PREFACE

In a bid to standardize higher education in the country, the University Grants Commission (UGC) has introduced Choice Based Credit System (CBCS) based on five types of courses viz. *core, generic, discipline specific, generic elective, ability and skill enhancement* for graduate students of all programmes at Honours level. This brings in the semester pattern, which finds efficacy in sync with credit system, credit transfer, comprehensive continuous assessments and a graded pattern of evaluation. The objective is to offer learners ample flexibility of choose from a wide gamut of courses, as also to provide them lateral mobility between various educational institutions in the country where they can carry their acquired credits. I am happy to note that the University has been recently accredited by National Assessment and Accreditation Council of India (NAAC) with grade "A".

UGC (Open and Distance Learning Programmes and Online Programmes) Regulations, 2020 have mandated compliance with CBCS for U. G. programmes for all the HEIs in this mode. Welcoming this paradigm shift in higher education, Netaji Subhas Open University (NSOU) has resolved to adopt CBCS from the academic session 2021-22 at the Under Graduate Degree Programme level. The present syllabus, framed in the spirit of syllabi recommended by UGC, lays due stress on all aspects envisaged in the curricular framework of the apex body on higher education. It will be imparted to learners over the six semesters of the Programme.

Self Learning Materials (SLMs) are the mainstay of Student Support Services (SSS) of an Open University. From a logistic point of view, NSOU has embarked upon CBCS presently with SLMs in English/Bengali. Eventually, the English version SLMs will be translated into Bengali too, for the benefit of learners. As always, all of our teaching faculties contributed in this process. In addition to this we have also requisitioned the services of best academics in each domain in preparation of the new SLMs. I am sure they will be of commendable academic support. We look forward to proactive feedback from all stakeholders who will participate in the teaching-learning based on these study materials. It has been a very challenging task well executed, and I congratulate all concerned in the preparation of these SLMs.

I wish the venture a grand success.

Professor (Dr.) Subha Sankar Sarkar
Vice-Chancellor

Netaji Subhas Open University
Under Graduate Degree Programme
Choice Based Credit System (CBCS)
Subject : Honours in Physics (HPH)
Course Code : GE-PH-21
Course : Thermal Physics

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: Course Writer :

Dr. Chinmay Basu
Retd. Associate Professor of Physics
Raigang University College
Indian Centre for Space Physics, Kolkata

: Course Editor :

Dr. Achintya Kumar Chatterjee
Associate Professor of Physics
Malda College and Prof. (Honorary),

: Format Editor :

Dr. Gahul Amin
Assistant Professor of Physics
Netaji Subhas Open University

Notification

Kishore Sengupta
Registrar

Netaji Subhas Open University

UG : Physics
(HPH)

Thermal Physics

GE-PH-21

Unit - 1 ❑ Laws of Thermodynamics

Structure

1.0 Objectives

An idea needs to develop about thermodynamics & different thermal processer is nature. By reeding this unit you will understand about different thermal process and about ideal heat engine. Eventually you will learn about thermal scale absolute zero.

1.1 Introduction

Thermodynamics is a branch of physical science that deals with the relation between heat and other forms of energy such as mechanical, electrical, chemical etc and by extension between all forms of energies.

Determination of the relationship among the various properties of substances, without consideration of the detailed structure of the materials is the subject of thermodynamics. Historically thermodynamics was developed before an understanding of the internal structure was achieved. The results of thermodynamics are all contained implicitly in certain apparently simple statements called laws of thermodynamics.

1.2 Thermodynamic description of System

The macro state variables such as temperature, pressure, entropy, internal energy etc. are known as thermodynamic state variables. A group of materials and/or radiative contents, whose properties are described by thermodynamics varibles are thermodynamic system.

A system is a finite quality of substances or a prescribed region of space.

Boundary of a system is an actual or a hypothetical envelope enclosing the system.

Universe outside the boundary is called surrounding.

Open, closed and isolated system :

In open system matter, heat and energy can be exchanged across the boundadry. In closed system heat and energy can be exchanged across the boundary not matter. In isolated system none of matter, heat or energy can be exchanged across the boundary.

1.3 Zeroth Law of thermodynamics and temperature

If two bodies are in thermal equilibrium with a third, they are in thermal equilibrium with each other.

This law gives the concept of temperature. All these above three systems can be said to process a properly that ensures their being in thermal equilibrium with one another. This property is known as temperature. Thus temperature of a system is a property that determines whether or not the system is with thermal equilibrium or can exchange heat will neighbouring system.

1.4 First Law of thermodynamics and internal energy

First law is the law of conservation of energy, states that energy cannot be created or destroyed in an isolated system. Joule's statement of first law is "Where work (W) is convented into heat (H), or heat is convented into work, they are always proportional to each other. i.e.

$$W = JH$$

Where J is constant of proportionality known as Joule's constant. In other words J Joule of heat is to be spent to get one calorie of heat. The value of J has been found to be 4.2 J/Cal. The law is adopted in thermodynamics as

$$dQ = dU + dW \text{ .... } (1)$$

Where dQ is the heat given to a system dU is the increase in internal energy of the system and dW is the work done by the system. Equation (1) can be written as for the increase in internal energy

$$dU = dQ - dW \text{ .... } (2)$$

The internal energy is an important property of the system. It is the heat energy stored in the system. If a certain amount of heat is supplied to a closed system temperature and/or volume may increase. If temperature increases internal energy will increase and if volume increases, work will be done by the system. Internal energy is a state function and depends only on the temperature. Change in internal energy depends on the change of the state not on the path the change has taken place.

