SYLLABUS

UNIT – I

Laws of Thermodynamics: Thermodynamic Description of system: Zeroth Law of thermodynamics and temperature. First law and internal energy, conversion of heat into work, Various Thermodynamical Processes, Applications of First Law: General Relation between C_P and C_V, Work Done during Isothermal and Adiabatic Processes, Compressibility and Expansion Coefficient, Reversible and irreversible processes, Second law, Entropy, Carnot's cycle & theorem, Entropy changes in reversible and irreversible processes, Entropy-temperature diagrams,Third law of thermodynamics, Unattainability of absolute zero

THERMODYNAMICS

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

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

THERMODYNAMIC SYSTEMS

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

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

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

ZEROTH LAW AND CONCEPT OF TEMPERATURE

Zeroth law and concept of temperature was enunciated by Fowler, stated "if two systems are separately in thermal equilibrium with third, then they will be in thermal equilibrium with one another".

Consider two systems 1 and 2, each consists of a fluid in a cylinder, separated by adiabatic walls and a mercury thermometer. If the thermometer is placed in thermal contact with them and both exhibit thermal equilibrium, then the zeroth law implies there will be no change in 1 or 2 then they are in thermal contact, when the adiabatic wall between them is replaced by a diathermic wall. The state of this system is specified by a parameter called temperature. Thus temperature of a system is a property that determines whether or not a system is in thermal equilibrium with other systems. Let pressure and volume be used as independent variables to describe their equilibrium states. Choose system 3 and define by p_3 and V_3 as the reference system. Then the condition for thermal equilibrium between system 1 and 3 be expressed in the functional form as $f_{13}(p_1, V_1, p_3, V_3) = 0$ ------ (1)

This equation implies that when two systems are in thermal equilibrium, there is a definite relationship between the four variables and for fixed p_3, V_3 and p_1, V_1 will be uniquely determined. Out of the four variables, only three are independent. Similarly, for thermal equilibrium between system 2 and 3, $f_{23}(p_2, V_2, p_3, V_3) = 0$ --------------- (2)

Eqn., (1) and (2) can be, $p_3 = F_{13}(p_1, V_1, V=)$ ------------ (3)

and $p_3 = F_{23}(p_2, V_2, V_3)$ ----------------- (4)

Eliminating p_3 between these equations, $F_{13}(p_1, V_1, V_3) = F_{23}(p_2, V_2, V_3)$ --------- (5)

$p_1 = G(V_1, p_2, V_2, V_3)$ ----------------- (6)

According to zeroth law, if system 1 and 2 are separately in thermal equilibrium with system 3, then they will also be in thermal equilibrium with one another. This requires

$f_{12}(p_1, V_1, p_2, V_2) = 0$ -------------- (7)

Again, $p_1 = F_{12}(V_1, p_2, V_2)$ --------------- (8)

Under given condition p_1 is uniquely determined by V_1, p_2 and V_2 must cancel out. The functions F_{13} and F_{23} must be of the form, $F_{13} = \phi_1(p_1, V_1)\eta(V_3)+\xi(V_3)$ ---------(9)

$$\text{and } F_{23} = \phi_2(p_2, V_2)\eta(V_3)+\xi(V_3) \text{ ----------(10)}$$

$$\phi_1(p_1, V_1) = \phi_2(p_2, V_2) \text{ ------------ (11)}$$

This is the condition for thermal equilibrium between the system 1 and 2. In general,

$$\phi_1(p_1, V_1) = \phi_2(p_2, V_2) = \phi 3(p_3, V_3) \text{ ----------------- (12)}$$

$$\text{In general, } \phi(p, V) = \theta$$

This equation is called equation of state.

LAWS OF THERMODYNAMICS

The four main laws of Thermodynamics are,

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

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

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

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

Internal Energy and first law of thermodynamics

Internal energy can be described as the sum of kinetic and potential energies of individual molecules in the material. But in thermodynamics U is simply a macroscopic variable of the system.

U is thermodynamic state variable and its value depends only on the given state of the system and not on path taken to arrive the state. Transfer of heat and performance of work are two mean of adding or subtracting energy from a system. On transfer of energy, system is said to have undergone a change in internal energy. Thus the sum of heat put into the system plus works done on the system equals increase in internal energy of the system for any process. If, U_1 is internal energy of state 1 and U_2 is internal energy of state 2 than change in internal energy would be $\Delta U=U_2 - U_1$. If W is the work done by the system on its surroundings then -W would be the work done on the system by the surroundings.

If Q is the heat put into the system then, $Q+(-W)=\Delta U$ usually written as $Q=\Delta U+W$ -------- (1). Equation (1) is then known as first law of thermodynamics and it can be applied when Q, W and U are expressed in same units. Q is positive when heat is given to the system and Q is negative when heat is taken from the system. W is positive when system expands and does work on surroundings. Hence we may say that when a certain amount of heat Q is given to the system then some part of it is used in increasing internal energy ΔU of the system while remaining part leaves the system in form of work done by the system on its surroundings.

From equation 1 we see that first law of thermodynamics is a statement of conservation of energy stated as ' The energy put into the system equals the sum of the work done by the system and the change in internal energy of the system'. If the system undergoes any process in which $\Delta U=0$ i.e., charge in internal energy is zero then from (1) Q = W that is heat supplied to the system is used up entirely in doing work on the surroundings.

Heat Engine and efficiency

Any device which convents heat continuously into mechanical work is called a heat engine.

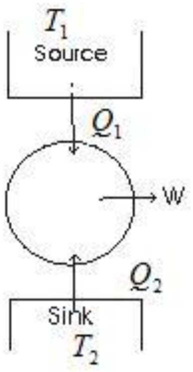
For any heat engine there are three essential requirements.

(i) SOURCE: A hot body at fixed temperature T_1 from which heat engine can draw heat

(ii) Sink : A cold body, at a fixed lower temperature T_2, to which any amount of heat can be rejected.

(iii) WORKING SUBSTANCE: The material, which on being supplied with heat will do mechanical work.

- In heat engine, working substance could be gas in a cylinder with a moving piston.
- In heat engine working substance takes heat from the source, convents a part of it into mechanical work, gives out rest to the sink and returns to the initial state. This series of operations constitutes a cycle.
- This cycle is represented in fig below



- Work from heat engine can be continously obtained by performing same cycle again and again.

  Consider, Q_1 - heat absorbed by working substance from a source

  Q_2 - heat rejected to the sink

  W - net amount of work done by working substance

  Q_1-Q_2 - net amount of heat absorbed by working substance.

  $\Delta U = 0$ since in the cycle Working Substance returns to its initial condition.

  So on application of first law of thermodynamics $Q_1 - Q_2 = W$

Thermal efficiency of heat engine

η= work output in energy units / Heat input in same energy units

$= W / Q_1 = (Q_1 - Q_2)/ Q_1$

Or, $\eta = 1-(Q_2/Q_1)$

from this equation it is clear that Q = 1 for $Q_2=0$ and there would be 100% conversion of heat absorbed into work but such ideal engines are not possible in practice.

Isothermal Process

- In isothermal process temperature of the system remains constant throughout the process.
- For an isothermal process equation connecting P, V and T gives.

  PV = constant

  i.e., pressure of given mass of gas varies inversely with its volume this is nothing but the Boyle's law.
- In isothermal process there is no change in temperature, since internal energy for an ideal gas depends only on temperature hence in isothermal process there is no change in internal energy.

  Thus,

  $\Delta U=0$ therefore, $\Delta Q =\Delta W$
- Thus during isothermal process

  Heat added (or subtracted) from the system = work done by (or on) the system

Adiabatic Process

- Process in which no heat enters or leaves a system is called an adiabatic process
- For every adiabatic process Q=0
- Prevention of heat flow can be accomplished by surrounding system with a thick layer of heat insulating material like cork, asbestos etc.
- Flow of heat requires finite time so if a process is performed very quickly then process will be practically adiabatic.
- On applying first law to adiabatic process we get

  $\Delta U = U_2 - U_1 = -\Delta W$ (adiabatic process)
- In adiabatic process change in internal energy of a system is equal in magnitude to the work by the system.
- If work is done on the system contracts i.e. ΔW is negative then.

  $\Delta U = \Delta W$

  and internal energy of system increases by an amount equal to the work done on it and temperature of system increases.
- If work is done by the system i.e., ΔW is negative

  $\Delta U = -\Delta W$

  here internal energy of systems decreases resulting a drop in temperature.

Isochoric process v

- In an isochoric process volume of the system remain uncharged throughout i.e. ΔV = O.
- When volume does not change no work is done ; ΔW = 0 and therefore from first law

  $U_2 - U_1 = \Delta U = \Delta Q$
- All the heat given to the system has been used to increase the intenal energy of the system.

Isobaric Process

- A process taking place at constant pressure is called isobaric process.
- From equation (3) we see that work done in isobaric process is

  $W = P(V_2 - V_1)\ nR\ (T_2 - T_1)$

  where pressure is kept constant.

- Here in this process the amount of heat given to the system is partly used in increasing temperature and partly used in doing work.

Application of First law

The first law of thermodynamics has been successfully applied to physical and chemical process. This law is universal.

Heat Capacity of gas

First law becomes, $\delta Q = dU + pdV$ -------- (1)

Let us choose T and V as independent variables. Since U is a function of state, U=U(T,V) and write the differential of U as $dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$

Sub. this in eqn., (1), $\delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(p + \left(\frac{\partial U}{\partial V}\right)_T\right) dV \quad ------(2)$

At constant volume, Cv = $\left(\frac{\delta Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V \quad ----- (3)$

If there is no charge in volume, no work will be done and change in internal energy will be equal to the heat entering the system. The corresponding specific heat is

$$Cv = \frac{1}{m}\left(\frac{\partial U}{\partial T}\right)_V = \frac{Cv}{m} --- (4)$$

Similarly at constant pressure eqn.,(2 &3) becomes, Cp =$\left(\frac{\delta Q}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right)\left(\frac{\partial V}{\partial T}\right)_p$

$$= \mathrm{Cv} + \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right)\left(\frac{\partial V}{\partial T}\right)_p$$

$$\mathrm{Cp\text{-}Cv} = \left(\left(\frac{\partial U}{\partial V}\right)_T + p\right)\left(\frac{\partial V}{\partial T}\right)_p \text{ -------- (5)}$$

The first term indicates how the internal energy changes with time. The second term indicates how much of work is done in pushing back the surroundings at constant p.

(i) *Perfect gas*

A perfect gas is defined in following two properties:

1. There are no intermolecular attractions so that its internal energy is wholly kinetic. As a result, it remains unchanged in Joule expansion.
2. Its molecules are point masses and its equation of state is the perfect gas law: pV=RT.

Eqn. (5) reduces to Cp-Cv = p $\left(\frac{\partial V}{\partial T}\right)_p$ ------- (6)

The difference in two capacities depends on how the volume of a system at constant pressure changes as its temperature increases. This difference is large because a small change in temperature gives rises to a large change in volume of a gas.

$$p\left(\frac{\partial V}{\partial T}\right)_p = R \; so \; that \; \mathrm{Cp\text{-}Cv = R} \qquad \text{---------- (7)}$$

This result is known as Mayer’s formula. Eqn., (4) can be Cv= dU/dT so that, dU=CvdT

Using this result, we get $\delta Q = C_V dT + pdV$ ---------- (a)

From equation of state of a perfect gas is pdV +Vdp = RdT

Or pdV=RdT – Vdp

So that, $\delta Q = C_V dT + RdT - Vdp = C_p dT - Vdp$ ------- (b)

On other hand if eliminate dT from (a) and (b)

$\delta Q = (C_V Vdp + C_p pdV)/R$ -------- (c)

Real gas:

For a real gas, the internal energy changes with volume because work has to be done against the intermolecular forces. Use the Van der Waal's equation as the equation of state:

$(p+\frac{a}{V^2})\ (V-b) = RT$ ------- (8)

For a real gas, $\left(\frac{\partial U}{\partial V}\right)_T = \frac{a}{V^2}$

Using this result, Cp-Cv = $\frac{RT}{(V-b)}\left(\frac{\partial V}{\partial T}\right)_p$ ------------ (9)

To evaluate $\left(\frac{\partial V}{\partial T}\right)_p$, $\left(p+\frac{a}{V^2}-(V-b)\frac{2a}{V^3}\right)\left(\frac{\partial V}{\partial T}\right)_p = R$

So that $\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{\left(p+\frac{a}{V^2}-(V-b)\frac{2a}{V^3}\right)}$

Multiply the numerator and denominator by (V-b) and simplify.

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R\ (V-b)}{\left(RT-(V-b)^2\frac{2a}{V^3}\right)} \text{ or } \frac{1}{V-b}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T(1-(V-b)^2\frac{2a}{V^3})}$$

Using binomial expansion we can write for a very small a,

$$\frac{1}{(V-b)}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{T}\left(1+(V-b)^2\frac{2a}{RTV^3}\right) - - - (10)$$

Substituting this in eqn., (9), we obtain Cp-Cv=R$\left(1+(V-b)^2\frac{2a}{RTV^3}\right) - - - - - - (11)$

The difference is more for a real gas than a perfect gas.

Work done in Isothermal process

In an isothermal process temperature remains constant. Consider pressure and volume of ideal gas changes from (P_1, V_1) to (P_2, V_2) then, from first law of thermodynamics $\Delta W = P\Delta V$ Now taking ΔV approaching zero i.e. ΔV and summing ΔW over entire process we get total work done by gas so we have $W = \int PdV$

where limits of integration goes from V_1 to V_2 as $PV = nRT$ we have $P = nRT / V$

$$W = \int(nRT/V)dV$$

where limits of integration goes from V_1 to V_2 on integrating we get,

$$W=nRT \ln(V_2/V_1)$$

Where n is the number of moles in sample of gas taken.

Work done in an Adiabatic process

For an adiabatic process of ideal gas equation we have $PV^\gamma = K$ (Constant)

Where γ is the ratio of specific heat (ordinary or molar) at constant pressure and at constant volume $\gamma = C_p/C_v$

Suppose in an adiabatic process pressure and volume of a sample of gas changes from (P_1, V_1) to (P_2, V_2) then we have $P_1(V_1)^\gamma=P_2(V_2)^\gamma=K$

Thus, $P = K/V^\gamma$

Work done by gas in this process is $W = \int PdV$

where limits of integration goes from V_1 to V_2, substituting for $P=K/V^\gamma$, and integrating we get, $W = (P_1V_1-P_2V_2)/(\gamma-1)$

In an adiabatic process if W>0 i.e., work is done by the gas then $T_2 < T_1$. If work is done on the gas (W<0) then $T_2 > T_1$ i.e., temperature of gas rises.

Compressibility and Expansion coefficient

In a single phase region, where pressure and temperature are independent, the volume as being a function of pressure and temperature.

$$V = V(T, p) \quad \text{-------} \quad (1)$$

$$\text{Or, } v = v(T, p) \text{-------} (2)$$

Applying the chain rule of the calculus, $dv = \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial v}{\partial p}\right)_T dp$. The derivative $\left(\frac{\partial v}{\partial T}\right)_p$ represents the slope of a line of constant pressure on V - T a plane. A similar interpretation can be given for the second derivative. These derivatives are themselves intensive thermodynamic properties, since they have definite values at any fixed thermodynamic state. The first represents the sensitivity of the specific volume changes in temperature at constant pressure, and the second is a measure of the change in specific volume associated with a change in pressure at constant temperature. Isothermal compressibility, isentropic compressibility and volume expansivity are defined as

Isothermal compressibility: $k_T = -\frac{1}{V}\left(\frac{\partial v}{\partial p}\right)_T --------(3)$

Volume expansivity: $\beta = \frac{1}{V}\left(\frac{\partial v}{\partial T}\right)_p$ --------- (4)

3β Young's modulus of elasticity is proportional to k_T in terms of β and k_T, Eq. 4 can be written as $dv = \beta\, vdT - k_T\, vdp$ ------- (5)

Usefulness of Eq. 5 arises from the fact that β and k_T are sometimes slowly varying functions of T and P. Another term in use is the isothermal compressibility defined as

$$k_s = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_s \quad C_p - C_V = \frac{TV\beta^2}{k_T}$$

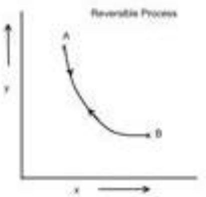
REVERSIBLE AND IRRERVERSIBLE PROCESS

There are two main types of thermodynamic processes: the reversible and irreversible. The reversible process is the ideal process which never occurs, while the irreversible process is the natural process that is commonly found in the nature.

When the system undergoes a change from its initial state to the final state, the system is said to have undergone a process. During the thermodynamic process, one or more of the properties of the system like temperature, pressure, volume, enthalpy or heat, entropy, etc. changes. The second law of thermodynamics enables us to classify all the processes under two main categories: reversible or ideal processes and irreversible or natural processes.

The process in which the system and surroundings can be restored to the initial state from the final state without producing any changes in the thermodynamic properties of the universe is called a reversible process. In the figure below, let us suppose that the system has undergone a change from state A to state B. If the system can be restored from state B to state A, and there is no change in the universe, then the process is said to be a reversible process. The reversible process can be reversed completely and there is no trace left to show that the system had undergone thermodynamic change.

For the system to undergo reversible change, it should occur infinitely slowly due to infinitesimal gradient. During reversible process all the changes in state that occur in the system are in thermodynamic equilibrium with each other.



Thus, there are two important conditions for the reverse process to occur. Firstly, the process should occur in infinitesimally small time and secondly all of the initial and final state of the system should be in equilibrium with each other. If during the reversible process the heat content of the system remains constant, i.e. it is adiabatic process, then the process is also isentropic process, i.e. the entropy of the system remains constant.

The phenomenon of undergoing reversible change is also called reversibility. In actual practice the reversible process never occurs, thus it is an ideal or hypothetical process.

The irreversible process is also called the natural process because all the processes occurring in nature are irreversible processes. The natural process occurs due to the finite gradient between the two states of the system. For instance, heat flow between two bodies occurs due to the temperature gradient between the two bodies; this is in fact the natural flow of heat. Similarly, water flows from high level to low level, current moves from high potential to low potential, etc.

1) In the irreversible process the initial state of the system and surroundings cannot be restored from the final state.

2) During the irreversible process the various states of the system on the path of change from the initial state to final state are not in equilibrium with each other.

3) During the irreversible process the entropy of the system increases decisively and it cannot be reduced back to its initial value.

4) The phenomenon of a system undergoing an irreversible process is called as irreversibility.

Second law of thermodynamics

- First law of thermodynamics states the equivalence of heat and energy.

- It does not state anything about the limitation in the conversion of heat into work or about the condition necessary for such conversion.
- Second law of thermodynamics is generalization of certain experience and observation and is concerned with tine direction in which energy flow takes place.
- This law can be stated in number of ways. Although differently said, they are essentially equivalent.

(i) Kelvin Plank Statement :

- "It is impossible to construct a device which, operating in a cycle, has a sole effect of extracting heat from a reservoir and performing an equivalent amount of work".

(ii) Clasius Statement :

- "It is impossible for a self acting machine, unaided by external agency, to transfer heat from a colder body to a hotter body".
- It can be proved that these two statements of second law are completely equivalent and violation of Kelvin Plank statement leads to violation of Clasius statement and vice-versa.

ENTROPY

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

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

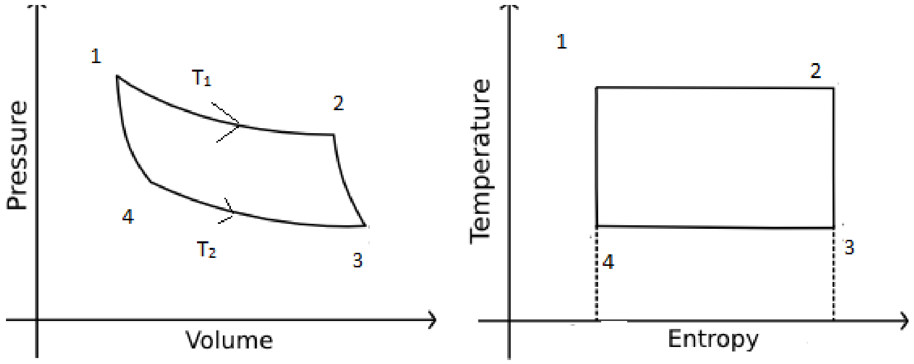
(i) Entropy of a system remains constant during an adiabatic change,
(ii) Entropy of a system remains constant in all reversible processes.
(iii) Entropy of a system increases in all irreversible processes.

ENTROPY CHANGE IN REVERSIBLE PROCESS

Entropy is a thermodynamic property of a system. T-S diagrams are often useful in engineering and meteorology.

(i) Carnot Cycle

The most efficient heat engine cycle is the Carnot cycle, consisting of two isothermal processes and two adiabatic processes. The Carnot cycle can be thought of as the most efficient heat engine cycle allowed by physical laws. When the second law of thermodynamics states that not all the supplied heat in a heat engine can be used to do work, the Carnot efficiency sets the limiting value on the fraction of the heat which can be so used.

