p_i} \frac{dp_i}{dt} \qquad \ldots(11)$$

Comparing equations (10) and (11), we get

$$\frac{d\rho}{dt} = 0. \qquad \ldots(\text{A})$$

According to Gibbs, this form of expression may be called the *principle of conservation of density in phase space. Therefore, the density of a group of points remains constant along their trajectories in the phase space. If at any time the phase points are distributed uniformly in phase space they will for ever have uniform density.*

Second Part : *Principle of conservation of extension in space :*

For this part, we have to prove that $\frac{d}{dt}(\delta\Gamma)=0$. We know that

$$\delta N=\rho\,\delta\Gamma,$$

or

$$\frac{d}{dt}(\delta N)=\frac{d\rho}{dt}\delta\Gamma+\rho\frac{d}{dt}(\delta\Gamma). \qquad ...(12)$$

Since the number of phase points δN in a given region of the phase space must remain fixed, as the system can neither be created nor destroyed, we have $\frac{d}{dt}(\delta\Gamma)=0$.

$$\therefore \qquad \frac{d\rho}{dt}(\delta\Gamma)+\rho\frac{d}{dt}(\delta\Gamma)=0 \qquad ...(13)$$

We have proved that $\frac{d\rho}{dt}=0$. Hence it follows that

$$\rho\frac{d}{dt}(\delta\Gamma)=0. \qquad ...(14)$$

Since $\rho\neq 0$, we have

$$\frac{d}{dt}(\delta\Gamma)=0. \qquad ...(B)$$

Following Gibbs, the equation gives the *principle of conservation of extension in phase space.*

Alternate proof of the second part :

Let $q_1...q_f$ and $p_1...p_f$ be the position and momenta coordinates which constitute the phase space. Let $\delta p_1...\delta p_f\ \delta q_1...\ \delta q_f=\delta\Gamma_1$ be an element of volume. Let $\delta\Gamma_2$ be the element of volume after an interval of time dt. The new coordinates, therefore, are

$$\left(p_1+\frac{\partial p_1}{\partial t}dt\right)...\left(p_f+\frac{\partial p_f}{\partial t}dt\right)$$

and

$$\left(q_1+\frac{\partial q_1}{\partial t}dt\right)...\left(q_f+\frac{\partial q_f}{\partial t}dt\right) \qquad ...(15)$$

because the rate of change of momenta and position coordinates is $\sum_i\frac{\partial p_i}{\partial t}$ and $\sum_i\frac{\partial q_i}{\partial t}$ and after a time dt, the change will be $\sum_i\frac{\partial p_i}{\partial t}.dt$ and $\sum_i\frac{\partial q_i}{\partial t}\,dt$.

Let the volume element be $\delta\Gamma_2$, then

$$\delta\Gamma_2=\delta(p_1+\dot p_1 dt)...\delta(p_f+\dot p_f dt)\,\delta(q_1+\dot q_1 dt)...\delta(q_f+\dot q_f dt), \qquad ...(16)$$

where $\frac{\partial p_1}{\partial t}=\dot p_1$ and $\frac{\partial q_1}{\partial t}=\dot q_1$.

Equation (16) can be written as

$$\delta\Gamma_2=\delta p_1...\delta p_f\delta q_1...\delta q_f\left(1+\frac{\partial\dot p_1}{\partial p_1}dt\right)...\left(1+\frac{\partial\dot p_f}{\partial p_f}dt\right)\left(1+\frac{\partial\dot q_1}{\partial q_1}dt\right)...\left(1+\frac{\partial\dot q_f}{\partial q_f}dt\right). \qquad ...(17)$$

$$\delta q_1 \delta q_2 \ldots\ldots \delta q_f \delta p_1 \delta p_2 \ldots\ldots \delta p_f . \qquad \ldots (1)$$

The dimensions of this volume element are those of (length × momentum). If a finite volume of the phase space is divided into a large number of cells, then the size of each cell will be h^f, where h is any arbitrary constant, given by

$$h = \delta q_i \delta p_i \qquad \ldots (2)$$

∴ Number of phase cells in the volume element is

$$= \frac{\delta q_1 \delta q_2 \ldots \delta q_f \delta p_1 \delta p_2 \ldots \delta p_f}{h^f} \qquad \ldots (3)$$

2•7. CLASSICAL MAXWELL-BOLTZMANN DISTRIBUTION LAW :

The assemblies, in general, consist of three types of particles :

1. *Identical but distinguishable particles :* Molecules of a gas are the particles of this kind. The particles obey Maxwell-Boltzmann distribution law.

2. *Identical but indistinguishable particles of zero or integral spin :* Photons are the particles of this kind. The particles obey Bose-Einstein statistics and hence are known as Bose-particles (Bosons).