1.5 Various Thermodynamic process

There are four main thermodynamic Process.

1. Isothermal : An isothermal process is one in which there is no temperature change ($\Delta T = 0$). There may be energy flow into or out of the system, however the exchange of heat is just enough to keep the temperature of the system constant.

As for example during phase change viz melting of solid or boiling of liquid. The internal energy of this system remains constant.

2. Adiabatic : The adiabatic process is one in which no heat or mass is transferred between the system and the surrounding ($\Delta m = 0$, $\Delta Q = 0$). In practice this assumption is most often used for rapidly acting system. The adiabatic process provides a rigorous conceptual basis for the theory used to explain fist law of thermodynacmics.

3. Isobaric : The isobaric process is one in which pressure is held constant ($\Delta P = 0$). The heat transferred to the system does work and also changes the the internal energy of the system.

4. Isochoric Process : It is an isovolumatric for an isometric process during which the volume of the closed system remaing constant ($\Delta V = 0$). Increase in internal energy of the system is due to absorption of heat from the surrounds or decrease in internal energy of the system is due to release of heat from the system to the surrounding.

We also speak of isolated system and cyclic process. An isolated system does not interact with the surroundings. In this case there no heat flow and no work is done and internal energy remains constant. A cyclic process in one in which a system returnes to its initial state after passing through various intermediate states. In this process change in internal energy is zero. The amount of heat given to the system is equal to net work done by the system. This is the principle of heat engine whose purpose is to absorb heat and perform work in a cyclic process.

Over and above said processes in thermodynamics other process are worth mentioning. They include isenthalpic, isentropic, isotropic, reversible and irreversible process.

1.6 General relation between C_p and C_v

Heat capacity, specific heat capacity and molar heat capacity.

Except during phase change application of heat increase, temperature of the body. Heat required to increase temperature of a body by 1 degree is known as heat capacity of the body. We write

$$C = \frac{dQ}{dT}, \text{ C (in upper case), whose unit is } JK^{-1}$$

Heat required to increase the temperature of unit mass of the body is known as specific heat capacity (c) (in lower case)

$$c = \frac{1}{m}\frac{dQ}{dT}, \; m = \text{mass of the body}$$

The unit of specific heat capacity is $JKg^{-1}K^{-1}$.

$$c = \frac{C}{m}$$

One mole (or mol) is the amount of substance that contains as many elementary entities (atoms, molecules, ions, electrons etc.) as there are atoms in 0.012 Kg of ^{12}C. This number of atoms of ^{12}C is called Avogadro No. (N_A) and is equal to 6.022×10^{23} particls per mole. Molar mass of a substance = $M = m_aN_A$. Where m_a is the mass of an atom.

Total number of moles $n = \frac{m}{M}$.

The molar heat capacity = $c = \frac{C}{n} = \frac{1}{n}\frac{dQ}{dT}$

For an infinitesimal quasi static process, 1st law of thermodynamics can be written as.

$$dQ = dU + pdV. \; .... \; (1)$$

Heat capacity of constant volume is given by

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

In case of an ideal gas U is a function of temperature only and we can write.

$$C_v = \frac{dU}{dT}$$

Equation (1) can be re written as.

$$dQ = C_v dT + pdV \; .... \; (2)$$

For n mole of gas we write

$$pV = nRT$$

differentiating

$$pdV + Vdp = nRdT.$$

$$\text{or,}\quad pdV = nRT - Vdp$$

putting in equaiton (2)

$$dQ = C_v dT + nRdT - Vdp$$

At constant pressure

$$C_p = \left(\frac{dQ}{dT}\right)_p = C_v + nR$$

$$\text{Or,}\ C_p - C_v = nR$$

1.7 Work done during isothermal process

We consider an ideal gas whose pressure and volume are changed from an initial value p_1, V_1 to a final value p_2 and V_2 keeping temperature constant at T.

The work done is

$$W = \int_{V_1}^{V_2} pdV$$

$$= \int_{V_1}^{V_2} \frac{nRT}{V} dV, \qquad \because\ pV = nRT$$

$$= nRT \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\text{or,}\quad W = nRT \ln \frac{V_2}{V_1}$$

$$\text{or,}\quad W = nRT \ln \frac{p_1}{p_2} \qquad [\because\ p_1V_1 = p_2V_2]$$

1.8 Adiabetic process

Relations between p, V, T in a reversible adiabatic process.