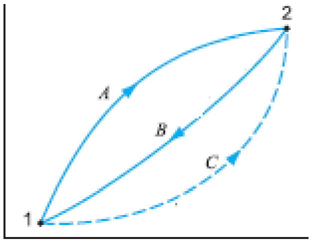


In order to approach the Carnot efficiency, the processes involved in the heat engine cycle must be reversible and involve no change in entropy. This means that the Carnot cycle is an idealization, since no real engine processes are reversible and all real physical processes involve some increase in entropy. The temperature in the Carnot efficiency expression must be expressed in Kelvin. The conceptual value of the Carnot cycle is that it establishes the maximum possible efficiency of the engine cycle operating between T_H and Tc. It is not a practical engine cycle because the heat transfer into the engine in the isothermal process is too slow to be of practical value.

ENTROPY CHANGE IN IRREVERSIBLE PROCESS

Consider a system that undergoes the cycle changes. For the reversible cycle 1A2B1 made up of reversible process A and B we write the equations as

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q_R}{T}\right)_{via\ A} + \int_2^1 \left(\frac{\delta Q_R}{T}\right)_{via\ B} = 0$$



Now consider the irreversible cycle 1A2C1 made up of reversible process A and irreversible process C. For this cycle, the inequality of Clausius implies that

$$\oint \frac{\delta Q}{T} = \int_1^2 \left(\frac{\delta Q_R}{T}\right)_{via\ A} + \int_2^1 \left(\frac{\delta Q_R}{T}\right)_{via\ C} < 0$$

On combining these two equations, we get

$$\int_2^1 \left(\frac{\delta Q_R}{T}\right)_{via\ C} < \int_2^1 \left(\frac{\delta Q_R}{T}\right)_{via\ B}$$

Since B is reversible and entropy is a function of state,

$$S_1\text{-}S_2 = \int_2^1 \left(\frac{\delta Q_R}{T}\right)_{via\ B} = \int_2^1 (dS)_B = \int_2^1 (dS)_C$$

Therefore in irreversible process

$$\int_2^1 (dS)_C > \left(\frac{\delta Q_1}{T}\right) \text{---------} (1)$$

For the general case we write, $\Delta S \geq \left(\frac{\delta Q}{T}\right)$ --------------- (2)

For a change from state 1 to 2, the difference in entropy is given by $S_2\text{-}S_1 \geq \int_1^2 \frac{\delta Q}{T}$

The equality and greater sign hold for reversible and irreversible process respectively.

CARNOT'S HEAT ENGINE

According to the second law of thermodynamics, no heat engine can have 100% efficiency.

Carnot heat engine is an idealized heat engine that has maximum possible efficiency consistent with the second law. Cycle through which working substance passed to Carnot engine is known as Carnot Cycle.

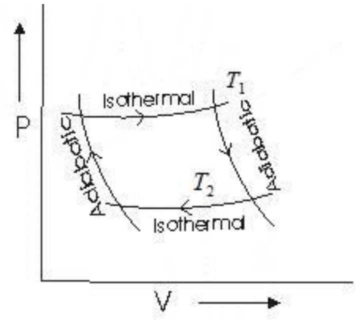
Carnot's engine works between two temperatures

T_1 - temperature of hot reservoir

T_2 - temperature of cold reservoir

In a Complete Carnot's Cycle system is taken from temperature T_1 to T_2 and then back from temperature T_2 to T_1.

- We have taken ideal gas as the working substance of Carnot engine.



(i) In step b→c isothermal expansion of gas taken place and thermodynamic variables of gas changes from (P_1, V_1, T_1) to (P_2, V_2, T_1)

If Q_1 is the amount of heat absorbed by working substance from the source and W_1 the work done by the gas.

$$Q_1 = W_1 = nRT_1 \ln (V_2/V_1) \text{ -----------(1)}$$

as process is isothermal.

(ii) Step c→d is an adiabatic expansion of gas from (P_2, V_2, T_1) to (P_3,V_3,T_2). Work done by gas in adiabatic expansion.

$$W_2 = nR\,(T_1-T_2)/(\gamma-1) \qquad \text{-----------}\ (2)$$

(iii)Step d→a is isothermal compression of gas from (P_3,V_3,T_2) to (P_4,V_4,T_2). Heat Q_2 would be released by the gas to the at temperature T_2

Work done on the gas by the environment is $W_3 = Q_2 = nRT_2\ln(V_3/V_4)$ ----------- (3)

(iv)Step a→b is adiabatic compression of gas from (P_4, V_4, T_2) to (P_1, V_1, T_1)

- Work done on the gas is

  $W_4 = nR\,(T_1-T_2)/(\gamma-1)$ ---------- (4)

- Now total work done in one complete cycle is

  $W = W_1 + W_2 - W_3 - W_4 = nRT_1\ln(V_2/V_1)-nRT_2\ln(V_3/V_4)$ -------- (5)

  as $W_2 = W_4$

- Efficiency of Carnot engine

  $\eta=W/Q_1 = 1-(Q_2/Q_1)$

  $= 1-(T_2/T_1)\ln(V_3/V_4)/\ln(V_2/V_1)$ ---------- (6)

  or $\eta= 1-[T_2\ln(V_3/V_4)/T_1\ln(V_2/V_1)]$ ----------- (7)

  Since points b and c lie on same isothermal

  $\Rightarrow P_1V_1=P_2V_2$ ------------ (8)

  also points c and d lie on same adiabatic

  $\Rightarrow P_2(V_2)^{\gamma}=P_3(V_3)^{\gamma}$ ----------- (9)

  also points d and a lie on same isothermal and points a and b on sum adiabatic thus,

  $P_3V_3=P_4V_4$ ----------- (10)

  $P_4(V_4)^{\gamma}=P_2(V_1)^{\gamma}$ ----------- (11)

  multiplying all the above four eqn. me get

  $V_{3/4} = V_2/V_1$ ----------- (12)

  substituting this in equation (7) we get

  $\eta= 1-(T_2/T_1)$ ----------- (13)

From above eqn. we can draw following conclusions that efficiency of Carnot engine is

(i) independent of the nature of working substance

(ii) depend on temperature of source and sink

Carnot Theorem

Carnot Engine is a reversible engine. Carnot theorem consists of two parts:

(i) No engine working between two given temperatures can be more efficient than a reversible Carnot engine working between same source and sink.

(ii) All reversible engines working between same source and sink (same limits or temperature) have the same efficiency irrespective the working substance.

Third law of thermodynamics statement

The third law of thermodynamics states that" **The entropy of a perfect crystal at absolute zero temperature is exactly equal to zero."**

At absolute zero that is zero Kelvin, the system is said to possess minimum energy. This statement of the third law of thermodynamics holds true only when the perfect crystal has minimum energy state. If the system has minimum disturbances it means that the temperature has approached zero Kelvin where molecular motion seizes to exist. Standard molar entropy is defined as the entropy per mole of a substance at standard conditions and specified temperature.

Unattainability of absolute Zero

$$Q_1/Q_2 = \tau_1/\tau_2$$

If $\tau = 0$, no heat will be exchanged with the cold reservoir (Q1=0). In such case, complete conversion of heat into work is possible. However, this contradicts the second law of thermodynamics. Therefore we conclude that the thermodynamic temperature of zero degrees absolute or less cannot be achieved by any mechanical means. That is unattainabilitiy of absolute zero is implied by the second law of thermodynamics.

Posible Questions

2marks

1. State Zeroth law of thermodynamics.
2. State first law of thermodynamics.
3. State second law of thermodynamics.
4. State third law of thermodynamics.
5. Give a note on Reversible and irreversible processes.
6. Give a note on Isothermal and adiabatic process.
7. What is called isentropic process?
8. Give a note on the open and close system.
9. What is called internal energy?
10. What is the relation between Cp and Cv?
11. Define Compression and Expansion.
12. What is called Entropy?
13. State Carnot theorem?
14. Give a note on unattainability of absolute zero.

6 marks

1. Find the relation between Cp and Cv.
2. Explain Carnot cycle.
3. Explain Zeroth Law of thermodynamics and temperature.
4. Explain Carnot theorem.
5. How a heat can be converted into work? Explain it.
6. Calculate the entropy change in reversible process.
7. How much amount of work done during isothermal and adiabatic process.
8. Calculate the entropy change in irreversible process.
9. State different laws of thermodynamics.
10. What is application of first law of thermodynamics? Explain it.

KARPAGAM ACADEMY OF HIGHER EDUCATION

Coimbatore – 641021

(For Candidates Admitted From 2017 Onwards)

DEPARTMENT OF PHYSICS

UNIT I: Objective Type/Multiple choice Questions each Question carries one Mark

Sl.No	Questions	OPTION A	OPTION B	OPTION C	OPTION D	KEY
1	The term “thermodynamics” comes from Greek. words “therme” and “dynamis” which means _______.	Heat power	Heat transfer	Heat energy	Heat motion	Heat power
2	The term “thermodynamics” was first used in 1849 in the publication of a	Rudolph Clausius	William Rankine	Lord Kelvin	Thomas Savery	Lord Kelvin
3	The macroscopic approach to the study of thermodynamics does not require a knowledge of the behavior of individual particles is called _____.	Dynamic thermodynamics	Static thermodynamics	Statistical thermodynamics	Classical thermodynamics	Classical thermodynamics
4	What law asserts that energy is a thermodynamic property?	First law of Thermodynamics	Second law of Thermodynamics	Third law of Thermodynamics	Zeroth law of Thermodynamics	First law of Thermodynamics
5	What law asserts that energy has quality as well as quantity?	First law of Thermodynamics	Second law of Thermodynamics	Third law of Thermodynamics	Zeroth law of Thermodynamics	Second law of Thermodynamics
6	The first law of thermodynamics is based on which of the following principles?	mass of energy	Conservation of energy		The entropy-temperature relationship	Conservation of energy
7	Thermodynamics is applicable to	microscopic systems only	macroscopic systems only	homogeneous systems only	heterogeneous systems only.	macroscopic systems only
8	Which is not true about thermodynamics ?	it ignores the internal structure of atoms and molecules	it involves the matter in bulk	it is concerned only with the initial and final states of the system	it is not applicable to macroscopic systems.	it is not applicable to macroscopic systems.
9	A system that can transfer neither matter nor energy to and from its surroundings is called	closed system	an isolated system	an open system	a homogeneous system	an isolated system

10	Which of the following is incorrect, for an ideal gas ?	PV= nRT	V= nRT/P	P=nRT/V	P =RT	PV= nRT
11	The heat capacity at constant pressure is related to heat capacity at constant volume by the relation	Cp-R =Cv	Cv-R =Cp	Cp-Cv =R	R-Cp =Cv	Cp-Cv =R
12	A system is in ______ equilibrium if the temperature is the same throughout the entire system.	Static	Thermal	Mechanical	Phase	Thermal
13	A system is in ______ equilibrium if there is no change in pressure at any point of the system with time.	Pressure	Thermal	Mechanical	Phase	Mechanical
14	If a system involves two phases, it is in ______ equilibrium when the mass of each phase reaches an equilibrium level and stays there.	Chemical	Thermal	Mechanical	phase	phase
15	A system is in ______ equilibrium of its chemical composition does not change with time, i.e., no chemical reaction occurs.	Chemical	Thermal	Mechanical	Phase	Chemical
16	A system is said to be in thermodynamic equilibrium if it maintains ______ equilibrium.	Mechanical and phase	Thermal and chemical	Thermal, mechanical and chemical	Thermal, phase, mechanical and chemical	Thermal, phase, mechanical and chemical
17	What is a process with identical end states called?	Cycle	Path	Phase	Either path or phase	Cycle
18	What is a process during which the temperature remains constant?	Isobaric process	Isothermal process	Isochoric process	Isometric process	Isothermal process
19	What is a process during which the pressure remains constant?	Isobaric process	Isothermal process	Isochoric process	Isometric process	Isobaric process
20	What is a process during which the specific volume remains constant?	Isobaric process	Isothermal process	Isochoric or isometric process	Isovolumetric process	Isochoric or isometric process
21	What states that if two bodies are in thermal equilibrium with a third body, they are also in equilibrium with each other?	Zeroth law of thermodynamics	First law of thermodynamics	Second law of thermodynamics	Third law of thermodynamics	Zeroth law of thermodynamics

22	What is the study of energy and its transformations?	Thermostatics	Thermophysics	Thermochemistry	Thermodynamics	Thermodynamics
23	What is considered as the heat content of a system?	Enthalpy	Entropy	Internal heat	Molar heat	Enthalpy
24	What refers to the amount of heat needed to raise the temperature of an object by one degree Celsius or 1K?	Heat capacity	Specific heat	Latent heat	Molar heat	Heat capacity
25	What is the heat capacity of one mole of substance?	Molecular heat	Specific heat	Latent heat	Molar heat	Specific heat
26	What refers to the measure of the disorder present in a given substance or system?	Enthalpy	Entropy	Heat capacity	Molar heat	Entropy
27	Entropy is measured in ______.	Joule/Kelvin	Joule-Meter/Kelvin	Meter/Kelvin	Newton/Kelvin	Joule/Kelvin
28	What is the energy absorbed during chemical reaction under constant volume conditions?	Entropy	Ion exchange	Enthalpy	Enthalpy of reaction	Enthalpy
29	Which of the following equation is used to calculate the heats of reaction when ΔG at two temperatutes are given?	Gibbs Helmholtz equatioin	Clapeyron equation	Kirchoffs equation	Nernst equation	Gibbs Helmholtz equatioin
30	_____________ is applicable to macroscopic systems only.	thermochemistry	thermokinetics	thermodynamics	thermochemical studies.	thermodynamics
31	ΔE =q-w for an isochoric process	first law of thermodynamics	second law of thermodynamics	zeroth's law	third law of thermodynamics	first law of thermodynamics
32	Who proposed the Carnot cycle?	Sammy Carnot	Sonny Carnot	Sadi Carnot	Suri Carnot	Sadi Carnot
33	Entropy is transferred by ______.	Work	Heat	Energy	Work and heat	Heat
34	The specific heat of a gas in isothermal process is	Zero	Negative	Remains constant	Infinite	Infinite
35	The difference between the principal specific heats of nitrogen is 300 J/kg °K and ratio of the	1050 J/kg °K	650 J/kg °K	750 J/kg °K	150 J/kg °K	650 J/kg °K

	two specific heats is 1.4. then the CP is					
36	Which of the following variables controls the physical properties of a perfect gas?	Pressure	Temperature	Volume	Atomic mass	Atomic mass
37	A system in which state variables have constant values throughout the system is called in a state of	equilibrium	non- equilibrium	isothermal equilibrium	none of these.	equilibrium
38	In an adiabatic process ______ can flow in to or out of the system.	no heat	heat	matter	no matter	no heat
39	The mathematical relation for the first law of thermodynamics is	$\Delta E = q - w$	$\Delta E = 0$ for a cyclic process	$\Delta E = -q$ for an isochoric process	$\Delta E = W - q$.	$\Delta E = q - w$
40	For an adiabatic process according to first law of thermodynamics,	$\Delta E = -w$	$\Delta E = w$	$\Delta E = q - w$	$\Delta q = E - w$	$\Delta E = q - w$
41	The enthalpy change, ΔH of a process is given by the relation	$\Delta H = \Delta E + p\Delta v$	$\Delta H = \Delta E + \Delta nRT$	$\Delta H = \Delta E + w$	$\Delta H = \Delta E - \Delta nRT$	$\Delta H = \Delta E + p\Delta v$
42	The amount of heat required to raise the temperature of one mole of the substance by 1 K is called	heat capacity	molar heat capacity	molar heat	molar capacity.	molar heat capacity
43	Which of the following is not correct ?	$H=E+PV$	$H-E=PV$	$H-E-PV=0$	$H=E-PV$	$H=E-PV$
44	The enthalpy of a system is defined by the relation	$H=E+PV$	$H=E-Pv$	$E=H+PV$	$PV+E-H$	$H=E+PV$
45	Which of the following quantities is not the property of the system	Pressure	temperature	heat	density	density
46	Solid and liquids have	Only one value of specific heat	Two value of specific heat	Three value of specific heat	No value of specific heat	Only one value of specific heat
47	The term N.T.P stands for	Nominal temperature and pressurre	Natural temperature and pressure	Normal temperatuere and pressure	Normal thermodynamic pressure	Normal temperatuere and pressure

48	The property of a working substance which increases or decreases as the heat is supplied or removed in a reversible manner is known as	enthalpy	internal energy	entropy	external energy.	entropy
49	In an irreversible process there is a	loss of heat	no loss of heat	gain of heat	no gain of heat	loss of heat
50	The efficiency of the Carnot cycle may be increased by	increasing the highest temperature	decreasing the highest temperature	increasing the lowest temperature	decreasing the lowest temperature	decreasing the lowest temperature
51	Workdone in a free expansion process is	zero	minimum	maximum	positive	zero
52	The entropy of water at 0°C is assumed to be	1	0	-1	10	0
53	During which of the following process does heat rejection takes place in Carnot cycle?	Isothermal expansion	Isentropic expansion	Isothermal compression	Isentropic compression	Isothermal compression
54	The gas constant (R) is equal to the ___________ of two specific heats.	sum	difference	product	ratio	difference
55	Producer gas is obtained by	partial combustion of coal, coke, anthracite coal or charcoal in a mixed air steam blast	carbonisation of bituminous coal	passing steam over incandescent coke	passing air and a large amount of steam over waste coal at about 650°C	partial combustion of coal, coke, anthracite coal or charcoal in a mixed air steam blast
56	Kelvin-Planck's law deals with	conservation of work	conservation of heat	conversion of heat into work	conversion of work into heat	conversion of heat into work
57	If the value of n = 0 in the equation pvn = C, then the process is called	constant volume process	adiabatic process	constant pressure process	isothermal process	constant pressure process
58	For a reversible adiabatic process, the change in entropy is	zero	minimum	maximum	positive	zero
59	For any irreversible process the net entropy change is	zero	Negative	infinity	positive	positive

60	For any reversible process, the change in entropy of the system and surroundings is	zero	Negative	infinity	positive	zero

SYLLABUS

Thermodynamic Potentials: Enthalpy, Gibbs, Helmholtz and Internal Energy functions, Maxwell's relations and applications - Joule-Thompson Effect, Clausius-Clapeyron Equation, Expression for (C_P – C_V), C_P/C_V, TdS equations.

THERMODYNAMIC POTENTIALS

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

$$dQ = dU+PdV$$

$$dQ = TdS$$

Combining

$$TdS= dU+PdV$$

$$dU = TdS - PdV$$

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

Enthalpy or Heat content H

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

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

On diff., $dH=dU+PdV+VdP$

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

$= TdS+VdP$

$dH = Tds$ ------ (2)

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

Let H_i and H_f be the initial and final enthalpy,

$$H_f-H_i = Q$$

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

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

External work done by gas = $P_fV_f - P_iV_i$

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

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

$$U_i+P_iV_i = P_f V_f + U_f$$

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

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

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

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

As dH is perfect diff.

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

Using (3), we get

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

Which is third thermodynamical relation

Helmholtz Function F

On combining I & II law of thermodynamics,

dU = Tds – dW

suppose the temp of the system remain constant, then

d(TS) = Tds

⇨ dU=d(TS)-dW

d(U-TS) = –dW

where the fn. F=U-TS

dF=-dW --------- (1)

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

on diff. Eqn. (1), we pet

dF=dU-TdS-SdT

sub. dU=TdS-PdV

⇨ dF=TdS-PdV-TdS-SdT

= -PdV-SdT - (2)

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

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

As dF is a perfect diff,

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

using eq. (3) we get

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

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

Gibbs potential (G)

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

dH=T(ds)

= d (TS) [from Helmholtz fn.]

d(H-TS) = 0

dG = 0

Where G = H – TS

G = U+PV-TS

is called gibb's fn. or free energy

on diff. (5), we get

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

$$= (T\cancel{d}S - pd\cancel{V}) + pd\cancel{V}+VdP-Td\cancel{S}-SdT$$

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

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

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

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

This is called a fourth thermodynamical relation

MAXWELL RELATIONS

For a PVT system undergoing an infinitesimal reversible process, the combined form of the I and II law of thermodynamics is dU=TdS-pdV ---------- (1)

This equation involves 5 fn of state: p,V, T, S & U. For instance, the pressure and temperature is independent of variables U,V & S will be fn. of p & T. Let the independent variables be x & y. Then, U=U (x,y); S=S (x,y); V=V(x,y)

It is possible to eliminate internal energy from equation 1, general relations linking 4 thermodynamic variables. These relations are known as Maxwell relations. To derive these relations, dU, dS & dV are exact differentials.

$$dU= \left(\frac{\partial U}{\partial x}\right)_y dx + \left(\frac{\partial U}{\partial y}\right)_x dy$$

$$dS = \left(\frac{\partial S}{\partial x}\right)_y dx + \left(\frac{\partial S}{\partial y}\right)_x dy$$

$$dV = \left(\frac{\partial V}{\partial x}\right)_y dx + \left(\frac{\partial V}{\partial y}\right)_x dy \qquad \text{--------(2)}$$

On substituting these in equation (1) & comparing the coefficient of x & y.

$$\left(\frac{\partial U}{\partial x}\right)_y = T\left(\frac{\partial S}{\partial x}\right)_y - p\left(\frac{\partial V}{\partial x}\right)_y \qquad \text{---------} \; (3)$$

$$\& \; \left(\frac{\partial U}{\partial y}\right)_x = T\left(\frac{\partial S}{\partial y}\right)_x - p\left(\frac{\partial V}{\partial y}\right)_x \qquad \text{---------} \; (4)$$

U, V & S be perfect diff. of x & y

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right)_y$$

$$\left(\frac{\partial}{\partial y}\left(\frac{\partial V}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial y}\right)_x\right)_y$$

$$\& \left(\frac{\partial}{\partial y}\left(\frac{\partial S}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial S}{\partial y}\right)_x\right)_y \qquad \text{--------} \; (5)$$

Diff. eqn. (3) w.r.to y, keeping x fixed & Diff. eqn. (4) w.r.to x, keeping y fixed. The result is

$$s\left(\frac{\partial}{\partial y}\left(\frac{\partial U}{\partial x}\right)_y\right)_x = \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y + T\left(\frac{\partial}{\partial y}\left(\frac{\partial S}{\partial x}\right)_y\right)_x - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y - p\left(\frac{\partial}{\partial y}\left(\frac{\partial V}{\partial x}\right)_y\right)_x$$

$$\& \; \left(\frac{\partial}{\partial x}\left(\frac{\partial U}{\partial y}\right)_x\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x + T\left(\frac{\partial}{\partial x}\left(\frac{\partial S}{\partial y}\right)_x\right)_y - \left(\frac{\partial V}{\partial y}\right)_x\left(\frac{\partial p}{\partial x}\right)_y - p\left(\frac{\partial}{\partial x}\left(\frac{\partial V}{\partial y}\right)_x\right)_y$$

Compare these equations, on simplifying the resultant expression & rearranging terms,

$$\left(\frac{\partial V}{\partial y}\right)_x\left(\frac{\partial p}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y$$

In the determinant form, this eqn., can be $\begin{vmatrix} \left(\frac{\partial p}{\partial x}\right)_y & \left(\frac{\partial P}{\partial y}\right)_x \\ \left(\frac{\partial V}{\partial x}\right)_y & \left(\frac{\partial V}{\partial y}\right)_x \end{vmatrix} = \begin{vmatrix} \left(\frac{\partial T}{\partial x}\right)_y & \left(\frac{\partial T}{\partial y}\right)_x \\ \left(\frac{\partial S}{\partial x}\right)_y & \left(\frac{\partial S}{\partial y}\right)_x \end{vmatrix}$ ------- (6a)

In Jacobian notation, this relation can be written as $\frac{\partial(p,V)}{\partial(x,y)} = \frac{\partial(T,S)}{\partial(x,y)}$ ------- (6b)

Where x & y are diff., variables chosen out of T, S, P & V. This can be done in 6 diff. ways but only 4 choices give useful thermodynamic relation.