3. *Identical but indistinguishable particles of spin* 1/2 : Electrons, protons, neutrons are the particles of this kind. They obey Pauli's exclusion principle and Fermi-Dirac statistics. The particles are known as fermions.

The Maxwell-Boltzmann distribution law which is applicable to identical but distinguishable particles tells us how a total fixed amount of energy is distributed among the various members of an assembly of identical particles in the most probable distribution.

Let us consider a system of large number of similar but distinguishable molecules, enclosed in a vessel of constant volume. Suppose that what we know about the system is that its energy is constant. To obtain further information about the most probable behaviour of the system, it is necessary to choose an appropriate ensemble of similar system and to consider their behaviour. The ensemble suitable for this type of system is microcanonical ensemble. The points representing the systems are distributed uniformly through a thin shell lying between two surfaces in the μ space representing constant energies of E and $(E + \delta E)$, respectively. When δE is permitted to approach zero, the uniformity of distribution is not disturbed, while the energy of every system approaches the required constant value E. The probability ω of finding the n_1 molecules in first cell, n_2 in the second cell and so on, is given by

$$\omega = \frac{n!}{n_1 ! n_2 ! \ldots . n_i !}$$

$$\ldots (1)$$

or

$$\omega = \frac{n!}{\Pi \, n_i !} \times \text{constant}$$

To find out the most probable distribution of molecules among the cells in the μ space*, we must calculate the maximum of the probability ω for a variation of the numbers, n_1, n_2, n_3 ..... etc. subject to the subsidiary condition $n_1 + n_2 \ldots . + n_i = n$.

---

*An ensemble consisting of a large number of systems can be represented in phase space. Each representative point in phase space defines the exact state of the system as a whole. Similarly, a system consisting of a large number of similar molecules can be represented in μ space where μ stands for molecule. Then each point in the μ space indicates the precise state *i.e.*, position and momentum of a single molecule. The number of axes in μ space will be less than the number of axes in phase space. If the molecule has f degree of freedom, then μ space consists of $2f$ dimensions and if there are n similar molecules in the system, the phase space will have $2\,fn$ dimensions of axes.

From equation (1) we have

$$\log \omega = \log n! - \sum_i \log n_i! + \text{constant}, \quad \ldots (2)$$

Using Stirling's approximation, we have

$$\log \omega = n \log n - n - \sum_i (n_i \log n_i - n_i) + \text{constant}, \quad \ldots (3)$$

because the number of molecules, n is very large and we can also take $n_1, n_2, \ldots n_i$ to be sufficiently large.

From equation (3)

$$\log \omega = -\sum_i n_i \log n_i + \text{constant} \quad \ldots (4)$$

Here we have included the term $n \log n$ in the constant and the two factors n and $\sum_i n_i = n$ are cancelled. Differentiating equation (4), we have

$$\delta \log \omega = -\sum_i \delta(n_i \log n_i)$$

$$= -\sum_i (\log n_i + 1)\, \delta n_i. \quad \ldots (5)$$

Applying the condition of maximum probability *i.e.*, log ω = 0 we have

$$-\sum_i (\log n_i + 1)\, \delta n_i = 0 \quad \ldots (6)$$

As the total number of molecules n cannot be altered, the variation δn_i must always add up to zero *i.e.*,

$$\sum_i n_i = n = \text{constant}$$

$$\therefore \quad \sum_i \delta n_i = \delta n = 0. \quad \ldots (7)$$

Let us consider a particular configuration such that n_1 particles go to the first cell with energy ε_1, n_2 particles to second cell with energy ε_2 and so on. Then

$$\sum_i n_i \varepsilon_i = E$$

or

$$\delta E = \sum \varepsilon_i \delta n_i = 0. \quad \ldots (8)$$

Applying the Lagrange method of undetermined multipliers *i.e.*, on multiplying equation (7) by α and equation (8) by β and adding the resulting expression to equation (6) we have

$$\sum_i (\log n_i + 1 + \alpha + \beta \varepsilon_i)\, \delta n_i = 0 \quad \ldots (9)$$

For convenience adding the integer 1 to α and putting it equal to α, we have

$$\sum (\log n_i + \alpha + \beta \varepsilon_i)\, \delta n_i = 0 \quad \ldots (10)$$

Equation (10) will be satisfied only when each term in the summation is separately zero. Thus

$$\log n_i + \alpha + \beta \varepsilon_i = 0.$$

Now $$\log n_i = -(\alpha + \beta\varepsilon_i)$$

or $$n_i = \frac{1}{\exp.[\alpha + \beta\varepsilon_i]}. \quad \ldots (11)$$

The result is of great importance in statistical physics and is known as Maxwell Boltzmann distribution law of particles.