We consider our adiabatic process on an ideal gas. Let pressure, volume and temperature change from p, V, T to p + dp, V + dV and T + dT respectively. The internal energy changes from U to U + dU. Since in adiabatic process the amount of heat supply is zero, we write first law of thermodynamics as.

$$O = dU + pdV$$

$$\text{or,}\quad nC_v dT + pdV = 0 \text{ .... (1)}$$

For ideal gas we know $pV = nRT$

$$pdV + Vdp = nRdT$$

$$\text{or,}\quad dT = \frac{pdV + Vdp}{nR}$$

Putting in (1)

$$C_v \frac{pdV + Vdp}{R} + pdV = 0$$

$$\text{or,}\quad (C_v + R)\, pdV + C_v\, Vdp = 0$$

$$\text{or,}\quad C_p\, pdV + C_v\, Vdp = 0$$

$$\text{or,}\quad \frac{C_p dV}{C_v V} + \frac{dp}{p} = 0$$

$$\text{or,}\quad \gamma \frac{dV}{V} = -\frac{dp}{p} \text{ ....(3)} \qquad \because \frac{C_p}{C_v} = \gamma$$

Integrating between initial to final state are get from (3)

$$\int_{V_1}^{V_2} \gamma \frac{dV}{V} = -\int_{p_1}^{p_2} \frac{dp}{p}$$

$$\text{or,}\quad \gamma \ln \frac{V_2}{V_1} = -\ln \frac{p_2}{p_1}$$

$$\text{or,}\quad \ln \left(\frac{V_2}{V_1}\right)^{\gamma} = \ln\left(\frac{p_1}{p_2}\right)$$

$$\text{or, } \left(\frac{V_2}{V_1}\right)^{\gamma} = \frac{p_1}{p_2}$$

or, $p_1V_1^{\gamma} = p_2V_2^{\gamma}$, or pV^{γ} = constant

Again $pV = nRT$

$$V = \frac{nRT}{p}$$

$$\therefore \quad p\left(\frac{nRT}{p}\right)^{\gamma} = \text{constant}$$

$$\text{or, } \quad p^{1-\gamma}\,T^{\gamma} = \text{constant}$$

$$\text{or, } \quad \frac{T^{\gamma}}{p^{\gamma-1}} = \text{constant}$$

Similarly $TV^{\gamma-1}$ = constant.

1.9 Work done during isothermal and adiabatic processes

Work done in an isothermal process. We consider an ideal gas where pressure and volume are changed from p_1, V_1 to p_2, V_2 isothermally. In such process $p_1V_1 = p_2V_2 = nRT$

Work done in this process

$$W = \int_{V_1}^{V_2} p\,dV = \int_{V_1}^{V_2} \frac{nRT}{V}\,dV$$

$$= nRT \ln \frac{V_2}{V_1}$$

$$= nRT \ln \frac{p_1}{p_2}$$

Work done in adiabatic process.

In case of adiabatic process

$$pV^{\gamma} = p_1V_1{}^{\gamma} = p_2V_2{}^{\gamma} = k$$

The work done is

$$W = \int_{V_1}^{V_2} pdV = \int_{V_1}^{V_2} \frac{kdV}{V^{\gamma}} = \int_{V_1}^{V_2} kV^{-\gamma}dV$$

$$= \frac{K}{1-\gamma}\left[\frac{1}{V_2^{\gamma-1}} - \frac{1}{V_1^{\gamma-1}}\right]$$

$$= \frac{1}{1-\gamma}\left[\frac{K}{V_2^{\gamma-1}} - \frac{K}{V_1^{\gamma-1}}\right]$$

$$= \frac{p_1V_1 - p_2V_2}{\gamma-1}$$

Slopes of adiabatic and isothermal curves.

The graph giving variation of pressure with volume at constant temperature is known as isothermal and that at constant heat is adiabatic. We denote the pressure p, volume V and temperature T of a gas by a point O on the p – V curve. If we vary

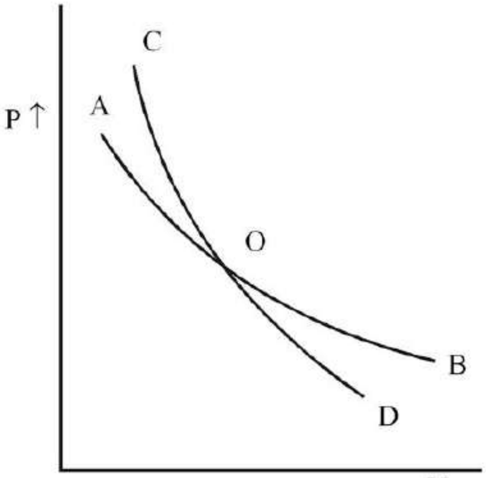


Fig. 1

p and V keeping T constant we get the curve AOB, on the other hand it p and V are changed adiabatically to the same extent, the heat will remain confind in the gas and the variation of p with V will be given by COD.

For isothermal process we have

$$pV = \text{constant}$$

$$pdV + Vdp = 0$$

$$\frac{dp}{dV} = -\frac{p}{V} \text{ is the slope of the isothermal curve.}$$

For adiabatic process we know

$$pV^{\gamma} = \text{constant, differentiating.}$$

$$\gamma pV^{\gamma-1}dV + V^{\gamma}dp = 0$$

$$\text{or,} \quad \frac{dp}{dV} = -\gamma\frac{p}{V} \text{ is the slope of the adiabatic curve.}$$

Since $\gamma > 1$, the slope of the adiabatic curve is greater than that of the isothermal curve.