1st Relation

Let take the temp. & volume as independent variables & sub. x= T & y=V in eqn., (6b)

$\frac{\partial(T,S)}{\partial(T,V)} = \frac{\partial(p,V)}{\partial(T,V)}$ which simplifies to $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V$ ------- (7)

For any thermodynamic system, the increase in entropy per unit increases of volume at constant temp. is equal to the increase of pressure per unit increase of temp. when volume is constant. Apply eqn. (7) to the equilibrium b/n two stages of the same substance, phase change such as vaporization of liquid or melting of a solid. Multiply eqn. (7) by T.

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

$$\text{Or } \left(\frac{\delta Q}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V \qquad \text{-------- (8)}$$

Which means that in isothermal expansion heat is absorbed per unit volume at constant temperature T is equal to the product of absolute temperature and the rate of increase of P with temperature in isochoric process.

2nd Relation

Temperature & pressure is independent variables. x = T, y = p.

$$\frac{\partial(T,S)}{\partial(T,p)} = \frac{\partial(p,V)}{\partial(T,p)}$$

$$\text{Which gives, } \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p \quad \text{------ (9)}$$

States that decrease in entropy per unit increase of pressure during an isothermal process is equal to increase of volume per unit rise of temperature for an isobaric process.

Multiply both sides by T, $\left(\frac{\delta Q}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p = -TV\alpha$

Where $\propto = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ is the volume expansion coefficient at constant pressure.

3rd & 4th Relation

S and V are independent, x= S & y = V.

$$\frac{\partial(T,S)}{\partial(S,V)} = \frac{\partial(p,V)}{\partial(S,V)}$$

$$gives \left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_v$$

States that increase of temperature per unit increase of volume in an isentropic process is equal to decrease of pressure per unit increase in entropy in an isochoric process.

S and p are independent, x=S & y=p.

$$\frac{\partial(T,S)}{\partial(S,p)} = \frac{\partial(p,V)}{\partial(S,p)}$$

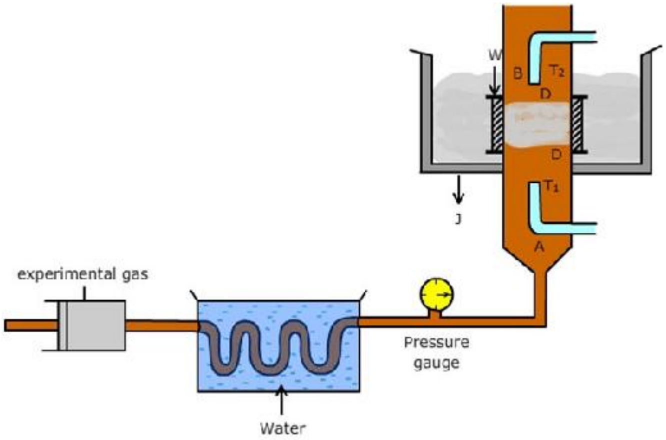
$$gives \left(\frac{\partial T}{\partial p}\right)_S = -\left(\frac{\partial V}{\partial S}\right)_p$$

States that increase of temperature per unit increase of pressure during an isentropic process is equal to increase of volume per unit increase of entropy in an isobaric process.

Joule-Thomson effect- Porous plug experiment

James Joule and William Thomson (later Lord Kelvin) had devised an experiment known as ‘porous plug experiment’. This experiment was quite sensitive to detect the existence of change in temperature and subsequently the existence of inter-molecular forces in real gases.

In their experimental arrangement, a gas is allowed to pass through a porous plug from constant higher pressure region to a constant lower pressure region.



A **porous plug** consists of silk fiber or cotton wool packed in a space between two perforated brass discs (DD) and has a number of fine holes such that heat cannot flow smoothly through it and this process is considered to be adiabatic. Thus, porous plug maintains a constant pressure difference on the opposite sides of the plug.

This plug is fitted in a cylindrical non conducting tube W, separating it into two parts. This arrangement is surrounded by a vessel (J) containing cotton wool to avoid any loss or gain of heat from the surroundings. The lower end of this tube is connected to a pump through a long spiral tube. 'T_1' and 'T_2' are two platinum resistance thermometers to measure the temperature of incoming and outgoing gas respectively. The gas is compressed to a high pressure with the help of a piston and it is passed through the spiral tube immersed in a water bath maintained at a constant temperature. If there is any heating of the gas due to compression, this heat is taken away by the circulating water in the water bath. A pressure gauge is used to measure the pressure of the inlet gas. The upper portion of the tube 'C' is open. Thus, the pressure of this side 'P_2' is maintained at atmospheric pressure.

In this process gas flows through a large number of narrow orifices in the porous plug. The molecules of the gas are gradually pulled apart and the gas expands slowly from a constant higher pressure to a constant lower pressure state. This process is termed as **throttling process.** Due to this reason a porous plug is also called as throttled valve.

The behavior of large number of gases has been studied after passing through the porous plug at various inlet temperatures and the following conclusions were drawn:

1. All of the gases show change in temperature, proving existence of molecular attraction between the molecules and that no gas is perfect one.
2. At ordinary temperature all gases show cooling effect except hydrogen and helium which show heating effect.
3. At sufficiently low temperature all gases show cooling effect.
4. The fall in temperature is directly proportional to the pressure differences on the two sides of the porous plug.
5. For a given pressure difference, the fall in temperature is more if the initial temperature is less.
6. There is a particular inlet temperature for every gas at which gases show no change in temperature when they are passed through the porous plug. This temperature is called as

the **'temperature of inversion (T_i)'**. Below this temperature gases show cooling effect while above this temperature, they show heating effect.

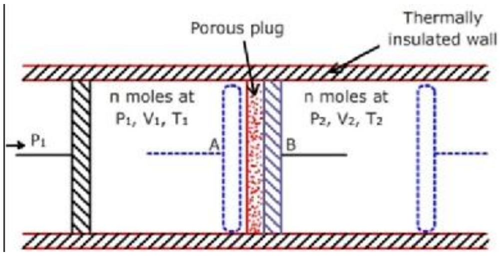
Theory of Porus Plug experiment:

The gas is allowed to pass through the porous plug from higher pressure side to the lower pressure side. Let P_1, V_1, T_1 and P_2, V_2, T_2 represents the pressure, volume and temperature on the two sides of the porous plug. When the piston A is moved through a certain distance, the piston B also moves through the same distance.

The work done on the gas by the piston A, $W_1= P_1V_1$

The work done by the gas on the piston B, $W_2= P_2V_2$.

Thus net work done by the gas, $\delta W = W_2-W_1 = P_2V_2-P_1V_1$



The dotted lines in the figure indicate the final position of the piston.

Since the system is thermally isolated, we can apply the law of conservation of energy. The work done by the gas on the piston is: $\delta W=P_2V_2-P_1V_1$

Since no heat enters the system, this work has to be performed at the cost os its internal energy. According to first law, $\delta Q=dU+\delta W$

Here, $\delta Q=0$

$\delta W=P_2V_2-P_1V_1$ and $dU=U_2-U_1$. Here U_1 & U_2 represents the internal energy of the gas on the two sides of the porous plug. $U_1+P_1V_1 = U_2+P_2V_2$

$$\text{or } H_1= H_2$$

Here H_1 and H_2 are the enthalpy on the two sides of the porous plug. Thus we conclude that the **enthalpy** is conserved. So, in the throttling process, enthalpy remains constant. This process is known as Joule Thomson or Joule Kelvin expansion which is **'quasistatic isenthalpic'** in nature.

CLASUSIS CLAYPERON EQUATION

Maxwell second thermo dynamical relation is

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

Multiply both sides by T,

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

From II law of thermodynamics,

$$TdS = dQ$$

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

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

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

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

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

$$dP/dT = \frac{L}{T(V_2 - V_1)}$$

which is called Clausius Clapyeron latent heat equitation

Difference of two specific heats

By equating 2 TdS eqn., $C_v dT + T\left(\frac{\partial p}{\partial T}\right)_v dV = C_p dT - T\left(\frac{\partial v}{\partial T}\right)_p dp$

$$\text{(or) } C_v dT - C_p dT = -T\left(\frac{\partial p}{\partial T}\right)_v dV - T\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$C_p dT - C_v dT = T\left(\frac{\partial p}{\partial T}\right)_v dV + T\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$dT = T\left(\frac{\partial p}{\partial T}\right)_v dV . \frac{T}{(C_p - C_v)} + \frac{T}{(C_p - C_v)}\left(\frac{\partial v}{\partial T}\right)_p dp \qquad \text{-------- (1)}$$

Here T is the fn. of v & p

$$T = T(v,p) \qquad dT \Rightarrow T\left(\frac{\partial T}{\partial v}\right)_p dv + T\left(\frac{\partial T}{\partial p}\right)_v dp \qquad \text{------- (2)}$$

$$\text{Compare (1) \& (2), } T\left(\frac{\partial T}{\partial p}\right)_v = \frac{T}{(C_p - C_v)}\left(\frac{\partial v}{\partial T}\right)_p$$

$$\& \left(\frac{\partial T}{\partial v}\right)_p = \frac{T}{(C_p - C_v)}\left(\frac{\partial p}{\partial T}\right)_v$$

Both these eqn. lead to same expression, $(C_p - C_v) = \left(\frac{\partial p}{\partial T}\right)_v \left(\frac{\partial v}{\partial T}\right)_p$ ------ (3)

Using Maxwell relation, $\left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial v}\right)_T$

Sub. in eqn. (3) $(C_p - C_v) = -T\left(\frac{\partial v}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial v}\right)_T$ ------(4)

Both eqn. (3) & (4) have their importance.

(i) Since increase in pressure reduces the volume, $\frac{\partial p}{\partial T}$ is always negative. Thus $\left(\frac{\partial v}{\partial T}\right)_p^2$ being a square term, (Cp-Cv) will always be positive quantity for all substance.

(ii) At T=0, (Cp-Cv) are equal to other.

(iii) Cp may become equal to Cv even at non-zero temperature, if $\left(\frac{\partial v}{\partial T}\right)_p=0$ which is a condition for maximum density. Thus at maximum density Cp=Cv for all substance. Water has maximum density at 4^oC at which Cp equals to Cv.

Ratio of specific heat

1st TdS equation can be rearranged in the form, CvdT=TdS - $\left(\frac{\partial p}{\partial T}\right)_v dV$ ------ (1)

$$dT = \frac{T}{C_v}\, dS - \frac{T}{C_v}\left(\frac{\partial p}{\partial T}\right)_v dV \text{ -------- (1a)}$$

T is the function of S & V, T = T (S, V)

$$\text{Which gives, } dT = \left(\frac{\partial T}{\partial S}\right)_v dS + \left(\frac{\partial T}{\partial V}\right)_S dU \text{ ------ (2)}$$

$$\text{Comparing (1a) \& (2), } \left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_v}\left(\frac{\partial p}{\partial T}\right)_v$$

$$Cv = -T\left(\frac{\partial v}{\partial T}\right)_S\left(\frac{\partial p}{\partial T}\right)_v \text{ ------ (3)}$$

Similarly from 2nd TdS equation,

$$CpdT = TdS + \left(\frac{\partial v}{\partial T}\right)_p dp$$

$$dT = \frac{T}{C_p}\, dS + \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_p dp \text{ ---------- (4)}$$

T is the function of S & p.

T = T (S,p)

$$dT = \left(\frac{\partial T}{\partial s}\right)_p dS + \left(\frac{\partial T}{\partial p}\right)_s dp \text{ ---------- (5)}$$

$$\text{compare (4) \& (5), } \left(\frac{\partial T}{\partial p}\right)_s dp = \frac{T}{C_p}\left(\frac{\partial v}{\partial T}\right)_p dp$$

$$Cp = T\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_s \text{ -------------- (6)}$$

From eqn. (6) & (3), $\frac{C_v}{C_p} = -\frac{\left(\frac{\partial v}{\partial T}\right)_S\left(\frac{\partial p}{\partial T}\right)_v}{\left(\frac{\partial v}{\partial T}\right)_p\left(\frac{\partial p}{\partial T}\right)_s}$

Or $\frac{C_p}{C_v} = \frac{\left(\frac{\partial T}{\partial V}\right)_S\left(\frac{\partial p}{\partial T}\right)_s}{\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial T}{\partial V}\right)_p}$ --------------- (7)

Right hand side becomes, $\left(\frac{\partial p}{\partial T}\right)_S\left(\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial p}{\partial T}\frac{\partial T}{\partial V}\right)_S = \left(\frac{\partial p}{\partial V}\right)_S \; ----(8)$

Denominator becomes, $\left(\frac{\partial T}{\partial V}\right)_p\left(\frac{\partial T}{\partial V}\right)_V = \left(\frac{\partial p}{\partial T}\right)_V \Big/ \left(\frac{\partial v}{\partial T}\right)_p$

Using 3rd & 4th Maxwell eqn., $-\left(\frac{\partial p}{\partial V}\right)_t$ ---------- (9)

Sub., (8) & (9) in eqn. (7) $\frac{C_p}{C_v} = -\left(\frac{\partial p}{\partial V}\right)_S \Big/ -\left(\frac{\partial p}{\partial V}\right)_t$

TdS Equation

S, p, T & V are the variables, where T & V are independent.

S=S(T, V)

On differentiating, dS = $\left(\frac{\partial S}{\partial T}\right)_v$dT+$\left(\frac{\partial S}{\partial v}\right)_T dV$ --------- (1)

Multiply both sides by T, TdS = T$\left(\frac{\partial S}{\partial T}\right)_v dT + T\left(\frac{\partial S}{\partial v}\right)_T dV$ --------- (2)

From 2nd law of thermodynamics, dq/T = dS, dq= TdS

Cv = T$\left(\frac{\partial S}{\partial T}\right)_v = \left(\frac{\partial S}{\partial T}\right)v \; ------(3)$

From (2 & 3), TdS = CvdT+ $\left(\frac{\partial S}{\partial v}\right)_T dV \; -------(4)$

Using 3rd Maxwell relation, dq = CvdT + $\left(\frac{\partial p}{\partial T}\right)_v dV$ ---------- (1st TdS equation)

Similarly, consider S as a function of T & p. S = S (T, p) -------- (5)

$\Longrightarrow$, dS = $\left(\frac{\partial S}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial p}\right)_T dp$

Or TdS = T$\left(\frac{\partial S}{\partial T}\right)_p dT + T\left(\frac{\partial S}{\partial p}\right)_T dp$ -------- (6)

From II second law of thermodynamics, TdS = dq

$$T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{dq}{dT}\right) = Cp \text{ -------- } (7)$$

Eqn. (6) becomes, $TdS = Cp\, dT + T\left(\frac{\partial S}{\partial p}\right)_T dp$

Using, Maxwell 2nd relation, $TdS = CpdT - T\left(\frac{\partial S}{\partial p}\right)_T dp$ --------- (8)

This is 2nd TdS equation in which both the coefficient of dT & dp are constant at volume

Possible Questions

2marks

1. Write four Maxwell's equation.
2. Write an expression for Helmhotz and internal energy.
3. Write a short note on Joule-Thomson effect.
4. Write down I and II Tds equation.
5. What is called thermodynamic potentials?
6. What is an expression for enthalpy and internal energy?
7. What are the applications of Maxwell's relations?

8. Write down an expression for C_p/C_v and (C_p-C_v).

6 marks

1. Obtain first and second relation of Maxwell equation.
2. Obtain an expression for Cp/Cv.
3. Obtain III and IV thermodynamic relation equations.
4. With a neat diagram explain Joule-Thompson Effect.
5. Obtain an expression for I and II thermodynamic relation.
6. Derive an expression for TdS equation.
7. What is thermodynamic potential? Obtain an equation for enthalpy and internal energy.
8. Obtain Clausius-clapeyron equation.
9. Obtain an expression for heat content and Helmhotz function.
10. Obtain an expression for Cp-Cv.