Also $$n = \sum_i n_i = \sum_i \exp.(-\alpha).\exp(-\beta\varepsilon_i) \quad \text{or} \quad \exp.(-\alpha) = \frac{n}{Z},$$

where $$Z = \sum_i \exp.(-\beta\varepsilon_i) \quad \ldots (12)$$

Z is known as ***partition function*** and is of immense importance as it leads to the solution of a large number of statistical mechanical problems.

2•8. MAXWELL BOLTZMANN DISTRIBUTION FOR MOLECULES OF MORE THAN A SINGLE KIND :

Now we shall consider the case of a system composed of interacting but not chemically reacting molecules of more than a single kind. For example, consider a mixture of $n, n', n'', \ldots\ldots$ molecules of different gases. Let $n_i, n'_j, n'_k \ldots$ etc. be the number of molecules of these different kinds which are assigned to the various equal cells $i, j, k \ldots$ etc. into which we divide the μ spaces for these different kinds of molecules. When the macroscopic equilibrium is attained, the probability ω of finding the conservative system in the specified state is given by

$$\omega = \frac{n!}{n_1!\ldots\ldots n_i!}\cdot\frac{n'!}{n'_1!\ldots\ldots n'_j!}\cdot\frac{n''!}{n''_1!\ldots\ldots n''_k!}\times \text{constant}. \quad \ldots (1)$$

Taking log, we have

$$\log\omega = \log n! - \sum_i \log n_i! + \log n'! - \sum_j \log n'_j! + \log n''! - \sum_k \log n''_k! + \ldots\ldots + \text{constant}. \quad \ldots (2)$$

Applying the Stirling approximation, we get

$$\log\omega = n\log n - \sum_i n_i \log n_i + n'\log n' - \sum_j n'_j \log n'_j + n''\log n''$$
$$- \sum_k n''_k \log n''_k + \ldots\ldots + \text{constant}. \quad \ldots (3)$$

The condition of maximum probability is

$$\delta(\log\omega) = -\sum_i (\log n_i + 1)\,\delta n_i - \sum_j (\log n'_j + 1)\,\delta n_j - \sum_k (\log n''_k + 1)\,\delta n''_k - \ldots = 0. \quad \ldots (4)$$

The total number of each kind of molecules remains separately constant; hence

$$\left.\begin{aligned} \delta n &= \sum_i \delta n_i = 0, \\ \delta n' &= \sum_j \delta n'_j = 0, \\ \delta n'' &= \sum_k \delta n''_k = 0, \end{aligned}\right\} \quad \ldots (5)$$

When $\lambda' = \lambda$, then $A = I_\lambda$

$$\therefore \qquad I_{\lambda'}\, d\lambda' = I_\lambda \exp.\left\{-\frac{mc^2}{2kT}\left(\frac{\lambda-\lambda'}{\lambda}\right)^2\right\} d\lambda' \qquad \ldots (5)$$

The distribution of intensity, thus, has a Gaussian line shape as shown in Fig. (3). The width of the spectral line is usually measured at the half intensity points as shown in the figure. If eq. (5) is expressed in terms of frequency, then half frequency width $\Delta\nu_d$ can be expressed as

$$\frac{\Delta\nu_d}{\nu} = 2\left(\frac{2kT\log_e 2}{mv_x^2}\right)^{3/2} \qquad \ldots (6)$$

The agreement between theory and experiment has been found to be excellent.

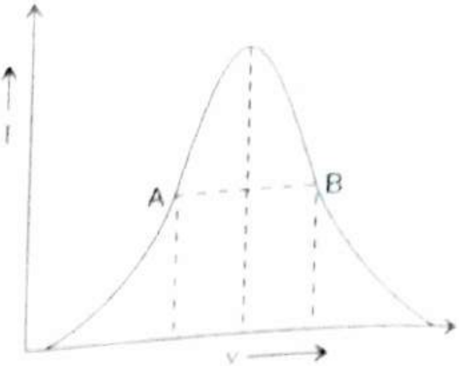


Fig. 3.