1.10 Compressibility and Expansion coefficient

The equation of state of any (pVT) system can be written as any one variable as a fucntion of two other viz.

$$V = V(T, p)$$

A fundamental theorem in partial differential calculus enable us to write the differential of the volume V as.

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp \quad \text{.........} \quad (1)$$

If the change of temperature is made smaller and smaller until if becomes infinitesimal, then the change in volume also become infinitesimal and we have what is known as the differential coefficient of volume expansion or volume expansivity, donoted by β, as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \quad \text{..........} \ (2)$$

β is almost always positive with a natural exception of water between 0°c to 4°c where β is negative.

If the change of pressure is made infinitesimal, then the volume change is also infinitesimal and we have differential bulk modulus. If we further require that temperature be kept constant the resulting quantily is called the isothermal bulk modulus, denoted by B as

$$B = -V\left(\frac{\partial p}{\partial V}\right)_T$$

For calculations in thermodynamies, the more useful quantity is the reciprocal of isothermal bulk modulus, called isothermal compressibility and is denoted by

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \quad \text{..........} \ (3)$$

The units of B and K_T are respectively K^{-1} and Pa^{-1}

For ideal gas we write $pV = nRT$ differentiating we get.

$$pdV + Vdp = nRdT$$

$$\text{or,} \quad dV = \frac{nR}{p}dT - \frac{V}{p}dp \quad \text{..........} \ (4)$$

Comparing equation (1) and (4) we get

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{nR}{p} \text{ and } \left(\frac{\partial V}{\partial p}\right)_T = -\frac{V}{P}$$

$$\therefore \quad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\frac{nR}{p} = \frac{nR}{nRT} = \frac{1}{T}$$

$$\text{and } K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(-\frac{V}{p}\right) = \frac{1}{p}$$

If volume changes repidly, so that no heat can flow we define adiabatic compressibility as.

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_s$$

In this case pV^γ = constant

$$\text{or,} \quad p\gamma V^{\gamma-1}dV + V^\gamma dp = 0$$

$$\frac{dV}{dp} = -\frac{V}{p\gamma}$$

$$\therefore \quad K_s = \frac{1}{p\gamma} = \frac{K_T}{\gamma}$$

$$\therefore \quad \frac{K_s}{K_T} = \frac{1}{\gamma} = \frac{C_v}{C_p} \qquad K_s < K_T$$

In reality it is found that it is harden to compress a fluid if heat does not flow out of it.

1.11 Reversible and irreversible process

The state of an ideas gas is described by specifying its pressure p, volume V and temperature T. If these parameters can be uniquely specified at a time, we say that the gas is in thermodynamic equlibrium. If a part of this gas is heated the equilibrium conditon is destroyed.

Let the initial state (p_1, V_1, T_1) of the gas be changed to a final state (p_2, V_2, T_2). If the process is performed in such a way that at any instant during the process, the system is very nearly in thermodynamic equilibrium, the process is called quasi-static. This means we can specify the parameters p, V. T uniquely at any instant during such a process. Actual processes are not quasi-static. However, in idealised processes where changes take place infinitely slowly, the processes may be assumed to be quasi-static.

A quasi-static processes on a gas can be represented by a curve on a p – V diagram. This is because at any instant we have a unique value of p and a unique value of V. Let the curve in the firgure shows such a quasi-static process, taking the system from an initial state (1) to a final state (2). AB is an arbitrary small part of the process. Suppose in this part the gas takes an amount dQ of heat from its surroundings and performs an amount dW of work on the surroung. It may be possible to design a reverse quasi-static process which takes the system from the state (2) to the state (1) satisfying the following conditions.

(1) The reverse process is represented by the same curve as the direct process with the arrow reversed.

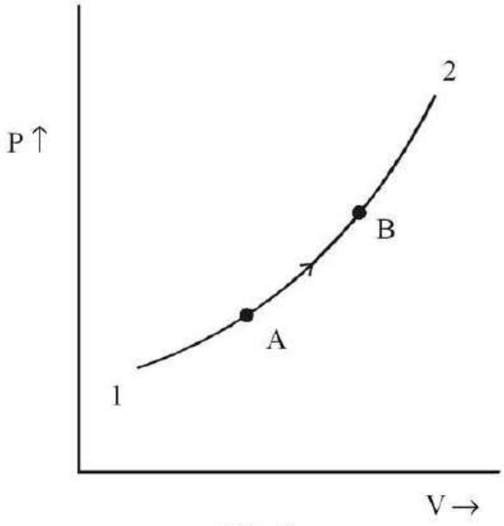


Fig. 2

(2) In the part BA the system gives an amount dQ of heat to the surrounding and an amount dW of work is performed on the system.