KARPAGAM ACADEMY OF HIGHER EDUCATION

Coimbatore – 641021

(For Candidates Admitted From 2017 Onwards)

DEPARTMENT OF PHYSICS

UNIT II: Objective Type/Multiple choice Questions each Question carries one Mark

SL. NO	QUESTION	OPTION A	OPTION B	OPTION C	OPTION D	KEY
1	The value of gas constant (R) in S. I. units is	0.287 J/kgK	2.87 J/kgK	28.7 J/kgK	287 J/kgK	287 J/kgK
2	Gibb’s function is expressed as,	G = H + TS	G = H / TS	G=H-TS	G = H * TS	G=H-TS
3	The sum of internal energy (U) and the product of pressure and volume (p.v) is known as	workdone	entropy	enthalpy	free energy	enthalpy
4	Internal energy of a perfect gas depends on	Temperature, specific heats and pressure	Temperature, specific heats and enthalpy	Temperature, specific heats and entropy	Temperature only	Temperature only
5	At critical point the enthalpy of vaporisation is	Only dependent on temperature	zero	minimum	maximum	zero
6	The term “enthalpy” comes from Greek “enthalpen” which means _______	warm	hot	heat	cold	heat
7	Total heat of a substance is a function of only	temperature	pressure	volume	none	none
8	CP and CV are the principal specific heat of a gas. In terms of mechanical units, CP – CV is equal to	R	R/J	R/MJ	R/M	R/MJ
9	Helmhotz free energy F of a system of particles is defined by ________.	F=U-TS	F=U/TS	F=U+TS	F=UTS	F=U-TS

10	__________of a system of particles is given by $F = U - TS$	Helmholtz free energy	free energy	helmholtz function	Gibb’s free energy	Helmholtz free energy
11	A decrease in the Helmholtz function of a system is equal to:	change in temperature	external work done	change in internal energy	change in energy	external work done
12	In a gas the transport of momentum gives rise to the phenomenon of	viscosity	conduction	diffusion	volume	viscosity
13	Joule-Thomson effect is related to	adiabatic compression	adiabatic expansion	isothermal expansion	isothermal compression	adiabatic expansion
14	The specific heat of a solid is 5 cal/g/ºC. Then heat required to raise its temperature by 20 ºC is:	150 cal	25 cal	100 cal	15 cal	100 cal
15	P, T are ρ are the pressure, absolute temperature and density of an ideal gas, then:	PT/ρ = constant	$P\rho/T$ = constant	$PT\rho$= constant	$P/\rho T$ = constant	$P/\rho T$ = constant
16	For the system of diatomic gas the number of degrees of freedom are:	2	4	5	6	6
17	If dQ is the amount of heat supplied and dW is the work done, then in isothermal process:	$dQ + dW = 0$	$dQ - dW = 0$	$dQ / dW = 0$	$dQ * dW = 0$	$dQ + dW = 0$
18	Increase in temperature of body is proportional to	amount of heat absorbed	amount of heat evolved	density of substance	average kinetic energy	amount oh heat absorbed
19	1 cal =	1.2 joule	3.2 joule	4.2 joule	2 joule	4.2 joule
20	Gases have	Only one value of specific heat	Two value of specific heat	Three value of specific heat	No value of specific heat	No value of specific heat

21	A pure substance which exists in a single phase has _____ independent variables.	zero	one	two	three	two
22	Maxwell’s equations consists of _____ equations.	four	one	two	three	four
23	Which of the following is not a Maxwell equation?	$(\partial T/\partial V) = -(\partial p/\partial S)$	$(\partial T/\partial p) = -(\partial V/\partial S)$	$(\partial p/\partial T) = (\partial S/\partial V)$	$(\partial V/\partial T) = -(\partial S/\partial p)$	$(\partial T/\partial p) = -(\partial V/\partial S)$
24	The condition for exact differential is	$(\partial N/\partial y) = (\partial M/\partial x)$	$(\partial M/\partial y) = (\partial N/\partial x)$	$(\partial M/\partial y) = -(\partial N/\partial x)$	$(\partial N/\partial y) = -(\partial M/\partial x)$	$(\partial M/\partial y) = (\partial N/\partial x)$
25	The first TdS equation is	$TdS=Cv*dT + T(\partial T/\partial p)dV$	$TdS=Cv*dT – T(\partial p/\partial T)dV$	$TdS=Cv*dT + T(\partial p/\partial T)dV$	$TdS=Cv*dT – T(\partial T/\partial p)dV$	$TdS=Cv*dT + T(\partial p/\partial T)dV$
26	The second TdS equation is	$TdS=Cp*dT + T(\partial V/\partial T)dp$	$TdS=Cp*dT – T(\partial V/\partial T)dp$	$TdS=Cp*dT + T(\partial T/\partial V)dp$	$TdS=Cp*dT – T(\partial T/\partial V)dp$	$TdS=Cp*dT – T(\partial V/\partial T)dp$
27	Which of the following is true?	$(\partial p/\partial V)*(\partial V/\partial T)*(\partial T/\partial p)=$ infinity	$(\partial p/\partial V)*(\partial V/\partial T)*(\partial T/\partial p)= 0$	$(\partial p/\partial V)*(\partial V/\partial T)*(\partial T/\partial p)= 1$	$(\partial p/\partial V)*(\partial V/\partial T)*(\partial T/\partial p)= -1$	$(\partial p/\partial V)*(\partial V/\partial T)*(\partial T/\partial p)= -1$
28	What do we get on equating the first and second TdS equations?	$Cp-Cv = T*(\partial T/\partial p)*(\partial V/\partial T)$	$Cp-Cv = T*(\partial p/\partial T)*(\partial V/\partial T)$	$Cp+Cv = T*(\partial p/\partial T)*(\partial V/\partial T)$	$Cp+Cv = T*(\partial p/\partial T)+(\partial V/\partial T)$	$Cp-Cv = T*(\partial p/\partial T)*(\partial V/\partial T)$
29	Consider the equation $Cp-Cv = -T*(\partial p/\partial V)(\partial V/\partial T)^2$, which of the following is correct?	$(\partial V/\partial T)^2$ is always positive	$(\partial p/\partial V)$ for any substance is negative	$(Cp-Cv)$ is always positive	all	all
30	For an ideal gas,	$Cp-Cv = R$	$Cp-Cv = mR$	$Cp=Cv$	$Cp=-Cv$	$Cp-Cv = mR$
31	The volume expansivity and isothermal compressibility is defined as	volume expansivity = $(1/V)*(\partial V/\partial T)$ at p and isothermal compressibility = $(-1/V)*(\partial V/\partial T)$ at	volume expansivity = $(1/V)*(\partial V/\partial T)$ at p and isothermal compressibility = $(1/V)*(\partial V/\partial T)$ at	volume expansivity = $(1/V)*(\partial V/\partial T)$ at p and isothermal compressibility = $(-1/V)*(\partial T/\partial V)$ at	volume expansivity = $(1/V)*(\partial V/\partial T)$ at p and isothermal compressibilit	volume expansivity = $(1/V)*(\partial V/\partial T)$ at p and isothermal compressibility

		T	T	T	y = (1/V)*(-∂T/∂V) at T	= (-1/V)*(∂V/∂T) at T
32	The equation Cp-Cv = -T*(∂p/∂V)(∂V/∂T)^2 can also be expressed as	Cp-Cv = T*V*(isothermal compressibility)^2 / (volume expansivity)	Cp-Cv = T*V*(isothermal compressibility) / (volume expansivity)	Cp-Cv = T*V*(volume expansivity)^2 / (isothermal compressibility)	Cp-Cv = T*V*(volume expansivity) / (isothermal compressibility)	Cp-Cv = T*V*(volume expansivity)^2 / (isothermal compressibility)
33	At constant entropy, the two TdS equations give us the relation	Cp+Cv = 0	Cp=Cv	Cp-Cv = mR	Cp/Cv = ɣ	Cp/Cv = ɣ
34	The slope of an isentrope is ____ the slope of an isotherm on p-v diagram.	less than	greater than	equal to	less than or equal to	greater than
35	Which of the following relation gives ɣ .	1/(isothermal compressibility *adiabatic compressibility)	isothermal compressibility * adiabatic compressibility	adiabatic compressibility / isothermal compressibility	isothermal compressibility / adiabatic compressibility	isothermal compressibility / adiabatic compressibility
36	According to the Clausius' theorem, the cyclic integral of ____ for a reversible cycle is zero.	dW/dT	dH/dT	dQ/dT	dE/dT	dQ/dT
37	The efficiency of a general cycle will be _____ the efficiency of a reversible cycle	equal to	less than	equal to or greater than	equal to or less than	equal to or less than
38	The cyclic integral of entropy is____	one	zero	infinity	cannot be determined	zero
39	Which of the following is known as the inequality of	cyclic integral of dQ/T<=0	cyclic integral of dQ/T>=0	cyclic integral of dW/T<=0	cyclic integral of dW/T>=0	cyclic integral of dQ/T<=0

	Clausius?					
40	If the cyclic integral of dQ/T is less than zero then the cycle is	irreversible but not possible	irreversible and possible	impossible	reversible	irreversible and possible
41	If the cyclic integral of dQ/T is zero then the cycle is	irreversible but not possible	irreversible and possible	impossible	reversible	reversible
42	If the cyclic integral of dQ/T is greater than zero then the cycle is	irreversible but not possible	irreversible and possible	impossible	reversible	impossible
43	If dQ is the heat supplied at T and dQ2 is the heat rejected at T2, then efficiency is given by	1-(dQ2/dQ)	1-(dQ/dQ2)	(dQ/dQ2)-1	(dQ2/dQ)-1	1-(dQ2/dQ)
44	Which of the following curves meet at triple point?	fusion curve and vaporization curve	fusion curve and sublimation curve	vaporization curve and sublimation curve	fusion curve and vaporization curve and sublimation curve	fusion curve and vaporization curve and sublimation curve
45	The slopes of sublimation and vaporization curves for all substances are	negative	positive	zero	infinity	positive
46	The slope of the fusion curve for water is	negative	positive	zero	infinity	negative
47	Which of the following represents the latent heat of vaporization at a particular pressure.	Hf-Hg	Hg-Hf	Hf+Hg	Hg+Hf	Hg-Hf

48	At critical pressure, value of Hg-Hf is	two	one	zero	infinity	zero
49	The locus of all points at which the Joule-Kelvin coefficient is ____ is the inversion curve.	negative	positive	zero	infinity	zero
50	The region inside the inversion curve has ____ Joule-Kelvin coefficient and the region outside the inversion curve has ____ Joule-Kelvin coefficient.	positive, positive	negative, negative	negative, positive	positive, negative	positive, negative
51	For a gas being throttled, the change in temperature can be	positive	negative	zero	all	all
52	Maximum temperature drop occurs if the initial state lies ____ the inversion curve.	above	on	below	zero	on
53	For an ideal gas,	volume expansivity = T and Joule-Kelvin coefficient = 0	volume expansivity = (1/T) and Joule-Kelvin coefficient = 1	volume expansivity = (1/T) and Joule-Kelvin coefficient = 0	volume expansivity = T and Joule-Kelvin coefficient = 1	volume expansivity = (1/T) and Joule-Kelvin coefficient = 0
54	The amount of heat required to raise the temperature of 1 kg by 1°C is called as:	work capcaity	heat capacity	energy capacity	specific heat capacity	specific heat capacity
55	SI unit of specific heat capacity is:	kg°C	j/kg°C	j/kg°	j/g°C	j/kg°C
56	Which of the following has highest heat capacity?	water	air	soil	wood	water

SYLLABUS

Kinetic Theory of Gases: Derivation of Maxwell's law of distribution of velocities and its experimental verification, Mean free path (Zeroth Order), Transport Phenomena: Viscosity, Conduction and Diffusion (for vertical case), Law of equipartition of energy (no derivation) and its applications to specific heat of gases; mono-atomic and diatomic gases.

Maxwell –Boltzmann speed Distribution Law

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

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

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

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

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

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

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

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

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

Discussion of the law:

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

From the distribution curves we get the following conclusions.

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

(2) As the speed increases the no of molecules in a given speed interval $\Delta\nu$ increases upto a certain maximum value.

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

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

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

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

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

Experiental Verification of distribution law

Finite width of spectral lines

In an excited atom electrons in the outermost orbit jump to higher orbits. If the energy is not sufficient to knock these electrons out, they fall back in the origin a position and the excess energy is emitted in the form of radiation. If an atom at rest is excites, there will be no Doppler broadening. The spectral line will have an exceedingly small width. In actual practice, we observe a finite width. This can be explained on the basis of the Maxwell distribution law for electrons.

For an atom at rest the frequeny of radiation is given by $v_0 = c/\lambda_0$

If we consider an assembly of electrons moving freely and behaves as the molecules of a gas, the changed frequency will be given by Doppler's effect.

Consider the motion along x-axis. If an electron is moving towards an observer with a velocity v_x, it will correspond to a frequency $v_0(1+v_x/c)$ where c is the velocity of light. On the other hand, if the electron moves away from the observer its frequency will corresponds to $v_0(1-v_x/c)$. Since v_x can have all possible values from 0 to infinity all frequencies about v_0 are possible. The spectral line will have an infinite width. Since the number of particles having velocity is small, the intensity falls off rapidly about a central maximum.

To understand it better, the frequency is inversely proportional to wavelength. So $v_0(1\pm v/c)$ will correspond to the wavelength λ_0 x.

Taking neutral of the form ln 2 $e^{-\left(\frac{mb^2v_0^2}{2k_BT}\right)}$Hence, $\lambda_0\text{-}x = \frac{c}{v_0\sqrt{1+v\frac{x}{c}}} = \frac{c}{v_0}(1+v\_x/c)^{-1}$

Using binomial expansion and relating terms upto first order in v_x/c, the $\lambda_0 - x = c/v_0 - v_x/v_0$

So that $x = v_x/v_0$

The spread of the spectral lines is related to molecular velocity. So the number of particles having velocity components between v_x and v_x+dv_x.

$$dNv_x = NAe^{-\left(\frac{mv^2}{2k_BT}\right)}dv_x$$

$$\text{So that } I_x = I_0e^{-\left(\frac{mv^2}{2k_BT}\right)}$$

Thus intensity at half width will be $I_b = I_0 e^{-\left(\frac{mb^2v_0^2}{2k_BT}\right)}$

$$I_0/I_b = 2 = \left(\frac{mb^2v_0^2}{2k_BT}\right)$$

$$\text{Or } b = \lambda_0/c \sqrt{\frac{2RT\ln 2}{M}}$$

Mean free path

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

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

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

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

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

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

where S is the total distance travelled in N collisions

Expression for mean free path:

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

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

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

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

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

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

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

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

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

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

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

Transport phenomena

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

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

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

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

Viscosity, conduction and diffusion represent the transport of momentum, energy and mass respect .These phenomena are called thermodynamic transport phenomena.

VISCOSITY

Viscosity is the property by virtue of which fluid opposes the relative motion between adjacent layers. It is quantitatively estimated in terms of the coefficient of viscosityη, which is defined as the tangential force per unit velocity gradient exists in a perpendicular direction. Mathematical,

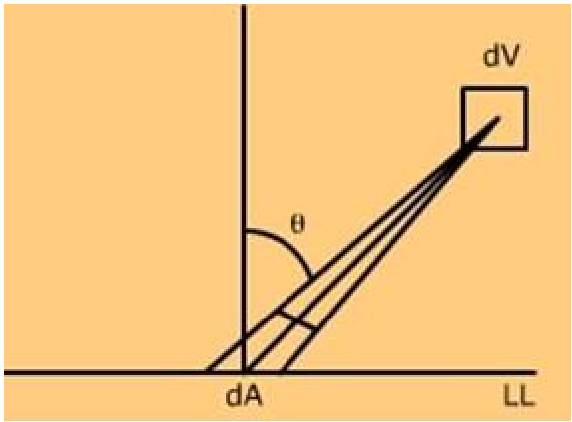
$$F=-\eta A\frac{du}{dy} \text{ ------------------ (1)}$$

Where F is the viscous force acting on an area A and du/dy is the velocity gradient along the +ve y direction. The negative sign indicates the viscous force acts in opposite direction.

To obtain an expression for η:

Consider a gas enclosed between two planes aa′ and bb′ separated through a distance h. The gas moves from left to right the layer of the gas in contact with the lower plane is at rest and a positive velocity gradient exists along a direction perpendicular to the direction of flow. Imagine a plane xx′ within the gas parallel to the direction of motion.

Let the velocity of flow xx′ be u and the velocity gradient du/dy. Because of their random motions, molecules continuously cross the surface both from above and below. To this end, we assume that its end last before crossing the surface, each molecule acquires a flow of velocity towards the right characteristics of the height at which it suffers the collision. Since the velocity gradients are positive upward molecules moving from above transport greater momentum than do molecules crossing from below.



Let us first discuss the average no. of molecules crossing the surface xx from above. Consider an element of volume dV at distance r from an element area dA in the plane xx' and the direction makes an angle θ with normal to the plane. Let n be the number density so that the number of molecules in the element is ndV. If z is the collision frequency, the total number of collision occurring within dv in time dt will be (1/2) 2ndVdt. This free path will start off in all 4π directions since all the directions of molecular motion are equally possible. Therefore, the fraction heading towards dA is

$$\Delta n = \frac{d\Omega}{4\pi} zndVdt$$

$$d\Omega = \frac{dA\ COS\theta}{r^2}$$

The number of molecules that will reach dA without making any further collision is given by the survival equation. Hence, $\Delta n_1 = \Delta n e^{\frac{-r}{\lambda}}$

In spherical polar coordinates, $dV = r^2 \sin\theta d\theta d\phi dr$.

$$\Delta n_1 = \frac{1}{4\pi} zn\ dA\ dt \sin\theta \cos\theta e^{\frac{-r}{\lambda}} d\theta d\phi dr \text{ --------- } (2)$$

To calculate the total number of molecules crossing dA in time dt from all half space and from all directions this expression over r from 0 to ∞, over θ from 0 to π/2 and ϕfrom 0 to 2π. This gives

$$n_1 = 1/4\,\pi\, zn\, dA\, dt\lambda\ ½\ 2\,\pi$$

$$= (\lambda/4)zndAdt$$

$$n_1/dAdt = n_s = 1/4\ \bar{v}n$$

On substituting n_1 from eqn (2) and integrate over r, θ and ϕ we get $\bar{y}=2/3\lambda$ -------- (3)

The momentum of this molecule will be m $(u+\frac{2}{3}\lambda\ \frac{du}{dy})$

Total momentum in the direction of flow, carried across the surface per unit area per unit time by all the molecules crossing the surface from above is

$$G^{+}=\frac{1}{4}n\bar{v}m\ (u+\frac{2}{3}\lambda\frac{du}{dy}) \qquad \text{------ (4)}$$

Similarly, the total momentum carried across the surface by the molecules crossing it in upward direction from below is

$$G- = \frac{1}{4}n\bar{v}m\ (u-\frac{2}{3}\lambda\frac{du}{dy}) \qquad \text{-------- (5)}$$

The net rate of transport of momentum in the upward direction per unit area per unit time is given by $G=G^{-}-G^{+} = -\frac{1}{3}n\bar{v}m\lambda\frac{du}{dy}$ -------- (6)

$$\eta=\frac{1}{3}nvm\lambda=\frac{1}{3}\rho V\lambda \qquad \text{-------- (7)}$$

On substituting the expression for λ we get, $\eta=(1/3\sqrt{2})\ (1/\pi d^2)\ mv$ ------ (8)

From this we note that the viscosity of a gas is proportional to $\bar{v}$. That is $\eta \propto T^{1/2}$ and is independent of n however, at very low or high pressure this low is not valid. This is because at very low pressure the intermolecular collisions are rare and mean free path becomes constant; comparable with the dimensions of apparatus. Consequently, the coefficient of viscosity decreases as pressure decreases. This fact was experimentally verified by crooks.

THERMAL CONDUCTIVITY: TRANSPORT OF ENERGY

The thermal conductivity of gas is treated in the same way as the viscosity. We again make a reference and consider heat flow across the gas lying between parallel surface aa′ and bb′ which are at rest but at different temperatures. That is, there is a temperature gradient be positive upwards and normal to the surface xx′ the heat flowing per second per unit area in the upward direction is given by

$$Q= -K\frac{dT}{dy} \text{----------------} (1)$$

Where k is thermal conductivity. As discussed earlier the thermal conductivity of a gas can be explained on the basis of the transport of molecular energy. We know that the average energy possessed by the molecules of a perfect gas can be written as

$$\varepsilon =\frac{f}{2}K_B T \quad \text{-----------} (2)$$

Where f is the number of degrees of freedom. We assume that

i) Each molecule crossing the given surface made its last collision at a distance of (2/3)λ above or below it , and

ii) The energy carried by a molecule is characteristic of that distance.

If T is the temperature at the surface xx′, the energy of a molecule at a distance (2/3)λ above or below its will be $\frac{f}{2}K_B(T\pm\frac{2}{3}\lambda\frac{dT}{dy})$. The particle moving in the downward direction per unit area per second is given by

$$Q^{+}=\frac{1}{2}nv\frac{f}{2}K_B(T+\frac{2}{3}\lambda\frac{dT}{dy})$$

The particle moving in upward direction per unit area per second is given by

$$Q^{-}=\frac{1}{2}nv\frac{f}{2}K_B(T-\frac{2}{3}\lambda\frac{dT}{dy})$$

Hence the net transport will be

$$Q = Q^{-}-Q^{+}=-\frac{1}{6}n\lambda v f\frac{k_B dT}{dy} \text{ ------}(3)$$

By comparing eqn (1) and (3) $K=f/6\, n\lambda\bar{v}\, k_B = (C_v/3)n\bar{v}\lambda$ ------ (4)

Where $C_v= f/2\, k_B$ is the molar heat capacity. Hence by combining, viscosity and thermal conductivity we note that $\frac{K}{\eta}=\frac{Cv}{m}=\frac{N_A C_V}{M}=C_V/M$

$$\text{Or } KM/\eta C_V=1 \text{ --------} (5)$$

Therefore our theory predicts that for all gases, this ratio should be equal to unity.

DIFFUSION

Consider two gases, say hydrogen and oxygen placed one above another, hydrogen being above. Let these gases be at the same temperature and pressure. As such there will be no large scale movement of the gas in either direction but after sometimes one finds that the two one finds that the two gases mix with each other even against gravity. This phenomenon, as a result of that which gives gradually permeate the other is called diffusion. It is a direct consequence of random molecular motion and continues so long as inequalities in concentration exist. This process is described in terms of the coefficient of diffusion, D. let n be the molecular concentration along a horizontal plane xx′ and let there be a positive concentration gradient dn/dy in the vertical plane. Then the number of particles crossing the given surface per unit area per unit time is given by

$$\Gamma=-D\frac{dn}{dy} \text{ --------- } (1)$$

Calculate the number in the reverse direction

For the general case the calculation of the diffusion coefficient is complicated due to the fact then the rates of diffusion of two gases may or may not be the same. One can simplify this problem and still being out the essential ideas by considering the diffusion of like molecules i.e., self-diffusion. The diffusion of isotope of the same element is an example for this type. As before we assume that each molecule makes its last collision before crossing a surface at a perpendicular distance (2/3) λ. if n_0 is the concentration of gas molecules t any point the number density at a distance (2/3)above or below the surface xx′ will be

$$n_0=n\pm\frac{2}{3}\lambda\frac{dn}{dy}$$

Hence the number of molecules crossing the given surface area per unit area per second from below is

$$\Gamma^-=\frac{1}{4}\,v\left(n-\frac{2}{3}\lambda\frac{dn}{dy}\right) \text{ ------- } (2)$$

Since the number of molecules crossing the given surface per unit area per unit time from above is

$$\Gamma^{+}=\frac{1}{4}\ v\ (n+\frac{2}{3}\lambda\frac{dn}{dy})\text{ ----- }(3)$$

Therefore the total number of molecules transferred upward across the given surface per unit area per second is

$$\Gamma = -\frac{1}{3}\bar{v}y\frac{dn}{dy}\text{ -------- }(4)$$

On comparing (1) and (4), we get $D=\frac{1}{3}v\lambda$ ----- (5)

Since $\lambda \propto T/P$ and $v=T^{1/2}$ it implies that the diffusion coefficient will vary inversely as p and directly as $T^{3/2}$. One finds that the predicted variation with pressure is in agreement with the observed result but the power of T lies between 1.75 and 2.