2·12. PRINCIPLE OF EQUIPARTITION OF ENERGY :

The law of equipartition of energy states that the total kinetic energy of a dynamical system consisting of a large number of particles, in thermal equilibrium, is equally divided among its all the degrees of freedom and the average energy associated with each degree of freedom is $\frac{1}{2}kT$, where k is Boltzmann constant and T is absolute temperature of the system. In a system, the average energy of the molecule is given by

$$\bar{\varepsilon} = \frac{\int \ldots \int \varepsilon\, e^{-\varepsilon/kT}\, dq_1 \ldots dp_r}{\int \ldots \int e^{-\varepsilon/kT}\, dq_1 \ldots dp_r} \qquad \ldots (1)$$

The value of $\bar{\varepsilon}$ can be evaluated provided the dependence of the energy on the coordinates and momenta are known. The treatment can be simplified when the energy components corresponding to one or more variables are separable from each other. For example, if the energy $\varepsilon\,(p_i)$ associated with momentum p_i may be treated as independent of the other forms of energy $\varepsilon\,(p, q)$, then we can write

$$\varepsilon = \varepsilon\,(p_i) + \varepsilon\,(p, q). \qquad \ldots (2)$$

Now equation (1) can be expressed as

$$\bar{\varepsilon}(p_i) = \frac{\int \ldots \int \varepsilon(p_i)\, e^{-\varepsilon/kT}\, dq_1 \ldots dp_r}{\int \ldots \int e^{-\varepsilon/kT}\, dq_1 \ldots dp_r}$$

$$= \frac{\int \ldots \int \varepsilon\,(p_i)\, e^{-\varepsilon(p_i)/kT}\, e^{-\varepsilon(p,q)/kT}\, dq_1 \ldots dp_r}{\int \ldots \int e^{-\varepsilon(p_i)/kT}\, e^{-\varepsilon(p,q)/kT}\, dq_1 \ldots dp_r} \qquad \ldots (3)$$

As $\varepsilon\,(p_i)$ and $e^{-\varepsilon\,(p_i)}$ depend on the variable p_i, other variables may be integrated, the result is the same for both numerator and denominator. The equation (3) now becomes

$$\bar{\varepsilon}(p_i) = \frac{\int \varepsilon(p_i)\, e^{-\varepsilon(p_i)/kT}\, dp_i}{\int e^{-\varepsilon(p_i)/kT}\, dp_i} \quad \ldots (4)$$

If the energy can be expressed as a quadratic function of p_i *viz.*,

$$\varepsilon(p_i) = \frac{p_i^2}{2m}$$

$$\therefore \qquad \bar{\varepsilon}(p_i) = \frac{\int_{-\infty}^{+\infty} \frac{p_i^2}{2m}\, e^{-p_i^2/2mkT}\, dp_i}{\int_{-\infty}^{+\infty} e^{-p_i^2/2mkT}\, dp_i} \quad \ldots (5)$$

Using the integrals

$$\int_{-\infty}^{+\infty} x^2 e^{-ax^2}\, dx = \frac{1}{2}\left(\frac{\pi}{a^3}\right)^{1/2}$$

and

$$\int_{-\infty}^{+\infty} e^{-ax^2}\, dx = \left(\frac{\pi}{a}\right)^{1/2}$$

We have

$$\bar{\varepsilon}(p_i) = \frac{1}{2m} \cdot \frac{\frac{1}{2}\left\{\frac{\pi}{(1/2mkT)^3}\right\}^{1/2}}{\left\{\frac{\pi}{(1/2mkT)}\right\}^{1/2}} = \frac{1}{2}kT. \quad \ldots (6)$$

This expression shows that the average energy associated with a single variable, coordinate or momentum, which contributes a quadratic term (or square term) to the total energy is $\frac{1}{2}kT$ per molecule in every case. This is known *as principle of the equipartition of energy*.

The component of the kinetic energy of a molecule in any direction may be expressed as a quadratic function of the corresponding momentum. *e.g.*, $\varepsilon_i = p_i^2/2m$; hence the mean value of the kinetic energy per molecule in that direction is $\frac{1}{2}kT$. In case of monatomic gas, the total energy is made up of three components corresponding to three momenta, hence the total energy is $\frac{3}{2}kT$ per molecule.

The rotational energy ε_r is given by

$$\varepsilon_r = \frac{p_\theta^2}{2I} \quad \ldots (7)$$

where p_θ is the angular momentum and I is the momentum of inertia about the axis of rotation. The rotational energy is a quadratic function of corresponding momenta and hence every type of rotation of the molecule as a whole will thus contribute $\frac{1}{2}kT$ per mole to the total energy.

The energy ε_v of linear harmonic oscillator is sum of two square terms (i) involving momentum p and (ii) involving coordinate q. Thus

$$\varepsilon_v = \frac{p^2}{2m} + \frac{1}{2} f q^2 \quad (f \text{ is force constant}) \qquad \ldots (8)$$

the first term on right hand side represents the vibrational kinetic energy and the second represents the potential energy. Thus the average energy of oscillator will be double of $\frac{1}{2}kT$ *i.e.*, kT, per molecule.