If such a reverse process is possible, the original process is called reversible process. In the direct process the system has passed through certain equlibium states in a sequence. When the process is reversed, the system passes through the same states in reverse sequence. Also, in any small part of the reverse process, it returns the same amount of heat to the surrounding as was taken during corresponding part of the direct process. Similarly any work done by the system in the direct process is compensated by the equal work done on the system in the corresponding reverse process.

A process can be reversible if it satisfies two conditions. The process must be quasi-static and should be nondissipative. This means friction, viscosity etc. should he completely absent.

1.12 Second law of thermodynamics and entropy

It is a fact of everyday experience that no heat engine has ever been developed that converts the heat extracted from a reservoir at a higher temperature into work without rejecting some heat to a reservoir at a lower temperature. This negative statement constitute the second law or thermodynamics. The law has been formulated in several ways.

Planck-Kelvin Statement

"It is impossible to construct an engine that operating in a cycle will produce no effect other than extraction of heat from a reservoir and performance of an equivalent amount of work."

Clausius Statement

"It is impossible to construct a refrigerator that operating in a cycle will produce no effect other than the transfer of heat from a lower temperature resevior to a higher temperature reservoir."

Though the above two statements are apparently different, it can be shown that they are equivalent in all respect.

Entropy

Entropy is the most important term in thermodynamics but its concept is rather a bit difficult to understand. There is no straight forward definition of entropy. Like pressure, temperature volume, internal energy etc, we have another thermodynamic variable of a system named entropy. In a given equilibrium state the system has a definite value of entropy. If the system has a temperature T and a small amount of heat ΔQ is added to it its entropy increases by

$$\Delta S = \frac{\Delta Q}{T}$$

The change of enuory from an initial to a final equilibrium states is

$$S_f - S_i = \int_i^f \frac{dQ}{T}$$

The value of the change depends on the two states only but not on the path of process of the change just as change of internal energy.

Clausius introduced the concept of entropy as a precise way of expressing the second law of thermodynamics. In terms of entropy the second law of thermodynamics is stated as "spontaneous changes for an irreversible process in an isolated system always proceeds in a direction of increasing entropy.

In a limiting view the entropy is sometimes stated to be the measure of randomness of the system.

The unit of entropy is Joule per kelvin (JK^{-1}).

1.13 Carnot's cycle and theorem

Sadi Carnot suggested as ideal engine, known as Carnot's engine which has an intimate relation with second law of thermodynamics.

We consider an ideal gas in a cylinder. The bottom of the cylinder is diathermic whereas the rest of which is adiabatic. An adiabatic piston is fitted into the cylinder. Also suppose we have two large bodies one at constant high temperature T_1 and other at constant low temperature T_2.

Four processes, togather known as Carnot's cycle, are performed in the following order.

1. The cylinder is in contact with the reservoir at temperature T_1 with the gas in a compressed state. This situation is shown by the point (1) in the $p - V$ and $T - S$ diagram. The gas is isothermally expanded from p_1, V_1, T_1 to p_2, V_2, T_1) (2). Work is done by the gas and Q_1 amount of heat is supplied to the gas by the reservoir at temperature T_1.
2. The cylinder is now kept on an adiabatic platform and the gas is allowed to expand further to the state from p_2, V_2, T_1 to the state p_3, V_3, T_2 shown by the point (3). The work is done by the gas and the temperature falls from T_1 and T_2.