Principle of equipartition of energy

The principle of equipartition of energy is stated as follows:

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

The principle may also be stated as follows:

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

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

Specific Heats of Gases

The specific heats of gases are generally expressed as molar specific heats. For a monoatomic ideal gas the internal energy is all in the form of kinetic energy, and kinetic theory provides the expression for that energy, related to the kinetic temperature. The expression for the internal energy is

$$U = nN_A KE_{avg} = nN_A \frac{3}{2}kT = \frac{3}{2}nRT$$

Two specific heats are defined for gases, one for constant volume (**C**$_V$) and one for constant pressure (**C**$_P$). For a constant volume process with a monoatomic ideal gas the first law of thermodynamics gives:

$$Q = C_V n\Delta T \qquad Q = \Delta U + P\Delta V = \Delta U$$

$$C_V = \frac{1}{n}\frac{\Delta U}{\Delta T} = \frac{3}{2}R$$

Possible Questions

2marks

1. State Law of equipartition of energy.
2. State the application of specific heat of diatomic gases.
3. What is called transport phenomena?
4. What is called mean free path?

5. Define viscosity.
6. Define conduction.
7. Define diffusion.
8. What is called specific heat?
9. What are the applications of specific heat of gas?

6 marks

1. What is mean free path? Explain it.
2. Discuss the application of specific heat of monoatomic gases.
3. Obtain an expression for Maxwell-Boltzmann law of distribution of velocities.
4. Discuss about application of specific heat to diatomic gases.
5. Discuss about transport phenomena.
6. Explain Maxwell-Boltzmann distribution experimentally.
7. State and explain mean free path.
8. What is called transport phenomenon? Explain any one of its types.
9. What is called diffusion? Explain it briefly.

SYLLABUS

Introduction – Liouville’s theorem – Measurement of macro-properties of a thermodynamic system – Ensemble – Microcanonical and Canonical ensembles – Entropy of an ideal gas – microcanonical ensemble – Application of Gibbs canonical ensembles – Fluctuations in thermodynamic variables – Stirling’s approximation or Stirling’s formula – Relation between entropy and probability – Boltzman theorem.

Liouville's Theorem

In Classical Mechanics, the complete state of a particle can be given by its coordinates and momenta. For example in three dimensions, there are three spatial coordinates and three conjugate momenta. If we consider a six dimensional phase space, a point in that space represents the state of a particle. A particle will follow a determined path through phase space, that is, given the particles full state (a point in phase space), our equations of motion will yield the phase space location of the particle at a later time (or even an earlier time). So particles follow determined paths through (six dimensional) phase space.

Consider a large number of particles, perhaps in a beam. These particles can be described by one point in phase space per particle. For really large numbers of particles in a system, or if we consider a theoretical ensemble of particles, the system can be described as a density $\rho(q_{i,}p_i)$ which is a function of the position in phase space.

Liouville's Theorem states that the density of particles in phase space is a constant $\frac{d\rho}{dt} = 0$, so to calculate the rate of change of the density of particles. Imagine shoot a burst of particles at the moon. The burst is localized in space and in momentum. The burst moves toward the moon and so clearly the density near the earth are decreased, however, the density we are interested in is essential, the density around one of the particles, not the density at some fixed point. That is, the point in phase space at which we wish to measure the density, moves with the particles. The bunch of particles spreads out in coordinates space but the coordinate is highly correlated with the momentum so the density in phase space can remain constant.

To ``prove'' Liouville's theorem, we will calculate the rate of change of the number of particles in an infinitesimal hypercube in phase space. Consider the cube face perpendicular to q_k for example. The flow of particles through the face is $\rho q_k dp_k$ times all the other dimensions of the face $dq_j dp_j$ for $j \neq k$. Then the rate of change of the number of particles in the hypercube, due to flow through this face and the one opposite it is.

$$\frac{\partial N}{\partial t} = -\frac{\partial(\rho \dot{q}_k)}{\partial q_K} \prod_j dq_j dp_j$$

and the net flow into the hypercube due to all of the faces is

$$\frac{\partial N}{\partial t} = -\sum_k \left[\frac{\partial(\rho \dot{q}_k)}{\partial q_K} + \frac{\partial(\rho \dot{p}_k)}{\partial p_K} \right] \prod_j dq_j dp_j .$$

Calculate the rate of change of the density by dividing by the volume of the hypercube.

$$\frac{\partial \rho}{\partial t} = -\sum_k \left[\frac{\partial(\rho \dot{q}_k)}{\partial q_K} + \frac{\partial(\rho \dot{p}_k)}{\partial p_K} \right]$$

So that is the rate of change due to the other particles flowing, the partial derivative. To this we should add the rate of change due to the particle we are following moving.

$$\frac{d\rho}{dt} = \frac{\partial \rho}{\partial t} + \sum_k \left[\frac{\partial \rho}{\partial q_K} \dot{q}_k + \frac{\partial \rho}{\partial p_K} \dot{p}_k \right]$$

$$\frac{d\rho}{dt} = -\sum_k \left[\frac{\partial(\rho \dot{q}_k)}{\partial q_K} + \frac{\partial(\rho \dot{p}_k)}{\partial p_K} \right] + \sum_k \left[\frac{\partial \rho}{\partial q_K} \dot{q}_k + \frac{\partial \rho}{\partial p_K} \dot{p}_k \right]$$

$$\frac{d\rho}{dt} = \sum_k \left[-\frac{\partial \rho}{\partial q_K} \dot{q}_k - \frac{\partial \dot{q}_k}{\partial q_K} \rho - \frac{\partial \rho}{\partial p_K} \dot{p}_k - \frac{\partial \dot{p}_k}{\partial p_K} \rho + \frac{\partial \rho}{\partial q_K} \dot{q}_k + \frac{\partial \rho}{\partial p_K} \dot{p}_k \right]$$

$$\frac{d\rho}{dt} = \sum_k \left[-\frac{\partial \dot{q}_k}{\partial q_K} - \frac{\partial \dot{p}_k}{\partial p_K} \right] \rho$$

Now, we apply Hamilton's equations.

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\frac{d\rho}{dt} = \sum_k \left[-\frac{\partial^2 H}{\partial q_K \partial p_K} + \frac{\partial^2 H}{\partial p_K \partial q_K} \right] \rho = 0$$

Ensembles

An ensemble is a collection of a large number of replicas (or mental copies) of the microstates of the system under the same macroscopic condition or having the same macrostate. However, the microstates of the members of an ensemble can be arbitrarily different. Thus, for a given macroscopic condition, a system of an ensemble is represented by a point in the phase space. The ensemble of a macroscopic system of given macrostate then corresponds to a large number of points in the phase space. During time evolution of a macroscopic system in a fixed macrostate, the microstate is supposed to pass through all these phase points.

Depending on the interaction of a system with the surroundings (or universe), a thermodynamic system is classified as isolated, closed or open system. Similarly, statistical ensembles are also classified into three different types. The classification of ensembles again depends on the type of interaction of the system with the surroundings which can either be by exchange of energy only or exchange of both energy and matter (particles or mass).

There are three types of ensembles:

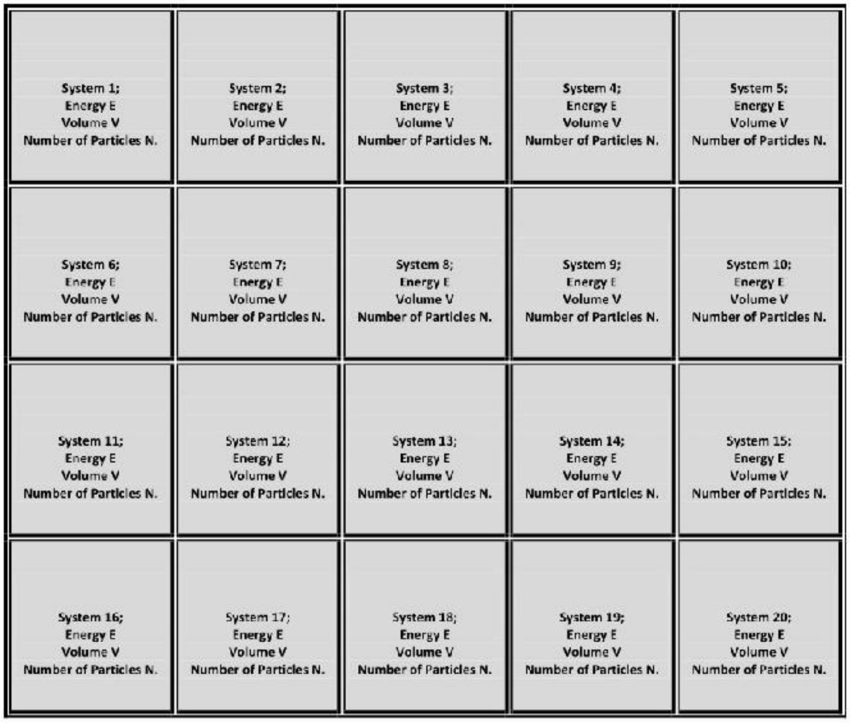
1. Micro-Canonical Ensemble
2. Canonical Ensemble
3. Grand Canonical Ensemble

Micro-canonical Ensemble

It is the collection of a large number of essentially independent systems having the **same energy E, volume V** and **total number of particles N.**

The systems of a micro-canonical ensemble are separated by rigid impermeable and insulated walls, such that the values of **E, V & N** are not affected by the mutual pressure of other systems.

This ensemble is as shown in the figure below:



System 1; Energy E Volume V Number of Particles N.	System 2; Energy E Volume V Number of Particles N.	System 3; Energy E Volume V Number of Particles N.	System 4; Energy E Volume V Number of Particles N.	System 5; Energy E Volume V Number of Particles N.
System 6; Energy E Volume V Number of Particles N.	System 7; Energy E Volume V Number of Particles N.	System 8; Energy E Volume V Number of Particles N.	System 9; Energy E Volume V Number of Particles N.	System 10; Energy E Volume V Number of Particles N.
System 11; Energy E Volume V Number of Particles N.	System 12; Energy E Volume V Number of Particles N.	System 13; Energy E Volume V Number of Particles N.	System 14; Energy E Volume V Number of Particles N.	System 15; Energy E Volume V Number of Particles N.
System 16; Energy E Volume V Number of Particles N.	System 17; Energy E Volume V Number of Particles N.	System 18; Energy E Volume V Number of Particles N.	System 19; Energy E Volume V Number of Particles N.	System 20; Energy E Volume V Number of Particles N.

Here all the borders are impermeable and insulated.

Canonical Ensemble

It's the collection of a large number of essentially independent systems having the same **temperature T, volume V** and **the number of particles N**.

The equality of temperature of all the systems can be achieved by bringing all the systems in thermal contact. Hence, in this ensemble the systems are separated by rigid impermeable but **conducting** walls, the outer walls of the ensemble are perfectly insulated and impermeable though.

This ensemble is as shown in figure:

System 1; **Temperature T** **Volume V** **Number of Particles N.**	System 2; **Temperature T** **Volume V** **Number of Particles N.**	System 3; **Temperature T** **Volume V** **Number of Particles N.**	System 4; **Temperature T** **Volume V** **Number of Particles N.**	System 5; **Temperature T** **Volume V** **Number of Particles N.**
System 6; **Temperature T** **Volume V** **Number of Particles N.**	System 7; **Temperature T** **Volume V** **Number of Particles N.**	System 8; **Temperature T** **Volume V** **Number of Particles N.**	System 9; **Temperature T** **Volume V** **Number of Particles N.**	System 10; **Temperature T** **Volume V** **Number of Particles N.**
System 11; **Temperature T** **Volume V** **Number of Particles N.**	System 12; **Temperature T** **Volume V** **Number of Particles N.**	System 13; **Temperature T** **Volume V** **Number of Particles N.**	System 14; **Temperature T** **Volume V** **Number of Particles N.**	System 15; **Temperature T** **Volume V** **Number of Particles N.**
System 16; **Temperature T** **Volume V** **Number of Particles N.**	System 17; **Temperature T** **Volume V** **Number of Particles N.**	System 18; **Temperature T** **Volume V** **Number of Particles N.**	System 19; **Temperature T** **Volume V** **Number of Particles N.**	System 20; **Temperature T** **Volume V** **Number of Particles N.**
System 21; **Temperature T** **Volume V** **Number of Particles N.**	System 22; **Temperature T** **Volume V** **Number of Particles N.**	System 23; **Temperature T** **Volume V** **Number of Particles N.**	System 24; **Temperature T** **Volume V** **Number of Particles N.**	System 25; **Temperature T** **Volume V** **Number of Particles N.**

Here, the borders in bold shade are both insulated and impermeable while the borders in light shade are conducting and impermeable.

Grand Canonical Ensemble

It is the collection of a large number of essentially independent systems having the same **temperature T, volume V & chemical potential μ.**

The systems of a grand canonical ensemble are separated by rigid permeable and conducting walls.

This ensemble is as shown in figure:

System 1; **Temperature T** **Volume V** **Chemical Potential μ .**	System 2; **Temperature T** **Volume V** **Chemical Potential μ.**	System 3; **Temperature T** **Volume V** **Chemical Potential μ.**	System 4; **Temperature T** **Volume V** **Chemical Potential μ.**	System 5; **Temperature T** **Volume V** **Chemical Potential μ.**
System 6; **Temperature T** **Volume V** **Chemical Potential μ.**	System 7; **Temperature T** **Volume V** **Chemical Potential μ.**	System 8; **Temperature T** **Volume V** **Chemical Potential μ.**	System 9; **Temperature T** **Volume V** **Chemical Potential μ.**	System 10; **Temperature T** **Volume V** **Chemical Potential μ.**
System 11; **Temperature T** **Volume V** **Chemical Potential μ.**	System 12; **Temperature T** **Volume V** **Chemical Potential μ.**	System 13; **Temperature T** **Volume V** **Chemical Potential μ.**	System 14; **Temperature T** **Volume V** **Chemical Potential μ.**	System 15; **Temperature T** **Volume V** **Chemical Potential μ.**
System 16; **Temperature T** **Volume V** **Chemical Potential μ.**	System 17; **Temperature T** **Volume V** **Chemical Potential μ.**	System 18; **Temperature T** **Volume V** **Chemical Potential μ.**	System 19; **Temperature T** **Volume V** **Chemical Potential μ.**	System 20; **Temperature T** **Volume V** **Chemical Potential μ.**
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Here inner borders are rigid, permeable and conducting while outer borders are impermeable as well as insulated. As the inner separating walls are conducting and permeable, the exchange of heat energy as well as that of particles between the system takes place, in such a way that all the systems achieve the same common temperature **T** and chemical potential **μ .**

ENTROPY OF AN IDEAL GAS

The entropy S of a monoatomic ideal gas can be expressed in a famous equation called the Sackur-Tetrode equation.

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right]$$

where

- N = number of atoms
- k = Boltzmann's constant
- V = volume
- U = internal energy
- h = Planck's constant

One of the things which can be determined directly from this equation is the change in entropy during an isothermal expansion where N and U are constant (implying Q=W). Expanding the entropy expression for V_f and V_i with log combination rules leads to

$$\Delta S = Nk\ln\frac{V_f}{V_i}$$

For determining other functions, it is useful to expand the entropy expression to separate the U and V dependence.

$$S = \frac{3}{2}Nk\ln U + Nk\ln V + Nk\left[\ln\left(\frac{1}{N}\left(\frac{4\pi m}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right]$$

Then making use of the definition of temperature in terms of entropy:

$$\frac{\partial S}{\partial U} = \frac{3}{2}\frac{Nk}{U} \quad ; \quad T = \frac{1}{\frac{\partial S}{\partial U}} = \frac{2U}{3Nk}$$

This gives an expression for internal energy that is consistent with equipartition of energy.

$$U = \frac{3}{2}NkT$$

with kT/2 of energy for each degree of freedom for each atom.

For processes with an ideal gas, the change in entropy can be calculated from the relationship

$$S(B)-S(A)=\int_A^B \frac{dQ}{T}$$

Making use of the first law of thermodynamics and the nature of system work, this can be written

$$\Delta S=\int_A^B \frac{dQ}{T}=\int_A^B \frac{dU+PdV}{T}=\int_A^B \frac{nC_V dT}{T}+\int_A^B \frac{nRdV}{V}$$

$$\Delta S=nC_V \ln\frac{T_B}{T_A}+nR\ln\frac{V_B}{V_A}$$

This is a useful calculation form if the temperatures and volumes are known. Using the ideal gas law

$$\frac{T_B}{T_A}=\frac{P_BV_B}{P_AV_A} \quad then \quad \ln\frac{T_B}{T_A}=\ln\frac{P_B}{P_A}+\ln\frac{V_B}{V_A}$$

then

$$\Delta S=nC_V \ln\frac{P_B}{P_A}+(nC_V+nR)\ln\frac{V_B}{V_A}.$$

But since specific heats are related by $C_P = C_V + R$,

$$\Delta S=nC_V \ln\frac{P_B}{P_A}+nC_P\ln\frac{V_B}{V_A}.$$

Since entropy is a state variable, just depending upon the beginning and end states, these expressions can be used for any two points.

FLUCTUATIONS IN ENERGY

A system can be represented by a canonical ensemble. Since in this ensemble, system remains in thermal equilibrium with heat reservoir, fluctuations cannot occur in temperature but only in energy when the energy is exchanged between the system and the reservoir. For canonical ensemble, partition function is

$$Z=\sum_r e^{-\frac{E_r}{kT}}$$

And mean energy is $\langle E\rangle = \frac{\sum_r E_r e^{-\frac{E_r}{kT}}}{\sum_r e^{-\frac{E_r}{kT}}}$

Or $\langle E\rangle \sum_r e^{-\frac{E_r}{kT}} = \sum_r E_r e^{-\frac{E_r}{kT}}$

Differentiation above equation w.r.to temperature, we obtain

$$\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V}\sum_r e^{-\frac{E_r}{kT}} + \frac{\langle E\rangle}{kT^2}\sum_r E_r e^{-\frac{E_r}{kT}} = \frac{1}{kT^2}\sum_r {E_r}^2 e^{-\frac{E_r}{kT}}$$

Rearranging the term we obtain,

$$\frac{\sum_r {E_r}^2 e^{-\frac{E_r}{kT}}}{\sum_r e^{-\frac{E_r}{kT}}} - \langle E\rangle \frac{\sum_r E_r e^{-\frac{E_r}{kT}}}{\sum_r e^{-\frac{E_r}{kT}}} = kT^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V}$$

The first factoron left hand side represents $\langle E^2\rangle - \langle E\rangle^2 = kT^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V}$

But $\langle E^2\rangle - \langle E\rangle^2 = \langle\langle\langle E\rangle - E\rangle^2\rangle$

So that $\langle\langle\langle E\rangle - E\rangle^2\rangle = kT^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V}$ -------- (1)

When n is large and E≅ $\langle E\rangle$, $\frac{\langle\langle\langle E\rangle - E\rangle^2\rangle}{\langle\langle E\rangle\rangle^2} = \frac{kT^2}{E^2}\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V} = \frac{kT^2}{E^2}$ Cv --------- (2)

Where Cv is the specific heat at constant volume V and constant n. Experimentally, Cv= nk & E = nkT

$$\langle\frac{\Delta E}{E}\rangle^2 = \frac{\langle\langle\langle E\rangle - E\rangle^2\rangle}{\langle\langle E\rangle\rangle^2} = \frac{kT^2}{n^2k^2T^2}\,.nk = \frac{1}{n}$$

Or $\langle\frac{\Delta E}{E}\rangle$ = of the order of $(n)^{-1/2}$

The standard deviation from the mean value is of the order of $(n)^{-1/2}$. For $n=10^{22}$, fluctuations in energy will be small. On the other hand implies that the probability distribution in E, in an ordinary thermodynamics system consisting large number of molecules.

FLUCTUATIONS IN PRESSURE

The mean pressure of any phase is given by $\langle p\rangle = \frac{\sum_r e^{-\frac{E_r}{kT}}\left(-\frac{\partial E_r}{\partial V}\right)}{\sum_i e^{-\frac{E_r}{kT}}}$ ------- (1)

Differnetiating above eqn., and rearraging the terms, we get

$$\frac{\sum_r e^{-\frac{E_r}{kT}}\left(-\frac{\partial E_r}{\partial V}\right)^2}{\sum_r e^{-\frac{E_r}{kT}}} - \langle p\rangle \frac{\sum_r e^{-\frac{E_r}{kT}}\left(-\frac{\partial E_r}{\partial V}\right)}{\sum_i e^{-\frac{E_r}{kT}}} = kT[\left(\frac{\partial\langle p\rangle}{\partial T}\right)_{n,V} + \langle\frac{\partial^2 E}{\partial V^2}\rangle$$

$$\langle p^2\rangle - \langle p\rangle^2 = kT\left\{\left(\frac{\partial p}{\partial V}\right)_{n,V} + \langle\frac{\partial^2 E}{\partial V^2}\rangle\right\}$$

Or $\langle\langle\langle p\rangle - \langle p\rangle^2\rangle\rangle = kT\left\{\left(\frac{\partial\langle p\rangle}{\partial V}\right)_{n,V} - \langle\frac{\partial^2 p}{\partial V^2}\rangle\right\}$

Making the association with thermodynamics p≅ $\langle p\rangle$

$$\frac{\langle\langle\langle p\rangle - p\rangle^2\rangle}{\langle\langle p\rangle\rangle^2} = kT/p^2\left\{\left(\frac{\partial\langle p\rangle}{\partial T}\right)_{n,V} - \langle\frac{\partial^2 p}{\partial V^2}\rangle\right\} \text{----------- (2)}$$

The first term in the bracket on right hand side of above equation represents the variation of mean pressure with isothermal changes in volume. The second term involves the direct measurement of ratio at first and then averaging it.