For a non-linear molecule containing n-atoms there are three components of translational energy, three of rotational and $(3n - 6)$ of vibrational mode. The total energy per molecule is $(3n - 3)kT$.

Derivation of mean energy of harmonic oscillator :

Consider a particle of mass m performing simple harmonic oscillations in one dimension (say along X-axis). Its energy is given by

$$\varepsilon = \frac{1}{2m} p_x^2 + \frac{1}{2} f x^2 \qquad \ldots (1)$$

where first term on right hand side is the kinetic energy of the particle in terms of momentum and second term is its potential energy, f is the force constant.

Suppose that the oscillator is in equilibrium with a heat reservoir at temperature T. This temperature is high enough such that the oscillator may be described by classical mechanics.

The mean energy of the oscillator is given by

$$\bar{\varepsilon} = \frac{\int \varepsilon\, e^{-\beta\varepsilon}\, dx\, dp_x}{\int e^{-\beta\varepsilon}\, dx\, dp_x} \quad \text{where } \beta = 1/kT \qquad \ldots (2)$$

where the integrals extend over all possible values of x and p_x (*i.e.*, from $-\infty$ to $+\infty$).

Substituting the value of ε from eq. (1) in eq. (2), we get

$$\bar{\varepsilon}(p_i) = \frac{\int \frac{p_x^2}{2m} e^{-\beta p_x^2/2m}\, dp_x}{\int e^{-\beta p_x^2/2m}\, dp_x} + \frac{\int \frac{1}{2} f x^2 e^{-\beta f x^2/2}\, dx}{\int e^{-\beta f x^2/2}\, dx}$$

$$= \frac{-\frac{\partial}{\partial\beta}\left[\int e^{-\beta p_x^2/2m}\, dp_x\right]}{\int e^{-\beta p_x^2/2m}\, dp_x} + \frac{-\frac{\partial}{\partial\beta}\left[\int e^{-\beta f x^2/2}\, dx\right]}{\int e^{-\beta f x^2/2}\, dx}$$

$$= -\frac{\partial}{\partial\beta}\log_e\left[\int_{-\infty}^{+\infty} \exp.\left\{-\beta p_x^2/2m\right\} dp_x\right] - \frac{\partial}{\partial\beta}\log_e\left[\int_{-\infty}^{+\infty} \exp.\left\{-\beta f x^2/2\right\} dx\right]$$

Substituting $y = (\sqrt{\beta}\, p_x)$ in first integral and $z = (\sqrt{\beta}\, x)$ in the second integral,

$$\bar{\varepsilon} = -\frac{\partial}{\partial\beta}\left[-\frac{1}{2}\log_e\beta + \log_e\int_{-\infty}^{+\infty} e^{-y^2/2m} dy\right] - \frac{\partial}{\partial\beta}\left[-\frac{1}{2}\log_e\beta + \log_e\int_{-\infty}^{+\infty} e^{-fz^2/2} dz\right]$$

But $\int_{-\infty}^{+\infty} e^{-y^2/2m} dy$ and $\int_{-\infty}^{+\infty} e^{-fz^2/2}\, dz$ are zero.

$$\therefore \qquad \bar{\varepsilon} = -\frac{\partial}{\partial\beta}\left[-\frac{1}{2}\log_e \beta\right] - \frac{\partial}{\partial\beta}\left[-\frac{1}{2}\log_e \beta\right]$$

$$= \frac{1}{2\beta} + \frac{1}{2\beta} = \frac{1}{\beta} = kT.$$

2•13. CALCULATION OF GAS PRESSURE :

Let us consider a rectangular box of volume v containing n molecules of gas. Suppose m is the mass of a molecule. The molecules are moving in all possible directions; they are colliding with the walls of the box as well as with other molecules of the gas. Here we ignore the collision of the molecules amongst themselves. The pressure on the walls of the box is due to the bombardment of the molecules. Let a molecule strike the face which is perpendicular to x-axis. The pressure on this face may be regarded as due to the x-component of the velocities of all the molecules. Let $\bar{\dot{x}}$ be the mean velocity component in the x direction. The momentum of the molecule before collision on the face is $m\bar{\dot{x}}$ and after collision is $-m\bar{\dot{x}}$. Thus the change in momentum of a single molecule is $m\bar{\dot{x}} - (-m\bar{\dot{x}}) = 2m\bar{\dot{x}}$. All molecules within x should reach each square centimeter of the wall in unit time. Since there are n molecules in the volume v, it follows that $n\bar{\dot{x}}/v$ molecules strike the wall in unit time.