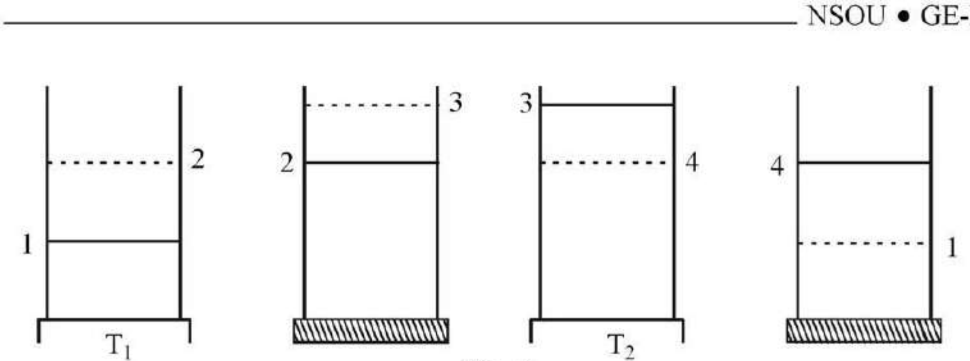


Fig. 3

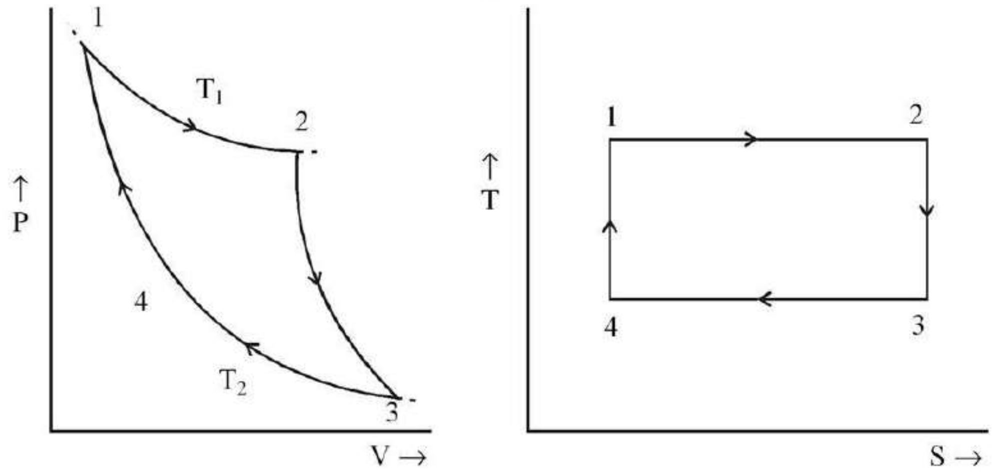


Fig. 4

3. The cylinder then is put in contact with the reservoir at the lower temperature T_2. The gas is isothermally compressed to p_4, V_4, T_2, shown by the point (4) in the $p - V$ and $T - S$ diagrams. The work is done on the gas and the gas rejects an amount of heat Q_1 to the reservoir at lower temperature T_2.
4. Finally the cylinder is kept on the adiabatic platform and further compressed to reach the state (1). Temperature uses from T_2 to T_1. The piston is frictionless and is moved very slowly during the entire cycle so that cycle is reversible.

The efficiency of Carnot's engine : Work done by the gas W_1 in the isothermal expansion in the first process is equal to the heat supplied to the gas.

$$Q_2 = W_1 = \int_{V_1}^{V_2} p dV = nRT_1 \ln \frac{V_2}{V_1}$$

The work done by the gas W_2 is equal to decrease in internal energy of the gas.

$$W_2 = nC_v\ (T_1 - T_2)$$

The work done on the gas W_3 in the third process is equal to the heat rejected by the gas.

$$W_3 = Q_1 = -\int_{V_3}^{V_4} pdV = -nRT_2 \ln \frac{V_4}{V_3}$$

The work done W_4 on the gas in the fourth process is equal to the increase in internal energy

$$W_4 = nC_v\ (T_1 - T_2)$$

$$\text{efficiency } \eta = \frac{\text{net work done}}{\text{heat aborbed at high temperature}}$$

$$= \frac{W_1 - W_2}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

Since V_2 and V_3 are on the same adiabatic curve.

$$\left(\frac{V_2}{V_3}\right)^{\gamma} = \frac{T_1}{T_2}$$

and V_1 and V_4 are on the same adiabatic curve.

$$\left(\frac{V_1}{V_4}\right)^{\gamma} = \frac{T_1}{T_2}$$

$$\therefore \quad \frac{V_2}{V_3} = \frac{V_1}{V_4} \quad \text{or} \quad \frac{V_2}{V_1} = \frac{V_3}{V_4}$$

Hence $\dfrac{Q_1}{Q_2} = \dfrac{T_1}{T_2}$

$$\therefore \quad \eta = 1-\frac{T_2}{T_1}$$

Carnot's Theorem :

All reversible engines operating between same two temperatures have equal efficiencies and no engine operating between same two temperatures can have efficiencies greater than this.

1.14 Entropy changes in reversible and irreversible processes

For a process that reversibly exchanges a quantity of heat Q_{rev} with surrounding, the entropy change is defined by $\frac{Q_{rev}}{T}$. The heat exchange occurs at temperature T.

Thus $\Delta S = \frac{Q_{rev}}{T}$, S is the entropy.

We consider and ideal gas expanding at constant temperature.

$$dQ = du + pdV \;;\; du = 0, \text{ for no change of temperature}$$

$$\text{or,} \quad dQ = RT\frac{dV}{V}. \quad pV = RT$$

$$\frac{dQ}{T} = R\frac{dV}{V}$$

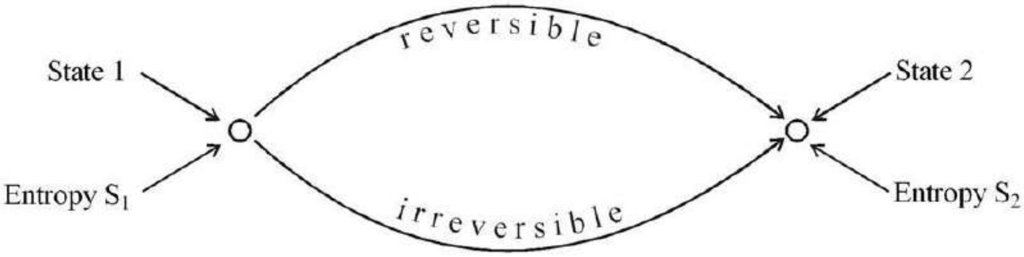
Integrating we get the change of entropy

$$\Delta S = \int\frac{dQ}{T} = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}$$

(p_1, V_1) and (p_2, V_2) are the pressure and volume respectively before and after expansion.