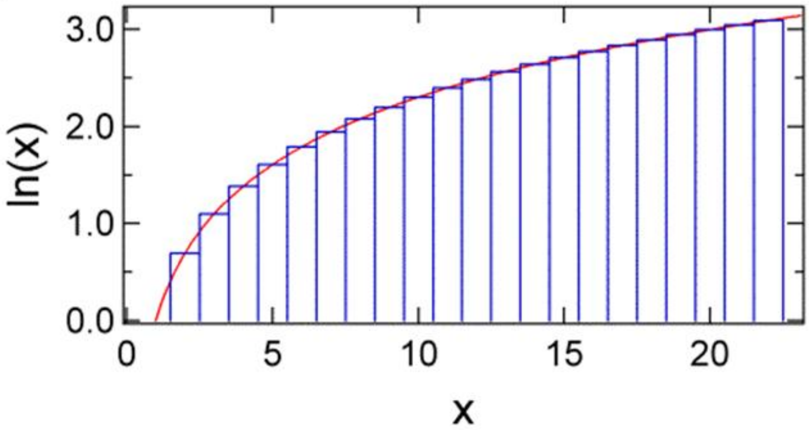
For an ideal gas, the first term on the right hand side is $\frac{kT}{p}x\left(-\frac{p}{V}\right) = \frac{1}{n}$ and the second term must be positive and larger in magnitude than the first hand side.

STIRLING'S APPROXIMATION

In confronting statistical problems we often encounter factorials of very large numbers. The factorial N! is a product N(N-1)(N-2)..(2)(1). Therefore, ln N! is a sum

$$\ln N! = \sum_{m=1}^{N} \ln m$$

where we have used the property of logarithms that log(abc) = log(a) + log(b) + log(c). The sum is shown in figure below.



The sum of the area under the blue rectangles shown below up to N is ln N!. As you can see the rectangles begin to closely approximate the red curve as m gets larger. The area under the curve is given the integral of ln x.

$$\ln N! = \sum_{m=1}^{N} \ln m \approx \int_{1}^{N} \ln x \, dx$$

To solve the integral use integration by parts

$$\int u \, dv = uv - \int v \, du$$

Here we let u = ln x and dv = dx. Then v = x and du = dx/x.

$$\int_{0}^{N} \ln x \, dx = x \ln x \Big|_{0}^{N} - \int_{0}^{N} x \frac{dx}{x}$$

Notice that x/x = 1 in the last integral and x ln x is 0 when evaluated at zero, so we have

$$\int_{0}^{N} \ln x \, dx = N \ln N - \int_{0}^{N} dx$$

Which gives us Stirling's approximation: ln N! = N ln N – N.

RELATION BETWEEN ENTROPY AND PROBABILITY

Entropy characterizes the disorder in a system. Since equilibrium is the most disordered state, its entropy is maximum. This suggests a connection between entropy and thermodynamic probability.

$$S=f\ (\Omega_0) \text{ ------- } (1)$$

This means that if S1 and S2 are the entropies of two systems, the entropy of the combined system will be given by

$$S_0 = S_1+S_2 \text{ ------- } (2)$$

On the other hand, probability is multiplicative and can be written as

$$\Omega_0 = \Omega_1 \, \Omega_2 \text{ ---------- } (3)$$

f is such that S increases with Ω and translates a product into a sum. This can achieved through a logarithmic function so that we can write as $S=k_B \ln \Omega$ ---------- (4)

where k_B is the Boltzmann's constant.

BOLTZMANN H-THEOREM

$$\left(\frac{\partial f_1}{\partial t}\right)_2 = \iiint u\,\sigma(\mathbf{v}_1; \mathbf{v}_2; \mathbf{v}_1'; \mathbf{v}_2')\,(f_1' f_2' - f_1 f_2)\, d^3\mathbf{v}_2\, d^3\mathbf{v}_1'\, d^3\mathbf{v}_2'.$$

…… (1)

Consider the quantity $H = \int f_1 \ln f_1 \, d^3\mathbf{v}_1.$ ……. (2)

It follows from Equation (1) that $\frac{dH}{dt} = \int (1 + \ln f_1) \frac{\partial f_1}{\partial t} d^3\mathbf{v}_1$

$$= \iiiint u\,\sigma\,(1+\ln f_1)\,(f_1'\,f_2' - f_1\,f_2)\,d^3\mathbf{v}_1\,d^3\mathbf{v}_2\,d^3\mathbf{v}_1'\,d^3\mathbf{v}_2', \quad \text{……. (3)}$$

where σ is short-hand for $\sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}_1', \mathbf{v}_2')$. Suppose that we swap the dummy labels **1** and **2** . This process leaves both $u = |\mathbf{v}_1 - \mathbf{v}_2|$ and the value of the integral unchanged. It also leaves the scattering cross-section $\sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}_1', \mathbf{v}_2')$ unchanged. Hence, we deduce that

$$\frac{dH}{dt} = \iiiint u\,\sigma\,(1+\ln f_2)\,(f_1'\,f_2' - f_1\,f_2)\,d^3\mathbf{v}_1\,d^3\mathbf{v}_2\,d^3\mathbf{v}_1'\,d^3\mathbf{v}_2'. \quad \text{…… (4)}$$

Suppose that we primed and unprimed dummy variables of integration in Equation (3). This leaves the value of the integral unchanged. we obtain

$$\frac{dH}{dt} = -\iiiint u\,\sigma\,(1+\ln f_1')\,(f_1'\,f_2' - f_1\,f_2)\,d^3\mathbf{v}_1\,d^3\mathbf{v}_2\,d^3\mathbf{v}_1'\,d^3\mathbf{v}_2'. \quad \text{….. (5)}$$

Finally, primed and unprimed variables in Equation (4) yields

$$\frac{dH}{dt} = -\iiiint u\,\sigma\,(1+\ln f_2')\,(f_1'\,f_2' - f_1\,f_2)\,d^3\mathbf{v}_1\,d^3\mathbf{v}_2\,d^3\mathbf{v}_1'\,d^3\mathbf{v}_2'. \quad \text{……. (6)}$$

The previous four equations can be combined to give

$$\frac{dH}{dt} = \frac{1}{4}\iiint \int u\sigma \ln\left(\frac{f_1 f_2}{f_1 f_2}\right)(f_1'f_2'-f_1f_2)\, d_3V_1 d_3V_2 d_3V'_1 d_3V_2'$$

Now, ln $(f_1f_2/f_1'f_2')$ is positive when $f_1'f_2'-f_1f_2$ is negative, and vice versa. Therefore, deduce that the integral on the right-hand side of the previous expression can never take a positive value. In other words,

$$dH/dt \le 0$$

This result is known as the *Boltzmann H-theorem*.

Possible Questions

2marks

1. Give a note on Stirling’s approximation.
2. What is the relation between entropy and probability?
3. Define microcanonical and canonical ensemble.
4. State Liouville’s theorem.
5. What is called ensemble?
6. Define entropy.
7. What are the applications of ensembles?
8. State Bolztman theorem.

6 marks

1. What is called ensemble? Explain it.
2. Give the relation between entropy and probability.
3. State Liouville’s theorem. Explain it briefly.
4. Explain microcanonical ensemble.
5. State Boltzmann Theorem. Explain it.
6. Explain the entropy of ideal gas.
7. Discuss about the fluctuations in thermodynamic variables.

SYLLABUS

Introduction – Liouville's theorem – Measurement of macro-properties of a thermodynamic system – Ensemble – Microcanonical and Canonical ensembles – Entropy of an ideal gas – microcanonical ensemble – Application of Gibbs canonical ensembles – Fluctuations in thermodynamic variables – Stirling's approximation or Stirling's formula – Relation between entropy and probability – Boltzman theorem.

Liouville's Theorem

In Classical Mechanics, the complete state of a particle can be given by its coordinates and momenta. For example in three dimensions, there are three spatial coordinates and three conjugate momenta. If we consider a six dimensional phase space, a point in that space represents the state of a particle. A particle will follow a determined path through phase space, that is, given the particles full state (a point in phase space), our equations of motion will yield the phase space location of the particle at a later time (or even an earlier time). So particles follow determined paths through (six dimensional) phase space.

Consider a large number of particles, perhaps in a beam. These particles can be described by one point in phase space per particle. For really large numbers of particles in a system, or if we consider a theoretical ensemble of particles, the system can be described as a density $\rho(q_{i,}p_i)$ which is a function of the position in phase space.

Liouville's Theorem states that the density of particles in phase space is a constant $\frac{d\rho}{dt} = 0$, so to calculate the rate of change of the density of particles. Imagine shoot a burst of particles at the moon. The burst is localized in space and in momentum. The burst moves toward the moon and so clearly the density near the earth are decreased, however, the density we are interested in is essential, the density around one of the particles, not the density at some fixed point. That is, the point in phase space at which we wish to measure the density, moves with the particles. The bunch of particles spreads out in coordinates space but the coordinate is highly correlated with the momentum so the density in phase space can remain constant.

To ``prove" Liouville's theorem, we will calculate the rate of change of the number of particles in an infinitesimal hypercube in phase space. Consider the cube face perpendicular to q_k for example. The flow of particles through the face is $\rho q_k dp_k$ times all the other dimensions of the face $dq_j dp_j$ for j≠k. Then the rate of change of the number of particles in the hypercube, due to flow through this face and the one opposite it is.

$$\frac{\partial N}{\partial t} = -\frac{\partial(\rho\dot{q}_k)}{\partial q_K}\prod_j dq_j dp_j$$

and the net flow into the hypercube due to all of the faces is

$$\frac{\partial N}{\partial t} = -\sum_k\left[\frac{\partial(\rho\dot{q}_k)}{\partial q_K}+\frac{\partial(\rho\dot{p}_k)}{\partial p_K}\right]\prod_j dq_j dp_j.$$

Calculate the rate of change of the density by dividing by the volume of the hypercube.

$$\frac{\partial \rho}{\partial t} = -\sum_k\left[\frac{\partial(\rho\dot{q}_k)}{\partial q_K}+\frac{\partial(\rho\dot{p}_k)}{\partial p_K}\right]$$

So that is the rate of change due to the other particles flowing, the partial derivative. To this we should add the rate of change due to the particle we are following moving.

$$\begin{aligned}
\frac{d\rho}{dt} &= \frac{\partial\rho}{\partial t}+\sum_k\left[\frac{\partial\rho}{\partial q_K}\dot{q}_k+\frac{\partial\rho}{\partial p_K}\dot{p}_k\right]\\
\frac{d\rho}{dt} &= -\sum_k\left[\frac{\partial(\rho\dot{q}_k)}{\partial q_K}+\frac{\partial(\rho\dot{p}_k)}{\partial p_K}\right]+\sum_k\left[\frac{\partial\rho}{\partial q_K}\dot{q}_k+\frac{\partial\rho}{\partial p_K}\dot{p}_k\right]\\
\frac{d\rho}{dt} &= \sum_k\left[-\frac{\partial\rho}{\partial q_K}\dot{q}_k-\frac{\partial\dot{q}_k}{\partial q_K}\rho-\frac{\partial\rho}{\partial p_K}\dot{p}_k-\frac{\partial\dot{p}_k}{\partial p_K}\rho+\frac{\partial\rho}{\partial q_K}\dot{q}_k+\frac{\partial\rho}{\partial p_K}\dot{p}_k\right]\\
\frac{d\rho}{dt} &= \sum_k\left[-\frac{\partial\dot{q}_k}{\partial q_K}-\frac{\partial\dot{p}_k}{\partial p_K}\right]\rho
\end{aligned}$$

Now, we apply Hamilton's equations.

$$\dot{q}_i = \frac{\partial H}{\partial p_i}$$

$$\dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$\frac{d\rho}{dt} = \sum_k \left[-\frac{\partial^2 H}{\partial q_K \partial p_K} + \frac{\partial^2 H}{\partial p_K \partial q_K} \right] \rho = 0$$

Ensembles

An ensemble is a collection of a large number of replicas (or mental copies) of the microstates of the system under the same macroscopic condition or having the same macrostate. However, the microstates of the members of an ensemble can be arbitrarily different. Thus, for a given macroscopic condition, a system of an ensemble is represented by a point in the phase space. The ensemble of a macroscopic system of given macrostate then corresponds to a large number of points in the phase space. During time evolution of a macroscopic system in a fixed macrostate, the microstate is supposed to pass through all these phase points.

Depending on the interaction of a system with the surroundings (or universe), a thermodynamic system is classified as isolated, closed or open system. Similarly, statistical ensembles are also classified into three different types. The classification of ensembles again depends on the type of interaction of the system with the surroundings which can either be by exchange of energy only or exchange of both energy and matter (particles or mass).

There are three types of ensembles:

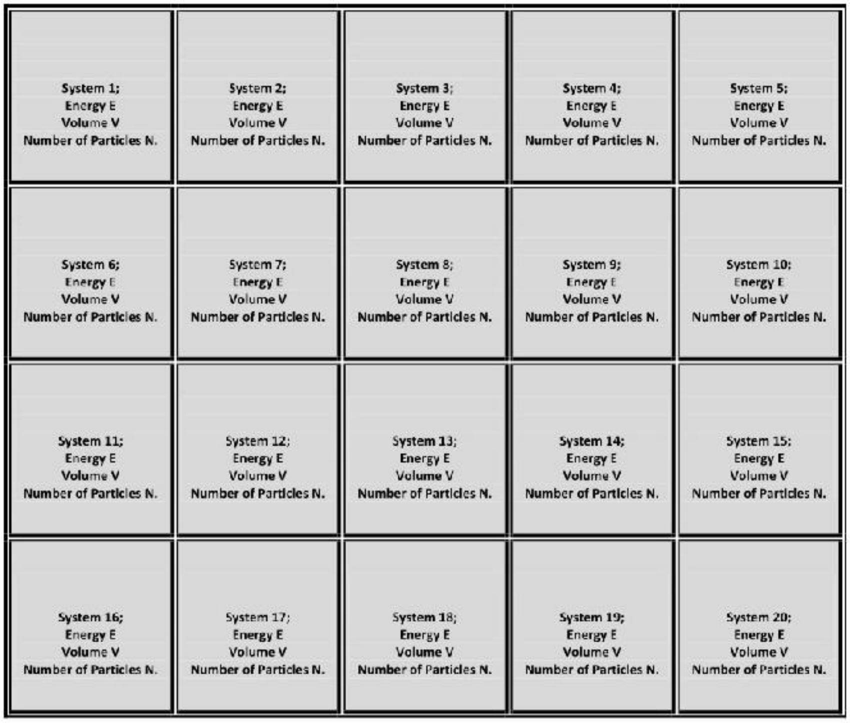
1. Micro-Canonical Ensemble
2. Canonical Ensemble
3. Grand Canonical Ensemble

Micro-canonical Ensemble

It is the collection of a large number of essentially independent systems having the **same energy E, volume V** and **total number of particles N.**

The systems of a micro-canonical ensemble are separated by rigid impermeable and insulated walls, such that the values of **E, V & N** are not affected by the mutual pressure of other systems.

This ensemble is as shown in the figure below:



System 1; Energy E Volume V Number of Particles N.	System 2; Energy E Volume V Number of Particles N.	System 3; Energy E Volume V Number of Particles N.	System 4; Energy E Volume V Number of Particles N.	System 5: Energy E Volume V Number of Particles N.
System 6; Energy E Volume V Number of Particles N.	System 7; Energy E Volume V Number of Particles N.	System 8; Energy E Volume V Number of Particles N.	System 9; Energy E Volume V Number of Particles N.	System 10: Energy E Volume V Number of Particles N.
System 11; Energy E Volume V Number of Particles N.	System 12; Energy E Volume V Number of Particles N.	System 13; Energy E Volume V Number of Particles N.	System 14; Energy E Volume V Number of Particles N.	System 15: Energy E Volume V Number of Particles N.
System 16; Energy E Volume V Number of Particles N.	System 17; Energy E Volume V Number of Particles N.	System 18; Energy E Volume V Number of Particles N.	System 19; Energy E Volume V Number of Particles N.	System 20; Energy E Volume V Number of Particles N.

Here all the borders are impermeable and insulated.

Canonical Ensemble

It's the collection of a large number of essentially independent systems having the same **temperature T, volume V** and **the number of particles N**.

The equality of temperature of all the systems can be achieved by bringing all the systems in thermal contact. Hence, in this ensemble the systems are separated by rigid impermeable but **conducting** walls, the outer walls of the ensemble are perfectly insulated and impermeable though.

This ensemble is as shown in figure:

System 1; **Temperature T** **Volume V** **Number of Particles N.**	System 2; **Temperature T** **Volume V** **Number of Particles N.**	System 3; **Temperature T** **Volume V** **Number of Particles N.**	System 4; **Temperature T** **Volume V** **Number of Particles N.**	System 5; **Temperature T** **Volume V** **Number of Particles N.**
System 6; **Temperature T** **Volume V** **Number of Particles N.**	System 7; **Temperature T** **Volume V** **Number of Particles N.**	System 8; **Temperature T** **Volume V** **Number of Particles N.**	System 9; **Temperature T** **Volume V** **Number of Particles N.**	System 10; **Temperature T** **Volume V** **Number of Particles N.**
System 11; **Temperature T** **Volume V** **Number of Particles N.**	System 12; **Temperature T** **Volume V** **Number of Particles N.**	System 13; **Temperature T** **Volume V** **Number of Particles N.**	System 14; **Temperature T** **Volume V** **Number of Particles N.**	System 15; **Temperature T** **Volume V** **Number of Particles N.**
System 16; **Temperature T** **Volume V** **Number of Particles N.**	System 17; **Temperature T** **Volume V** **Number of Particles N.**	System 18; **Temperature T** **Volume V** **Number of Particles N.**	System 19; **Temperature T** **Volume V** **Number of Particles N.**	System 20; **Temperature T** **Volume V** **Number of Particles N.**
System 21; **Temperature T** **Volume V** **Number of Particles N.**	System 22; **Temperature T** **Volume V** **Number of Particles N.**	System 23; **Temperature T** **Volume V** **Number of Particles N.**	System 24; **Temperature T** **Volume V** **Number of Particles N.**	System 25; **Temperature T** **Volume V** **Number of Particles N.**

Here, the borders in bold shade are both insulated and impermeable while the borders in light shade are conducting and impermeable.

Grand Canonical Ensemble

It is the collection of a large number of essentially independent systems having the same **temperature T, volume V & chemical potential μ.**

The systems of a grand canonical ensemble are separated by rigid permeable and conducting walls.

This ensemble is as shown in figure:

System 1; **Temperature T** **Volume V** **Chemical Potential μ .**	System 2; **Temperature T** **Volume V** **Chemical Potential μ.**	System 3; **Temperature T** **Volume V** **Chemical Potential μ.**	System 4; **Temperature T** **Volume V** **Chemical Potential μ.**	System 5; **Temperature T** **Volume V** **Chemical Potential μ.**
System 6; **Temperature T** **Volume V** **Chemical Potential μ.**	System 7; **Temperature T** **Volume V** **Chemical Potential μ.**	System 8; **Temperature T** **Volume V** **Chemical Potential μ.**	System 9; **Temperature T** **Volume V** **Chemical Potential μ.**	System 10; **Temperature T** **Volume V** **Chemical Potential μ.**
System 11; **Temperature T** **Volume V** **Chemical Potential μ.**	System 12; **Temperature T** **Volume V** **Chemical Potential μ.**	System 13; **Temperature T** **Volume V** **Chemical Potential μ.**	System 14; **Temperature T** **Volume V** **Chemical Potential μ.**	System 15; **Temperature T** **Volume V** **Chemical Potential μ.**
System 16; **Temperature T** **Volume V** **Chemical Potential μ.**	System 17; **Temperature T** **Volume V** **Chemical Potential μ.**	System 18; **Temperature T** **Volume V** **Chemical Potential μ.**	System 19; **Temperature T** **Volume V** **Chemical Potential μ.**	System 20; **Temperature T** **Volume V** **Chemical Potential μ.**
System 21; **Temperature T** **Volume V** **Chemical Potential μ.**	System 22; **Temperature T** **Volume V** **Chemical Potential μ.**	System 23; **Temperature T** **Volume V** **Chemical Potential μ.**	System 24; **Temperature T** **Volume V** **Chemical Potential μ.**	System 25; **Temperature T** **Volume V** **Chemical Potential μ.**

Here inner borders are rigid, permeable and conducting while outer borders are impermeable as well as insulated. As the inner separating walls are conducting and permeable, the exchange of heat energy as well as that of particles between the system takes place, in such a way that all the systems achieve the same common temperature **T** and chemical potential **μ .**

ENTROPY OF AN IDEAL GAS

The entropy S of a monoatomic ideal gas can be expressed in a famous equation called the Sackur-Tetrode equation.

$$S = Nk\left[\ln\left(\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right]$$

where

- N = number of atoms
- k = Boltzmann's constant
- V = volume
- U = internal energy
- h = Planck's constant

One of the things which can be determined directly from this equation is the change in entropy during an isothermal expansion where N and U are constant (implying Q=W). Expanding the entropy expression for V_f and V_i with log combination rules leads to

$$\Delta S = Nk\ln\frac{V_f}{V_i}$$

For determining other functions, it is useful to expand the entropy expression to separate the U and V dependence.

$$S = \frac{3}{2}Nk\ln U + Nk\ln V + Nk\left[\ln\left(\frac{1}{N}\left(\frac{4\pi m}{3Nh^2}\right)^{3/2}\right)+\frac{5}{2}\right]$$

Then making use of the definition of temperature in terms of entropy:

$$\frac{\partial S}{\partial U} = \frac{3}{2}\frac{Nk}{U} \quad ; \quad T = \frac{1}{\frac{\partial S}{\partial U}} = \frac{2U}{3Nk}$$

This gives an expression for internal energy that is consistent with equipartition of energy.

$$U = \frac{3}{2}NkT$$

with kT/2 of energy for each degree of freedom for each atom.