The rate of change of momentum per sq. cm. of wall

$$= m\bar{\dot{x}} \times \frac{n\bar{\dot{x}}}{v}$$

$$= \frac{2mn\bar{\dot{x}}^2}{v}$$

By definition, this is equal to the pressure P exerted by molecules. Thus

$$P = \frac{2mn\bar{\dot{x}}^2}{v} \qquad \ldots (1)$$

The values of $\bar{\dot{x}}^2$ may be derived as follows :

$$\bar{\dot{x}}^2 = \frac{\int_0^{\infty} \dot{x}^2\, e^{-m\dot{x}^2/2kT}\, d\dot{x}}{\int_0^{+\infty} e^{-\dot{x}^2/2kT}\, d\dot{x}} = \frac{kT}{2m}$$

Therefore,

$$P = \frac{nkT}{v}$$

If N is the number of molecules in one mole, and V is the corresponding volume, we have

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

which is the equation of state for an ideal gas. This is expected because Maxwell Boltzmann equation is applicable when no intermolecular forces are present.

We note that the quantity $(2\pi mkT)^{1/2}$ has the character of an average thermal momentum of a molecule, then

$$\lambda = \frac{h}{(2\pi mkT)^{1/2}}.$$

Putting this in equation (9), we get

$$S = nk\log\left[\left(\frac{V}{n}\right)\frac{1}{\lambda^3}\right] + \frac{5}{2}nk,$$

where the argument of logarithm has a ratio of volume per particle (V/n) to the volume λ^3 associated with de-Broglie wavelength.

(e) Chemical Potential, μ of a Perfect gas :

From chapter 1, we write

$$-\frac{\mu}{\tau} = \left(\frac{\partial\sigma}{\partial n}\right)_{E,V}$$

$$= \frac{\partial}{\partial n}[n\log(V/n) - n\log\lambda^3] + \frac{\partial}{\partial n}\left(\frac{5}{2}n\right)$$

$$= \frac{\partial}{\partial n}[n\log V - n\log n - n\log\lambda^3] + \frac{5}{2}$$

$$= \log V - 1 - \log n - \log\lambda^3 + \frac{5}{2}$$

$$= \log\left[\frac{V}{n\lambda^3}\right] + \frac{3}{2}$$

$$\frac{\mu}{\tau} = \log\left[\frac{n\lambda^3}{V}\right] - \frac{3}{2}$$

Putting $\frac{p}{\tau} = \frac{n}{V}$ from above part (c), we have

$$\frac{\mu}{\tau} = \log\left[\frac{p\lambda^3}{\tau}\right] - \frac{3}{2}$$

$$\mu = \tau\log p + \tau\log\left[\frac{\lambda^3}{\tau}\right] - \frac{3\tau}{2}$$

$$= \tau\log p + f(\tau)$$

where $f(\tau)$ is a function of temperature alone.

3·0–3. GIBBS PARADOX :

For equation (4a) art. 3·0–2, we have already stated that it does not satisfy the additive property of the entropy and which can be made more obvious if we take two systems denoted by indices a and b at the same temperature $T_a = T_b = T$. If the particles in the two systems are different, the entropy of the joint system ab will be (using equation $4a$).

$$S_{ab} = S_a + S_b$$
$$= n_a k[\log V_a + \frac{3}{2}\log T + C] + n_b k\,[\log V_b + \frac{3}{2}\log T + C]$$

where C is a constant term including constant factors *e.g.,* k, m of equation (4a).

Now, if the particles in the two systems are the *same* and if, for convenience, we take $V_a = V_b = V;\ n_a = n_b = n$, we have to consider $3n$ particles in a volume $2V$. We get

$$S_{ab} = 2nk\left[\log 2V + \frac{3}{2}\log T + C\right]$$
$$= 2nk\left[\log V + \frac{3}{2}\log T + C\right] + 2nk\log 2$$
$$= S_a + S_b + 2nk\log 2,$$

which shows that by joining two moles of two different gases by removing a partition between them, the entropy of the joint system increases by an additional factor $2nk\log_e 2$ which can not be accounted for. This is called Gibbs paradox.