The above definition of change of entropy is strictly valid for reversible processes. However, we can find ΔS precise even for real, irreversible processes. The reason is that the entropy S of a system, like internal energy depends only on the state of the system and not how it reached that condition. Entropy is a property of the state. Thus the change of entropy ΔS of a system between state 1 and state 2 is same no matter how the change occurs. We just need to find or imagine a reversible process than takes us from stae 1 to state 2 and calculate ΔS for that process. That will be the change in emtropy for any process going from state 1 and 2.

$$\Delta S = \left(\frac{Q}{T}\right)_{rev} = S_2 - S_1$$



$$\Delta S = S_2 - S_1 = \Delta S_{rev}$$

Fig. 5

1.15 Entropy-Temperature diagram

Entropy-temperature diagram is a thermodynamic diagram used in thermodynamics to visualize to temperature and entropy during thermodynamic process or cycle as a graph or a curve. It is useful and common tool particularly because it helps to visualise the heat transferred during a process. For reversible process the area under the curve of the process is the heat transferred to the system during the process.

Working fluids are often catagorised on the basis of the shape of their T-S (often so called) diagram. An isentropic process is depicted as a vertical line on a T-S diagram where as an isothermal process is a horizonal line. As an example of a T-S diagram we have considered a thermodynamic cycle taking place between a hot reservoir at a temperature T_1 and a cold reservoir at a temperature T_2.

For a resersible process the area ABCEF is the amount of heat Q aborbed from the reservior at higher temperature T_1. The area ADCFE is the amount of heat Q_2 rejected to the reservoir at lower temperature T_2. The thermal efficiency is the ratio of the area ABCD, (the net work done $W = Q_1 - Q_2$) to the area ABCFE (the heat

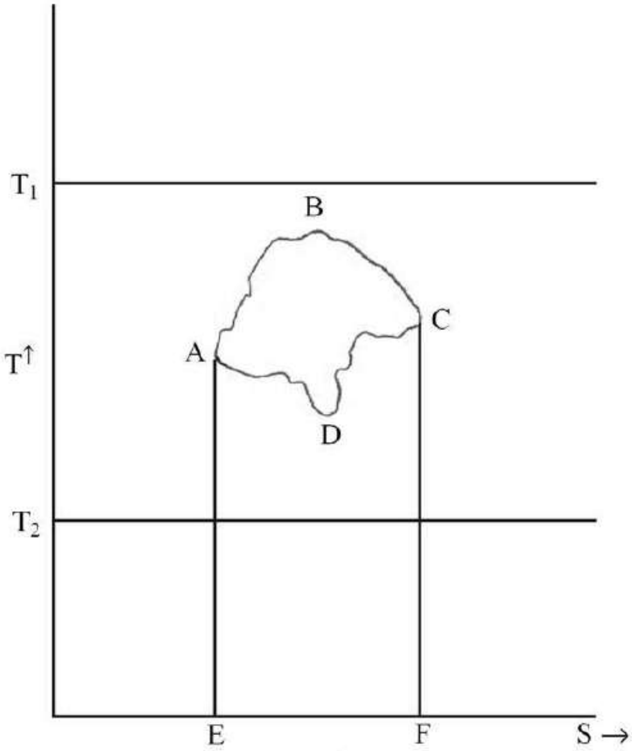


Fig. 6

absorbed from the hot reservoir). If the cycle moves in a clockwise sence, then it is a heat engine that output works. If the cycle moves in a counter clockwise sense, it is a heat pump.

1.16 Third law of thermodynamics and unattainability of absolute zero

Third law of thermodynamics states that the entropy of a system approaches a constant value as the temperature approaches absolute zero.

Unattainability of absolute zero.

Experiments show that the fundamental feature of all cooling processes is that the lower the temperature attained, the more difficult it is to cool further. For example, the colder as liquid is, the lower is the vapour pressure, and harder it is to produce further cooling. Similar reasons are there for other concluded that "By no finite series of processes is the absolute zero of temperature is attainable." This is known as unattainability of absolute zero.

1.17 Problems

Sloved Problems

1. A Carnot engine operates with $\eta = 40\%$. How much must the temperature of the hot reservoir increase so that η increase to 50%? Temperature of the cold reservoir is 9°c.

Solution

Let T_1 and T_1' he the temperatures of hot reservoir when efficiences are 40% and 50% respectively. Therefore

$$\frac{40}{100} = \frac{T_1 - T_2}{T_1} \qquad T_2 = \text{temperature of the cold reservoir} = 9 + 273 = 282\text{K}$$

$$\text{or, } \frac{T_1 - T_2}{T_1} = .4$$

$$\text{or, } T_1 - T_2 = 0.4\ T_1$$

$$\text{or, } (1 - 0.4)\ T_1 = T_2$$

$$\text{or, } T_1 = \frac{T_2}{0.6}$$

$$\text{Similarly } \frac{50}{100} = \frac{T_1' - T_2}{T_1'}$$

$$\text{or, } 0.5T_1' = T_1' - T_2$$

$$T_1' = \frac{T_2}{0.5}$$

$$\therefore\ T_1' - T = T_2 \left(\frac{1}{0.5} - \frac{1}{0.6}\right) = T_2 \frac{0.1}{0.3}$$