For processes with an ideal gas, the change in entropy can be calculated from the relationship

$$S(B) - S(A) = \int_A^B \frac{dQ}{T}$$

Making use of the first law of thermodynamics and the nature of system work, this can be written

$$\Delta S = \int_A^B \frac{dQ}{T} = \int_A^B \frac{dU + PdV}{T} = \int_A^B \frac{nC_V dT}{T} + \int_A^B \frac{nRdV}{V}$$

$$\Delta S = nC_V \ln \frac{T_B}{T_A} + nR \ln \frac{V_B}{V_A}$$

This is a useful calculation form if the temperatures and volumes are known. Using the ideal gas law

$$\frac{T_B}{T_A} = \frac{P_B V_B}{P_A V_A} \quad then \quad \ln \frac{T_B}{T_A} = \ln \frac{P_B}{P_A} + \ln \frac{V_B}{V_A}$$

then

$$\Delta S = nC_V \ln \frac{P_B}{P_A} + (nC_V + nR) \ln \frac{V_B}{V_A} .$$

But since specific heats are related by $C_P = C_V + R$,

$$\Delta S = nC_V \ln \frac{P_B}{P_A} + nC_P \ln \frac{V_B}{V_A} .$$

Since entropy is a state variable, just depending upon the beginning and end states, these expressions can be used for any two points.

FLUCTUATIONS IN ENERGY

A system can be represented by a canonical ensemble. Since in this ensemble, system remains in thermal equilibrium with heat reservoir, fluctuations cannot occur in temperature but only in energy when the energy is exchanged between the system and the reservoir. For canonical ensemble, partition function is

$$Z = \sum_r e^{-\frac{E_r}{kT}}$$

And mean energy is $\langle E\rangle = \frac{\sum_r E_r e^{-\frac{E_r}{kT}}}{\sum_r e^{-\frac{E_r}{kT}}}$

Or $\langle E\rangle \sum_r e^{-\frac{E_r}{kT}} = \sum_r E_r e^{-\frac{E_r}{kT}}$

Differentiation above equation w.r.to temperature, we obtain

$$\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V} \sum_r e^{-\frac{E_r}{kT}} + \frac{\langle E\rangle}{kT^2}\sum_r E_r e^{-\frac{E_r}{kT}} = \frac{1}{kT^2}\sum_r {E_r}^2 e^{-\frac{E_r}{kT}}$$

Rearranging the term we obtain,

$$\frac{\sum_r {E_r}^2 e^{-\frac{E_r}{kT}}}{\sum_r e^{-\frac{E_r}{kT}}} - \langle E\rangle \frac{\sum_r E_r e^{-\frac{E_r}{kT}}}{\sum_r e^{-\frac{E_r}{kT}}} = kT^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V}$$

The first factoron left hand side represents $\langle E^2\rangle - \langle E\rangle^2 = kT^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V}$

But $\langle E^2\rangle - \langle E\rangle^2 = \langle\langle\langle E\rangle - E\rangle^2\rangle$

So that $\langle\langle\langle E\rangle - E\rangle^2\rangle = kT^2\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V}$ -------- (1)

When n is large and E≅ $\langle E\rangle, \frac{\langle\langle\langle E\rangle - E\rangle^2\rangle}{\langle\langle E\rangle\rangle^2} = \frac{kT^2}{E^2}\left(\frac{\partial\langle E\rangle}{\partial T}\right)_{n,V} = \frac{kT^2}{E^2}$ Cv --------- (2)

Where Cv is the specific heat at constant volume V and constant n. Experimentally, Cv= nk & E = nkT

$$\langle\frac{\Delta E}{E}\rangle^2 = \frac{\langle\langle\langle E\rangle - E\rangle^2\rangle}{\langle\langle E\rangle\rangle^2} = \frac{kT^2}{n^2k^2T^2}\,.nk = \frac{1}{n}$$

Or $\langle\frac{\Delta E}{E}\rangle$ = of the order of $(n)^{-1/2}$

The standard deviation from the mean value is of the order of $(n)^{-1/2}$. For $n=10^{22}$, fluctuations in energy will be small. On the other hand implies that the probability distribution in E, in an ordinary thermodynamics system consisting large number of molecules.

FLUCTUATIONS IN PRESSURE

The mean pressure of any phase is given by $\langle p\rangle = \frac{\sum_r e^{-\frac{E_r}{kT}}\left(-\frac{\partial E_r}{\partial V}\right)}{\sum_i e^{-\frac{E_r}{kT}}}$ ------- (1)

Differnetiating above eqn., and rearraging the terms, we get

$$\frac{\sum_r e^{-\frac{E_r}{kT}}\left(-\frac{\partial E_r}{\partial V}\right)^2}{\sum_r e^{-\frac{E_r}{kT}}} - \langle p\rangle \frac{\sum_r e^{-\frac{E_r}{kT}}\left(-\frac{\partial E_r}{\partial V}\right)}{\sum_i e^{-\frac{E_r}{kT}}} = \text{kT}[\left(\frac{\partial\langle p\rangle}{\partial T}\right)_{n,V} + \langle\frac{\partial^2 E}{\partial V^2}\rangle$$

$$\langle p^2\rangle - \langle p\rangle^2 = kT\left\{\left(\frac{\partial p}{\partial V}\right)_{n,V} + \langle\frac{\partial^2 E}{\partial V^2}\rangle\right\}$$

$$\text{Or } \langle\langle\langle p\rangle - \langle p\rangle^2\rangle\rangle = kT\left\{\left(\frac{\partial\langle p\rangle}{\partial V}\right)_{n,V} - \langle\frac{\partial^2 p}{\partial V^2}\rangle\right\}$$

Making the association with thermodynamics p≅ $\langle p\rangle$

$$\frac{\langle\langle\langle p\rangle - p\rangle^2\rangle}{\langle\langle p\rangle\rangle^2} = kT/p^2\left\{\left(\frac{\partial\langle p\rangle}{\partial T}\right)_{n,V} - \langle\frac{\partial^2 p}{\partial V^2}\rangle\right\} \text{----------- (2)}$$

The first term in the bracket on right hand side of above equation represents the variation of mean pressure with isothermal changes in volume. The second term involves the direct measurement of ratio at first and then averaging it.

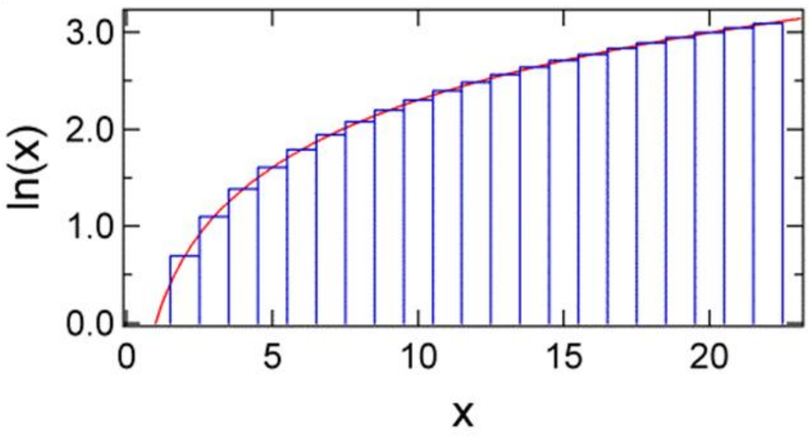
For an ideal gas, the first term on the right hand side is $\frac{kT}{p}x\left(-\frac{p}{V}\right) = \frac{1}{n}$ and the second term must be positive and larger in magnitude than the first hand side.

STIRLING'S APPROXIMATION

In confronting statistical problems we often encounter factorials of very large numbers. The factorial N! is a product N(N-1)(N-2)..(2)(1). Therefore, ln N! is a sum

$$\ln N! = \sum_{m=1}^{N} \ln m$$

where we have used the property of logarithms that log(abc) = log(a) + log(b) + log(c). The sum is shown in figure below.



The sum of the area under the blue rectangles shown below up to N is ln N!. As you can see the rectangles begin to closely approximate the red curve as m gets larger. The area under the curve is given the integral of ln x.

$$\ln N! = \sum_{m=1}^{N} \ln m \approx \int_1^N \ln x \, dx$$

To solve the integral use integration by parts

$$\int u \, dv = uv - \int v \, du$$

Here we let u = ln x and dv = dx. Then v = x and du = dx/x.

$$\int_0^N \ln x \, dx = x \ln x \Big|_0^N - \int_0^N x \frac{dx}{x}$$

Notice that x/x = 1 in the last integral and x ln x is 0 when evaluated at zero, so we have

$$\int_0^N \ln x \, dx = N \ln N - \int_0^N dx$$

Which gives us Stirling's approximation: ln N! = N ln N – N.

RELATION BETWEEN ENTROPY AND PROBABILITY

Entropy characterizes the disorder in a system. Since equilibrium is the most disordered state, its entropy is maximum. This suggests a connection between entropy and thermodynamic probability.

$$S=f\ (\Omega_0) \text{ ------- } (1)$$

This means that if S1 and S2 are the entropies of two systems, the entropy of the combined system will be given by

$$S_0 = S_1+S_2 \text{ ------- } (2)$$

On the other hand, probability is multiplicative and can be written as

$$\Omega_0 = \Omega_1\ \Omega_2 \text{ ---------- } (3)$$

f is such that S increases with Ω and translates a product into a sum. This can achieved through a logarithmic function so that we can write as $S=k_B \ln \Omega$ ---------- (4)

where k_B is the Boltzmann's constant.

BOLTZMANN H-THEOREM

$$\left(\frac{\partial f_1}{\partial t}\right)_2 = \iiint u\,\sigma(\mathbf{v}_1; \mathbf{v}_2; \mathbf{v}_1'; \mathbf{v}_2')\,(f_1' f_2' - f_1 f_2)\, d^3\mathbf{v}_2\, d^3\mathbf{v}_1'\, d^3\mathbf{v}_2'.$$

…… (1)

Consider the quantity $H = \int f_1 \ln f_1 \, d^3\mathbf{v}_1.$ ……. (2)

It follows from Equation (1) that $\frac{dH}{dt} = \int (1 + \ln f_1) \frac{\partial f_1}{\partial t} d^3\mathbf{v}_1$

$$= \iiiint u \, \sigma \, (1 + \ln f_1) \, (f_1' \, f_2' - f_1 \, f_2) \, d^3\mathbf{v}_1 \, d^3\mathbf{v}_2 \, d^3\mathbf{v}_1' \, d^3\mathbf{v}_2', \quad \text{……. (3)}$$

where σ is short-hand for $\sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}_1', \mathbf{v}_2')$. Suppose that we swap the dummy labels **1** and **2** . This process leaves both $u = |\mathbf{v}_1 - \mathbf{v}_2|$ and the value of the integral unchanged. It also leaves the scattering cross-section $\sigma(\mathbf{v}_1, \mathbf{v}_2; \mathbf{v}_1', \mathbf{v}_2')$ unchanged. Hence, we deduce that

$$\frac{dH}{dt} = \iiiint u \, \sigma \, (1 + \ln f_2) \, (f_1' \, f_2' - f_1 \, f_2) \, d^3\mathbf{v}_1 \, d^3\mathbf{v}_2 \, d^3\mathbf{v}_1' \, d^3\mathbf{v}_2'. \quad \text{…… (4)}$$

Suppose that we primed and unprimed dummy variables of integration in Equation (3). This leaves the value of the integral unchanged. we obtain

$$\frac{dH}{dt} = -\iiiint u \, \sigma \, (1 + \ln f_1') \, (f_1' \, f_2' - f_1 \, f_2) \, d^3\mathbf{v}_1 \, d^3\mathbf{v}_2 \, d^3\mathbf{v}_1' \, d^3\mathbf{v}_2'. \quad \text{….. (5)}$$

Finally, primed and unprimed variables in Equation (4) yields

$$\frac{dH}{dt} = -\iiiint u \, \sigma \, (1 + \ln f_2') \, (f_1' \, f_2' - f_1 \, f_2) \, d^3\mathbf{v}_1 \, d^3\mathbf{v}_2 \, d^3\mathbf{v}_1' \, d^3\mathbf{v}_2'. \quad \text{……. (6)}$$

The previous four equations can be combined to give

$$\frac{dH}{dt} = \frac{1}{4} \iiint \int u\sigma \ln\left(\frac{f_1 f_2}{f_1 f_2}\right)(f_1' f_2' - f_1 f_2) \, d_3V_1 d_3V_2 d_3V'_1 d_3V_2'$$

Now, ln ($f_1f_2/f_1'f_2'$) is positive when $f_1'f_2'-f_1f_2$ is negative, and vice versa. Therefore, deduce that the integral on the right-hand side of the previous expression can never take a positive value. In other words,

$$dH/dt \leq 0$$

This result is known as the *Boltzmann H-theorem*.

Possible Questions

2marks

1. Give a note on Stirling’s approximation.
2. What is the relation between entropy and probability?
3. Define microcanonical and canonical ensemble.
4. State Liouville’s theorem.
5. What is called ensemble?
6. Define entropy.
7. What are the applications of ensembles?
8. State Bolztman theorem.

6 marks

1. What is called ensemble? Explain it.
2. Give the relation between entropy and probability.
3. State Liouville’s theorem. Explain it briefly.
4. Explain microcanonical ensemble.
5. State Boltzmann Theorem. Explain it.
6. Explain the entropy of ideal gas.
7. Discuss about the fluctuations in thermodynamic variables.

KARPAGAM ACADEMY OF HIGHER EDUCATION

Coimbatore – 641021

(For Candidates Admitted From 2017 Onwards)

DEPARTMENT OF PHYSICS

UNIT IV: Objective Type/Multiple choice Questions each Question carries one Mark

SL NO	QUESTION	OPTION A	OPTION B	OPTION C	OPTION D	KEY
1	In a micro canonical ensemble, a system A of fixed volume is in contact with a large reservoir B. Then	A can exchange only energy with B	A can exchange only particles with B	A can exchange neither energy nor particles with B	A can exchange both energy and particles with B	A can exchange neither energy nor particles with B
2	In a canonical ensemble, a system A of fixed volume is in contact with a large reservoir B. Then	A can exchange only energy with B	A can exchange only particles with B	A can exchange neither energy nor particles with B	A can exchange both energy and particles with B	A can exchange only energy with B
3	In a grand canonical ensemble, a system A of fixed volume is in contact with a large reservoir B. Then	A can exchange only energy with B	A can exchange only particles with B	A can exchange neither energy nor particles with B	A can exchange both energy and particles with B	A can exchange both energy and particles with B
4	Those substances which have so far not been resolved by any means into other substances of simpler form are called	atom	molecules	element	compounds	element
5	The sum of internal energy (U) and the product of pressure and volume (p.v) is known as	workdone	enthalpy	entropy	gidds	enthalpy
6	What is the relation between thermodynamic probability *(W)* and entropy?	thermodynamic probability increases with entropy	thermodynamic probability decreases with entropy	thermodynamic probability does not change with change in with entropy	zero	thermodynamic probability increases with entropy
7	At the most probable state of a system the entropy of the system is	maximum	minimum	constatnt	zero	maximum

8	If the two parts A and B in a system are considered to be in equilibrium and having thermodynamic probabilities W_A and W_B, what will be the thermodynamic probability of the system?	$W = W_A . W_B$	$W = W_A + W_B$	$W = (W_A + W_B) / 2$	$W = \sqrt{}(W_A – W_B)$	$W = W_A . W_B$
9	What is the entropy chosen at the triple point of water?	zero	less than zero	more than zero	constant	zero
10	At the state of perfect order *(W = 1)* of pure crystalline substance, how is the zero entropy defined?	entropy at 0 °C temperature	entropy at absolute zero temperature	entropy at the freezing point of the substance	none	entropy at absolute zero temperature
11	The process which decreases the entropy of the universe is	reversible	irreversible	isochoric	impossible	impossible
12	When the potential gradient in a process is infinitesimal or zero, what will be the change in entropy of the universe?	entropy decreases	entropy increases	no change in entropy	zero	no change in entropy
13	What is the entropy transfer associated with work?	positive entropy transfer	negative entropy transfer	no entropy transfer	zero	no entropy transfer
14	Specific heat of metals can be expressed as	T^3	$AT + BT^2$	$AT^2 + BT^3$	$AT + BT^3$	$AT + BT^3$
15	What is the entropy change (dS_{iso}) of an irreversible isolated (dQ=0) process?	$dS_{iso} = 0$	$dS_{iso} > 0$	$dS_{iso} < 0$	dSiso=constant	$dS_{iso} > 0$
16	What is the entropy change (dS_{iso}) of a reversible isolated (dQ=0) process?	$dS_{iso} = 0$	$dS_{iso} > 0$	$dS_{iso} < 0$	dSiso=constant	$dS_{iso} = 0$
17	An ensemble usually refers to an equilibrium density distribution that does not change with __________	time	velocity	motion	mass	time
18	In the _______________ ensemble, we assume ρeq to be uniform inside the entire region between the two constant energy surfaces	microcanonical	macrocanonical	canonical	none	microcanonical
19	In molecular simulations, the microcanonical ensemble is usually referred to as the ____________ ensemble	VE	NV E	macrocanonical	N/VE	NV E

20	A canonical ensemble represents the possible states of a mechanical system in __________ equilibrium with a heat bath at a fixed temperature	Chemical	phase	thermal	mechanical	thermal
21	The canonical ensemble was first described by _________in 1884	Kelvin	Joule	Gibbs	Boltzmann	Boltzmann
22	The concept of ensemble put forward by ________	Einstein	Gibbs	Bose	Dirac	Gibbs
23	An ice cube in water or common salt in a water solution can be considered as members of a______________ ensemble	microcanonical	canonical	grand canonical	macro canonical	grand canonical
24	The entropy of the combined system will be given by	S0=S1+S2	S0=S1-S2	S0=S1*S2	S0=S1/S2	S0=S1+S2
25	The relation between entropy and probability is	S=f(x)	S=f(Ω)	S=f(-Ω)	S=-f(Ω)	S=f(Ω)
26	Water molecules in a tea pot is an example of ___________	microcanonical	canonical	grand canonical	macro canonical	canonical
27	The members of grand canonical can exchange	heat only	work only	mass only	heat and work	heat and work
28	Which canonical has idealised concept?	microcanonical	no canonical	grand canonical	macro canonical	microcanonical
29	The members of canonical ensemble can exchange	heat only	work only	mass only	thermal energy	thermal energy
30	Which ensemble do not interact with surroundings?	microcanonical	canonical	grand canonical	macro canonical	microcanonical

SYLLABUS

Statistical Mechanics: Phase space, Macrostate Thermodynamic probability, Maxwell-Boltzmann Quantum statistics, Fermi-Dirac distribution law, comparison of three statistics. and Microstate, Entropy and law, distribution of velocity, Bose-Einstein distribution law.

Phase Space

Statistics involves the counting of states, and the state of a classical particle is completely specified by the measurement of its position and momentum. If we know the six quantities

$$x,y,z,p_x,p_y,p_z$$

then we know its state. It is often convenient in statistics to imagine a six-dimensional space composed of the six position and momentum coordinates. It is conventionally called "phase space". The counting tasks can be visualized in a geometrical framework where each point in phase space corresponds to a particular position and momentum. That is, each point in phase space represents a unique state of the particle. The state of a system of particles corresponds to a certain distribution of points in phase space.

The counting of the number of states available to a particle amounts to determining the available volume in phase space. One might preclude that for a continuous phase space, any finite volume would contain an infinite number of states. But the uncertainty principle tells us that we cannot simultaneously know both the position and momentum, so we cannot really say that a particle is at a mathematical point in phase space. So when contemplate an element of "volume" in phase space

$$du = dxdydzdp_xdp_ydp_z$$

Different distribution in Statistical Mechanics

1. Identical but distinguishable particles - Maxwell Boltzmann distribution,Ex. Molecules of a gas
2. Identical but indistinguishable particles – Bose-Einstein distribution, Ex. Photons

3. Identical but indistinguishable particles obey the Pauli exclusion principle- Fermi-Dirac distribution, Ex. Protons & neutrons.