The explanation is quite simple. After the removal of partition, a molecule of each system, being *indistinguishable*, can be found anywhere within the volume $2V$ instead of V and hence external parameter becomes $2V$ and the possible states of energy are to be calculated with the total volume $2V$ instead of simply V. This explains the occurrence of the additional factor $nk\log 2$. So, if we take two systems as the same *e.g.,* two molecules of the same gas, in that case the molecules will be indistinguishable (as in quantum mechanics). Indeed, if we treat the gas by quantum mechanics, the molecules are to be regarded as completely indistinguishable, *i.e.,* in that case one can not say or observe and label the individual particle. So applying this idea of *indistinguishability* to classical approximation, we can correct the equation (4a) of art. 3.0–2. We note that if there are n molecules in a system, then they can not be distinguished in n ! ways and hence to arrive at the correct result, we must divide equation (4a) art. 3.0–2 by n ! which leads to equation (5) art. 3.0–2 which embodies the additive property of the entropy and then

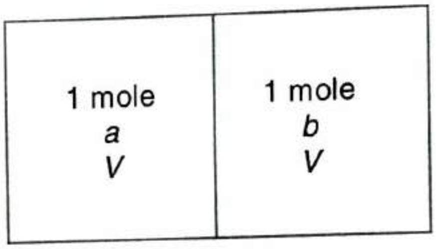


Fig. 1. Mixing of two gases.

$$S_{ab} = 2nk\,[\log 2V - \log 2 + \frac{3}{2}\log T + C]$$
$$= S_a + S_b.$$

Gibbs paradox is thus resolved by the concept of quantum mechanics.

While dealing with grand canonical ensemble (art. 3.2) we shall observe that entropy, deduced by the application of this ensemble, bears the additive property.

3·0–4. PARTITION FUNCTION AND ITS CORRELATION WITH THERMODYNAMIC QUANTITIES :

(a) Partition Function : Let us consider an assembly of ideal gas molecules obeying classical statistics *e.g.,* Maxwell Boltzmann distribution law. Following this distribution law, let n_r molecules occupy r^{th} state with energy between E_r and $(E_r + dE_r)$, and degeneracy, g_r. Then

$$n_r = g_r e^{-\alpha} . e^{-E_r/kT}$$

$$= g_r A e^{-\beta E_r} \qquad \dots (1)$$

where

$$A = e^{-\alpha} \text{ and } \beta = \frac{1}{kT}.$$

so that total number of molecules in the assembly

$$N = \sum_r n_r$$

$$= A \sum g_r e^{-\beta E_r}$$

or

$$\frac{N}{A} = \sum_r g_r e^{-\beta E_r} = Z \qquad \dots (2)$$

where Z is called the *Boltzmann partition function* or simply the *partition function*. The term

$$\sum_r g_r \, e^{-\beta E_r}$$

represents the sum of all the $g_r \, e^{-\beta E_r}$ terms for every energy state of the given molecule. Consequently, the *quantity, Z, indicates how the gas molecules of an assembly are distributed or partitioned among the various energy levels and is called a partition function.* Taking the weight, g_r, of an individual level as unity, we can write the equation (2) as

$$Z = \sum_r e^{-\beta E_r} \qquad \dots (3)$$

(b) Correlation with thermodynamic quantities.

(i) With entropy, S:

Entropy is related to the weight, ω, of most probable configuration by

$$S = k \log \omega_{\max}, \qquad \dots (4)$$

where for a classical system having total number of molecules as

$$N = \left(\sum_r n_r \right),$$

we have

$$\omega = N! \, \Pi_r \frac{g_r^{n_r}}{n_r!}$$

or

$$\log \omega = \log N! + \sum_r (n_r \log g_r - \log n_r!).$$

Using Stirling approximation

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

we get

$$\log \omega = N \log N - N + \sum_r (n_r \log g_r - n_r \log n_r + n_r).$$

According to Maxwell-Boltzmann distribution law, for the most probable configuration, we have

$$n_r = g_r e^{-\alpha} e^{-\beta E_r}$$

$$= g_r A \, e^{-\beta E_r}$$

so that $$\log \omega_{\max} = N\log N - N + \sum_r [n_r \log g_r - n_r \log(g_r A e^{-\beta E_r}) + n_r]$$

$$= N\log N - N + \sum_r n_r \log g_r - \sum_r n_r \log g_r - \sum_r n_r \log A + \sum_r n_r \beta E_r + \sum_r n_r.$$

Taking $\Sigma n_r = N$, total number of particles, and $\Sigma n_r E_r = E$ total energy of the gas molecules of the assembly, we get

$$\log \omega_{\max} = N\log N - N\log A + \beta E$$

$$= N\log\frac{N}{A} + \beta E$$

$$= N\log Z + \beta E \qquad \text{(Using eq. 2)} \qquad \ldots (5)$$

Putting in eq. (5), we find that entropy is

$$S = k\log\omega_{\max}$$

$$= kN\log Z + k\beta E$$

$$= kN\log Z + k.\frac{1}{kT}.E$$

$$= kN\log Z + \frac{E}{T}. \qquad \ldots (6)$$

For an ideal gas $$E = \frac{3}{2}NkT$$

so that $$S = kN\log Z + \frac{3}{2}Nk.$$

which gives the entropy of the assembly of ideal gas molecules.