Classical Maxwell Boltzmann Statistics

Consider distinguishable molecule, enclosed in a vessel of constant volume. Suppose energy is constant. The ensemble suitable for this type is microcanonical ensemble. The energy between two surface is noted as E & E+dE.The probability of finding the n1 molecules in the first cell, n2 in second cell is $\omega = \frac{n!}{n_1!n_2!\ldots\ldots n_i!}$

$$\text{Or } \omega = \frac{n!}{\Pi n_1!}\ x\ constant \text{ -------- (1)}$$

To find most probable distribution of molecules among the cell in μ space, we calculate the maximum probability $\omega\ for\ a\ variation\ of\ the$ numbers, n1, n2, n3, ……….

$$n_1+n_2+n_3+\ldots\ldots.+n_i= n$$

from eqn. (1), $\log\,\omega = \log n! - \Sigma i \log ni! + const$ ------- (2)

Using Stirling approximation, $\log\,\omega = n\log n - n - \Sigma i(n_i log n_i - n_i) + \ const.$ ------- (3)

Since n is large, $n_1, n_2, n_3\ldots\ldots.n_i$ is sufficiently large. Eqn., 3 becomes

$$\log\,\omega = -\Sigma i(n_i log n_i) + \ const. \text{ ------- (4)}$$

n log n is included in constant. On diff. eqn. (4) $\delta log\omega = -\Sigma\delta(n_i log n_i)$

$$= -\Sigma(\log n_i + 1)\ \delta n_i \text{ --- (5)}$$

Using the condition maximum probability, $\delta\log\,\omega = 0$

$$\text{So } \Sigma(log n_i + 1)\delta n_i = 0 \text{ ----- (6)}$$

As total no. of molecules cannot be altered, the variation δn_i must always be add to zero.

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

$$\Sigma\delta n_i = \ \delta n = 0 \text{-------- (7)}$$

Consider n_1 particles go to first cell with energy ε_1 & n_2 particles to second cell with energy ε_2.

$$\text{Then } \Sigma_i n_i\varepsilon_{i=}E \text{ or } \delta E = \ \Sigma\delta n_i\varepsilon_{i=}0 \text{ -------- (8)}$$

Using Lagrange method, on multiplying eqn. (7) by α and (8) by β and add to eqn. (6)

$$\Sigma_i(log n_i + 1 + \alpha + \beta\varepsilon_i)\delta n_i = 0 \text{-------- (9), where 1+ } \alpha = \alpha \text{ so that}$$

$$\Sigma_i(log n_i + \alpha + \beta\varepsilon_i)\delta n_i = 0 \text{------- (10)}$$

Eqn. (10) satisfied only when each term in summation is zero.

$$(logn_i + \alpha + \beta\varepsilon_i) = 0$$

$$(logn_i) = -(\alpha + \beta\varepsilon_i)$$

$$n_i = \frac{1}{\exp(\sim + \beta\varepsilon_i)} - - - - -(11)$$

Eqn. (11) is called Maxwell Boltzmann Statistics.

Fermi –Dirac distribution law

In F-D statistics, the condition are:

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

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

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

The Fermi – Dirac statistics is given by

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

Entropy

Entropy, the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Because work is obtained from ordered molecular motion, the amount of entropy is also a measure of the molecular disorder, or randomness, of a system. The concept of entropy provides deep insight into the direction of spontaneous change for many everyday phenomena. Its introduction by the German physicist Rudolf Clausius in 1850 is a highlight of 19th-century physics.

Microstate and Macrostate

Classical thermodynamics describes macroscopic systems in terms of a few variables such as temperature, volume and pressure. Such a system is really made of atoms, so a much richer description must be possible in principle. When the atoms interact, this state change rapidly 10^{35} times a second. But the observed macro state does not change. Many different microstates correspond to same macro state.

FERMI-DIRAC STATISTICS

In Maxwell Boltzmann statistics or Bose – Einstein statistics, there is no restriction for the particles to be present in any energy level. But in case of Fermi Dirac statistics, applied to energy particles like electrons and obeying the Pauli Exclusion Principle, only one particle can occupy only one energy state. The distribution of four particles (a, b, c and d) among two cells x and y each giving four energy state level such that there are three energy particles in cell x while one particle in cell y

In this case there will be 4×4=16 possible distribution. We consider a general case. This statistics is applied to indistinguishable particles having half integral spin. Though the particles are indistinguishable, the restriction imposed is that only one particle will be occupied by a single cell. The situation of distribution is of follows:

Energy level	$\varepsilon_1, \varepsilon_2, \ldots\ldots\varepsilon_i, \ldots\ldots \varepsilon_k$
Degeneracies	$g_1, g_2 \ldots\ldots g_i, \ldots\ldots g_k$
Occupation no.	$n_1, n_2 \ldots\ldots n_i, \ldots\ldots n_k$

So in case of Fermi Dirac statistics, we have the problem of assigning n_i distribution particles to g_i distinguishable particles levels under that restriction only one particle will be occupied by a single level; obviously, g_i must be greater than or equal to n_i, because there must be at least one elementary wave function available for every element of the system.

Thus in Fermi statistics the condition for every element in a group are:

1) The particles are indistinguishable from each other i.e, there is no restriction between different ways in which n_i particles are chosen
2) Each sublevel or cell may contain 0 or one particle. obviously g_i must be greater than or equal to n_i
3) The sum of energies of all the particles in the different quantum groups taken together constitutes the total energy of the system.

Now the distribution of n_i particles among the g_i states can be done in the following way:

We easily find that the first particle can be put in any one of the ith level in g_i ways. According to Pauli exclusive principle no more particles can be assigned to that filled state. Thus we are left (g_i-1) states in (g_i-1) ways, and so on. Thus the number of ways in which n_i, particles can assigned to g_i states is

$$g_i (g_i-1) (g_i-2)\ldots\ldots\ldots\ldots (g_i -n_i+1),$$

$$= g_i! / (g_i-n_i)!\ldots\ldots\ldots\ldots\ldots (1)$$

The permutations among the identical particles do not give distinct 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

$$=gi! /ni! (gi-ni)! \qquad \ldots\ldots\ldots\ldots (2)$$

The total number of Eigen states for whole system is given by

$$G=\P gi! /ni! (gi-ni)! \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The probability of ω of the specific state being proportional to G will be

$$\omega=\P gi! /ni! (gi-ni)! \times \text{Constant} \qquad \ldots\ldots\ldots (4)$$

To obtain the condition of maximum probability, we proceed as follows:

Taking log of equation (4), we have

$$\log=\Sigma [\log g_i! -\log n_i! \log (g_i-n_i)!]+ \text{Constant}$$

Differentiating equation (6) with respect to n_i

$$\log=\Sigma [\delta (n_i-g_i) \log (g_i-n_i) +g_i \log g_i-n_i \log n_i]$$

$$=\Sigma \{\delta n_i \log (g_i-n_i) +n_i-g_i/g_i-n_i (-\delta n_i)-\delta n_i \log n_i-n_i/n_i\delta n_i\}$$

$$=\Sigma \{\log n_i/ (g_i-n_i)\} \delta n_i$$

The condition for maximum probability gives

$$\Sigma [\log n_i/ (g_i-n_i) \delta n_i=0$$

Introducing the auxiliary condition.

$$\delta n=\Sigma\delta n_i=0$$

$$\delta E=\Sigma \varepsilon_i\delta n_i=0$$

Applying the Lagrange method of undermined multipliers i.e. multiplying equation (9) by α and equation (8) by β and adding the resulting expressions to equation (8) we have,

$$\Sigma [\log n_i/ (n_i-g_i) +\alpha+\beta\varepsilon_i] \delta n_i=0$$

Since δni can be treated as arbitrary

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

$$g_i/n_i-1=e^{(\alpha+\beta\varepsilon_i)}$$

$$n_i=g_i/e^{(\alpha+\beta\varepsilon_i)}+1$$

This is the most probable distribution according to Fermi-Dirac statistics

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

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

BOSE –EINSTEIN STATISTICS

In Maxwell –Boltzmann statistics, the particles are distinguishable from each other .Thus if the two particles interchange their positions or energy state, a new state is generated. But in case of Bose- Einstein statistics, the particles are indistinguishable. So the interchange of two particles between two energy states will not produce any new state. For example, let us distribute four particles (a, b, c and d) among two cells x and y such that there are three particles in cell x while one particles in cell there will be four compartments (states) in Maxwell – Boltzmann statistics while one in Bose Einstein distribution statistics.

Suppose that each cell is divided into four compartments. In this case 20 possible distributions are possible, three particles in cell x and 4 possible distributions of one particle in cell. Thus there will be 20×4=80 possible distributions. Consider a general case, suppose the system contain an independent identical particle. Let these particles be divided into quantum groups or levels such that there are n_1, n_2, n_i….respectively. n_1, n_2 and n_i are the occupation number of levels i.e. the number of particles that are in that level. Again let there be gig single particle states in the ith level, and we speak of this as the degeneracy or the statistical weight of the ith level. This situation is following as:

Energy levels	$\varepsilon_1, \varepsilon_2, \varepsilon_i.,\ldots\ldots\ldots \varepsilon_k$
Degeneracy	$g_1, g_2,\ldots\ldots.., g_i,\ldots\ldots.. g_k$
Occupation no.	$n_1, n_2, n_i\ldots\ldots.. n_k$

In case of Bose Einstein statistics, we have the problem of assigning n indistinguishable particles to g_i distinguishable levels when there is no restrictions to the number of particles that can occupy one level. g_i is also termed as density of states of function which gives number of one particle states per unit energy range.

Thus in Bose Einstein statistics, the conditions are:

1) The particles are indistinguishable from each other so that there is no distinction between the different ways in which Ni particles can be chosen.

2) Each cell or sublevel of ith quantum state may contain 0, 1, 2, n_i identical particles.

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

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

Thus total number of ways in realizing the distribution will be $g_i(n_i+g_i-1)!$ ……(1)

The particles are distinguished and therefore rearrangement of particle will not give rise to any distinguishable arrangement. There is $n_i!$ Permutations which correspond to the same configuration, hence term indicated by (1) should be divided by $n_i!$. Secondly, the distribution which can be derived from one another by mere permutation of the cells among themselves, do not produce different states, the term (1) should also be divided by $g_i!$

We thus obtain the required number of ways as $g_i\ (n_i+g_i-1)!\ /g_i!\ n_i!$

Or

$$(n_i+g_i-1)!\ /n_i!\ (g_i-1)!$$

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 ε_1, ε_2 to ε_i, the product of such expressions given below:

$$G= (n_1+g_1-1)!\ /n_1!\ (g_1-1)!(n_2+g_2-1)!/n_2!(g_2-1)!\ldots\ldots\ldots(n_i+g_i-1)!/n_i!(g_i-1)!$$

$$=¶\ (n_i+g_i-1)!\ /n_i!\ (g_i-1)!$$

According to the postulates of a priori probability of Eigen states, we have the probabilities ω of the system for occurring with the specified distribution to the total number of Eigen states, i.e.

$$\omega=¶\ (n_i+g_i-1)!\ /n_i!(g_i-1)!\ \times\text{constant}$$

We to obtain the condition of maximum probability, we proceed as follows:

Taking log of equation (3), we have

$$\log \omega=\Sigma\ [(n_i+g_i-1)!-\log n_i!\ –\log\ (g_i-1)!\ ]\ +\text{constant} \quad ..\ (4)$$

Using stirling's approximation, equation (4) becomes

$$\log \omega=\Sigma[(n_i+g_i)\log(n_i+g_i)-n_i \log n_i –g_i \log g_i]+ \text{constant} \quad ….(5)$$

Here we have neglected 1 in comparison to n_i and g_i as they are large numbers.

$$\Delta\ \log\omega=\Sigma\delta\ [(n_i+g_i)\ \log\ (n_i+g_i)—n_i \log n_i-g_i \log g_i]$$

$$=\Sigma\ \{\delta n_i \log\ (n_i+g_i) + (n_i+g_i)/\ (n_i+g_i)\ \delta n_i-\delta n_i \log n_i-n_i/n_i\ \delta n_i\}$$

$$=\Sigma\ \{\delta n_i \log\ (n_i+g_i)-\delta n_i \log n_i\}$$

$$=-\Sigma\ [\log n_i/\ (n_i+g_i)]\ \delta n_i \quad ……….\ (6)$$

The condition for maximum probabilities gives

$$=\Sigma\ [\log n_i/\ (n_i+g_i)]\ \delta n_i=0$$

The auxiliary conditions to be satisfied are

$$\delta n_i = \Sigma \delta n_i = 0$$

$$\delta E = \Sigma \varepsilon_i \delta n_i = 0$$

Applying the Lagrange method of undetermined multipliers i.e. multiplying equation (8) by α and equation (9) by β, and adding the resulting expressions to equation (7) we get,

$$\Sigma\, [\log n_i/\,(n_i+g_i) + \alpha + \beta\varepsilon_i]\ \delta n_i = 0$$

As the variations δni are independent of each other,

$$\log n_i/\,(n_i+g_i) + \alpha + \beta\varepsilon_i = 0$$

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

$$g_i/n_i = e^{(\alpha+\beta\varepsilon i-1)}$$

Therefore, $n_i = g_i/e^{(\alpha+\beta\varepsilon_i-1)}$

This represents the most probable distribution of the element s among various energy levels for a system obeying Bose Einstein statistics

Possible Questions

2marks

1. Compare two quantum statistics.
2. What is called microstate?
3. Give a note on MB statistics.
4. What is called phase space?
5. What is called macrostate?
6. Write a note on bosons.
7. Write a note on Fermions.
8. State FD statistics.

6 marks

1. Derive Maxwell-Boltzmann law.
2. Derive an expression for Bose-Einstein Statistics.
3. Obtain an expression for FD statistics.
4. Derive an expression for BE statistics.
5. Obtain an expression for classical statistical mechanics.
6. Derive an expression for Fermi Dirac distribution law.
7. Compare M.B, F.D and B.E statistics.
8. Discuss about thermodynamic probability.

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Coimbatore – 641021

(For Candidates Admitted From 2017 Onwards)

DEPARTMENT OF PHYSICS

UNIT V: Objective Type/Multiple choice Questions each Question carries one Mark

SL NO	QUESTION	OPTION A	OPTION B	OPTION C	OPTION D	KEY
1	M.B. distribution can be applicable to __________	identical molecule	indistinguishable molecule	gas	liquid	identical molecule
2	The number of quantum states is represented by _____	n_r	g_r	E_r	N	g_r
3	The degeneracy parameter A = __________	Z	e^{α}	$e^{-\alpha}$	e^{β}	$e^{-\alpha}$
4	In M.B. distribution, the unit of n(v) is ______	m/ sec	mol/sec	mol/m/sec	sec	mol/m/sec
5	The equation for total internal energy of one mole of an ideal gas is _______	U/N = 3/2 kT	U/N = 3/2	U/N = kT	U/N = 2/3 kT	U/N = 3/2 kT
6	The value of β = ______	kT	k	T	1/kT	1/kT
7	At absolute zero temperature the entropy may become ___________	Infinity	positive	Zero	Negative	Zero
8	The value of entropy becomes zero in perfectly _______	liquid	crystalline solid	gas	inert gas	crystalline solid
9	M.B. law cannot be applicable to ______ particles.	distinguishable	Indistinguishable	isolated	Isobaric	Indistinguishable
10	In dilute gas, the number of molecules per unit volume is _____	large	very small	infinity	small	small
11	In dilute gas, the average separation between the molecules is ______	large	very small	Infinity	small	large
12	In classical physics identical particles are ______	indistinguishable	distinguishable	symmetric	anti-symmetric	distinguishable
13	The dimensions of the phase space depends upon the ____ of the system.	entropy	heat content	degrees of freedom	enthalpy	degrees of freedom

14	B.E distribution function is given by	$\{1/(e^{a + bE}) \}$	$\{1/(e^{a + bE}) + 1\}$	$\{(e^{a + bE}) – 1\}$	{1/(ea + bE) – 1}	$\{(e^{a + bE}) – 1\}$
15	The degeneracy parameter e^{-a} =	N/V (h^2 / 2pmkT $)^{1/2}$	N/V (h^2 / 2pmkT $)^{3/4}$	N/V (h^2 / 2pmkT $)^{3/2}$	N/V (h^2 / 2pmkT$)^3$	N/V (h^2 / 2pmkT $)^{3/2}$
16	Maxwell first developed _____________theory	Equipartition	partition	classical	quantum	classical
17	According to classical mechanics a molecule can have	finite speed	infinite speed	variable speed	constant speed	infinite speed
18	B.E distribution law is used to derive ____________of radiation	Plank’s law	Weiss law	Widemann-Franz law	All the above	Plank’s law
19	Wave function of the system of identical Bosons is	Asymmetric	linear	non-linear	symmetric	symmetric
20	M.B. distribution can be applicable to __________	identical molecule	indistinguishable molecule	gas	liquid	identical molecule
21	In M.B. distribution the mean P.E. is ______ than/ to K.E. of ideal gas.	larger	very large	small	equal	small
22	When T=0, the value of entropy S = ______ in M.B. distribution.	infinity	negative infinity	zero	one	negative infinity
23	M.B. law cannot be applicable to ______ particles.	distinguishable	Indistinguishable	isolated	Isobaric	Indistinguishable
24	B.E distribution law is used to derive ____________of radiation	Planck's law	Weiss law	Widemann Franz law	Rayleigh's law	Planck's law
25	Wave function of the system of identical Bosons is	asymmetric	linear	non-linear	symmetric	symmetric
26	Which of the following obey Pauli exclusion principle?	M.B. statistics	B.E. statistics	F.D. statistics	Einstein’s equation	F.D. statistics
27	Which of the following do not obey Pauli exclusion principle?	M.B. statistics	B.E. statistics	F.D. statistics	Einstein’s equation	B.E. statistics

28	In B.E. distribution, the constant e^{α} must be __________	greater than 1	smaller than 1	equal to 1	zero	greater than 1
29	The molecules obey B.E. statistics are ____________	photons	phonons	fermions	bosons	bosons
30	_________ is the energy distribution function.	f(E)	g(E)	n(E)	f	f(E)
31	_____________ is the number of quantum states	f(E)	g(E)	n(E)	f	g(E)
32	In B.E. energy distribution, if e^{α} =1, for E=0, then n(0) dE =	postive infinity	negative infinitive	1	0	postive infinity
33	In B.E. energy distribution, if e^{α} <1, for E=0, then n(0) dE =	postive infinity	negative infinitive	1	0	negative infinitive
34	For an ideal B.E. distribution the degeneracy parameter A cannot be ____________-	greater than 1	smaller than 1	equal to 1	zero	greater than 1
35	For all known B.E. gases, T_B is very ________	high	low	small	0	low
36	E.Fermi developed the statistics for ________	photons	bosons	phonons	electrons	electrons
37	In B.E statistics the particles are identical and indistinguishable. These particles are called as	Bosons	fermions	leptons	baryons	Bosons
38	Particles with half-integral spin are called as	Bosons	fermions	leptons	baryons	fermions
39	Fermions obey _______________principle	Heisenberg	Le-chatlier	Pauli	Haber	Pauli
40	Condition for B.E distribution to approach M.B distribution is $1/A(e^{bE}) >> 1$ i.e	A<=1	A<<1	A>>1	A>>1	A<<1
41	In B.E statistics the particles are identical and indistinguishable. These particles	Bosons	fermions	leptons	baryons	Bosons

42	The Bosons has	spin 1	zero or half-integral spin	zero or whole number	zero	zero or half-integral spin
43	The examples for Bosons	photons	electrons	neutrons	protons	photons
44	Particles with half-integral spin are called as	bosons	Fermions	leptons	electrons	leptons
45	The examples for Fermions	Photons	phonons	electrons	antiparitcles	electrons
46	The spin of the photon is	0	1	2	½	1
47	In F.D statistics the particles are identical and indistinguishable. These particles	Fermions	bosons	photons	kryptons	Fermions
48	B.E distribution function is given by	{1/(ea + bE) }	{1/(ea + bE) + 1}	{(ea + bE) – 1}	{1/(ea + bE) – 1}	{1/(ea + bE) – 1}
49	Fermi energy Ef =	- aKT	aKT	–1/ aKT	1/ aKT	- aKT
50	Fermi-Dirac distribution function FD(E) =	{1/(ea + bE) + 1}	{1/(ea + bE) - 1}	{(ea + bE) - 1}	{-1/(ea + bE) + 1}	{1/(ea + bE) + 1}
51	In terms of Fermi energy F.D distribution function is fFD(E) =	{-1/(eE + EF) + 1}	{1/(eE - EF) + 1}	{1/(eE + EF) + 1}	{1/(eE + EF) - 1}	{1/(eE + EF) + 1}
52	B.E statistics is used to find the ___________among identical	energy distribution	frequency distribution	both a and b	mass distribution	energy distribution
53	According to B.E distribution law the number of Bosons having energies	g(E)dE/{(ea + bE) + 1}	g(E)dE/{(ea + bE) – 1}	g(E)dE/{(ea + bE) – 1}	g(E)dE/{(ea + bE) – 1}1/2	g(E)dE/{(ea + bE) – 1}1/2
54	Wave function of the system of identical Bosons is	Unsymmetric	linear	symmetric	zero	symmetric
55	The molecule of an ideal B.E gas in two phases at	T = TB	T > TB	T < TB	T <= TB	T < TB
56	Which type of statistics is used to describe the electron contribution to specific heat?	MB statistics	BE statistics	FD statistics	Classical statistics	FD statistics