(ii) With Helmholtz free energy, F :

Helmholtz free energy F is given by

$$F = E - TS$$

$$= E - T(kN\log Z + E/T) \qquad \text{(using eq. 6)}$$

$$= E - NkT\log Z - E$$

$$= -NkT\log Z. \qquad \ldots (7)$$

(iii) With total energy, E :

Average energy of a system of N particles (assembly) is given by

$$\bar{E} = \frac{E}{N} = \frac{\sum_r n_r E_r}{\sum_r n_r}$$

$$= \frac{\sum_r g_r A e^{-\beta E_r}.E_r}{\sum_r g_r A e^{-\beta E_r}} \qquad \text{(using eq. 1)}$$

$$= \frac{\sum_r g_r E_r e^{-\beta E_r}}{Z} \qquad \text{(using eq. 2)} \qquad \ldots (8)$$

Since
$$Z = \sum_r g_r e^{-\beta E_r}$$
$$= \sum_r g_r e^{-E_r/kT}$$

we have for *isothermal isochoric transformation*

$$\left(\frac{\partial Z}{\partial T}\right)_V = \sum_r g_r \times \frac{E_r}{kT^2} \times e^{-E_r/kT}$$
$$= \frac{1}{kT^2} \sum_r g_r e^{-E_r/kT} E_r$$
$$kT^2 \left(\frac{\partial Z}{\partial T}\right)_V = \sum_r g_r E_r e^{-E_r/kT}$$
$$= Z\,\bar{E} \quad \text{(using eq. 8)}$$

or
$$\bar{E} = \frac{kT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_V$$

or
$$N\bar{E} = \frac{NkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_V$$

or total energy, E is given by :

$$E = N\bar{E} = \frac{nkT^2}{Z}\left(\frac{\partial Z}{\partial T}\right)_V$$
$$= NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V \qquad \dots (9)$$

(iv) With enthalpy, H :

Enthalpy is given by

$$H = E + pV = E + RT \qquad \text{(for ideal gas } PV = RT\text{)}$$
$$= NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT \qquad \dots (10)$$

(v) With Gibb's potential, G :

Gibb's potential is given by

$$G = H - TS$$
$$= NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT - T\left(kN\log Z + \frac{E}{T}\right) \qquad \text{(Using eq. 5 and 10)}$$
$$= NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT - NkT\log Z - E$$
$$= NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V + RT - NkT\log Z - NkT^2\left[\frac{\partial}{\partial T}(\log Z)\right]_V$$
$$= RT - NkT\log Z \qquad \text{(Using eq. (9)} \qquad \dots (11)$$

(vi) With pressure, P, of the gas :

Pressure is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_V$$

$$= NkT\left[\frac{\partial}{\partial V}(\log Z)\right]_T \quad \dots (12)$$

using eq. (7).

(vii) With specific heat at constant volume, C_V :

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V$$

$$= \frac{\partial}{\partial T}\left[NkT^2 \frac{\partial}{\partial T}(\log Z)_V\right]$$

$$= Nk\left[2T\frac{\partial}{\partial T}(\log Z) + T^2\frac{\partial^2}{\partial T^2}(\log Z)\right]_V \quad \dots (13)$$

Ex. 1. *Show that if the partition function is given by Z, then mean energy, $\overline{E}$, is given by*

$$\overline{E} = -\frac{\partial}{\partial \beta}(\log Z), \quad \textit{where } \beta = \frac{1}{kT}$$

Refer to the case (iii) of relation of Z with total energy E. We have shown there in eq. (8) that

$$Z\overline{E} = \sum_r g_r E_r e^{-\beta E_r} \quad \dots (1)$$

Further

$$Z = \sum_r g_r e^{-\beta E_r}$$

or

$$\frac{\partial Z}{\partial \beta} = -\sum_r g_r E_r e^{-\beta E_r}$$

$$= -Z\overline{E} \quad \text{(Using eq. 1)}$$

or

$$\overline{E} = -\frac{1}{Z}\cdot\frac{\partial Z}{\partial \beta}$$

$$= -\frac{\partial}{\partial \beta}(\log Z)$$

which is desired.

Ex. 2. *Show that internal energy of harmonic oscillator of frequency* ν *is*

$$E = h\nu\left(\frac{1}{2} + \frac{1}{e^{\Theta}-1}\right) \quad \textit{where } \Theta = \frac{h\nu}{kT}$$

The energy levels of a harmonic oscillator of frequency, ν, are

$$E_j = \left(j + \frac{1}{2}\right)h\nu, \qquad j = 0, 1, 2, \dots$$

Hence the partition function per oscillator of an ensemble of identical oscillators is