$= \frac{282}{3} = 94\text{K}$ or, 94°c. $\qquad \because\ T_2 = 273 + 9 = 282\text{K}$

2. What is the increase in entropy of one gram of ice at 0°c when it is melted and heated to 50°c.

Solution

$\Delta Q = mL_f + mVC_w dT$, m = mass of ice = 1g, L_f = Latent heat of fusion = 8 cal g^{-1}, C_w = sp. heat of water = 1

$$\Delta S = \frac{1\times 80}{0+273} + \int_{0+273}^{50+273} \frac{dT}{T}$$

$$= 0.293 + \ln \frac{323}{273}$$

$$= 0.293 + 0.168 = 0461 \text{ Cal } k^{-1}.$$

3. What is the decrease in entropy of 25g of water that condenses on a bathroom minor at a temperature 35°c assuning no change in temperature and the latent heat of vaporization is 2450 KJ Kg^{-1}.

Solution

Mass of water condensed = $m = \frac{25}{100}$ kg heat liberated = $m \times L_v$

$$dQ = 25 \times 10^{-3} \times 2450 \times 10^3 \text{ J}$$

$$= 25 \times 2.45 \times 10^3 \text{ J}$$

Decrease in entropy

$$\Delta S = \frac{dQ}{T} = \frac{25\times 2.45}{35+273} \times 10^3 \text{ JK}^{-1}$$

$$= 199 \text{ JK}^{-1}$$

Problems

1. Calculate the efficiency of a Carnot engine operating between 10°c and 50°c.

2. Find the change of entropy if 1 kg of water at 80°c is added to 600 gm of water at 20°c.
3. Find the increase in entropy of 1 kg ice orginally at 0°c melts into water of 0°c.

1.18 Questions

1. Give the mathematical form of first law of thermodynamics. Explain each term.
2. What is meant by state function and path function? Give suitable example of each.
3. Distinguish between a reversible and irreversible process. Give examples.
4. What is the essential difference between first and second law of thermodynamics.
5. State second law of thermodynamics in terms of entropy.
6. Establish TdS relations in thermodynamics. What is their importance ?

Unit - 2 ❑ Thermodynamics Potentials

Structure

2.0 Objectives

You already learnt thermal process in privious unit. In this section we shall develop different equation related thermodynamical quantity and an idea of heat capacity of different material will also develop.

2.1 Introduction

Thermodynamic potentials are very important functions which give the insight of many processes leading to achievment of low temperature and different types of phase changes. Maxwell's relations are very convenient tools for the study of thermodynamic phenomena.

2.2 Thermodynamic potentials

The following four thermodynamics functions are of immense importance in the study of the subject. They are internal energy $U\ (S, V)$, Helmholtz function $F\ (T, V)$, Enthalpy $H\ (s, p)$ and Gibb's function $G\ (T, p)$. In mechanics potential has the capacity of doing mechanical work. In thermodynamics, internal energy U has capacity to do work and capacity to release heat. Helmholz function F has capacity to do mechanical and non mechanical work. Enthalpy H has capacity to do non mechanical work and capacity to release heat. Finally Gibb's function G has the capacity to do non mechanical work. Hence these functions are also known as thermodynamic potentials. They are defined as.

$$U = \int (TdS - pdV)$$

$$F = U - TS$$

$$H = U + pV$$

$$G = U + pV + TS$$

2.3 Maxwell's Relations

We start from first law of thermodynamics

$$dQ = TdS = dU + pdV$$

or, $$dU = TdS - pdV \text{ .... } (1)$$

Considering S and V as independent parameter

$$U = U\,(S,\ V)$$

Where from we write

$$dU = \left(\frac{\partial U}{\partial S}\right)_V ds + \left(\frac{\partial U}{\partial V}\right)_S dV \text{ .... } (2)$$

Comparing equs (1) and (2)

$$\left.\begin{aligned} \left(\frac{\partial U}{\partial S}\right)_V &= T \text{ and} \\ \left(\frac{\partial U}{\partial V}\right)_S &= -p \end{aligned}\right\} \text{ .... } (3)$$

The imporant content of the relation (1) is that the combination of parameters on right side is always equal to the exact differential of a quantity which in this case is U. Hence the parameters T, S, p, V which occurs in equ (1) can not be varied completely arbitranily, there must exist some connection between them to guarantee that their combination yields the differential dU.

To obtain this connection, it is only necessary to note that the second derivative of U must be independent of the order of differentiation. i.e.

$$\frac{\partial^2 U}{\partial V \partial S} = \frac{\partial^2 U}{\partial S \partial V}$$

or, $$\left(\frac{\partial}{\partial V}\right)_S \left(\frac{\partial U}{\partial S}\right)_V = \left(\frac{\partial}{\partial S}\right)_V \left(\frac{\partial U}{\partial V}\right)_S$$

Using eqn (3) we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \quad \text{............} \quad (4)$$

We write $pdV = d\,(pV) - Vdp$

Equation (1) is rewritten as

$$dU = TdS - d\,(pV) + Vdp$$

or, $d\,(U + pV) = TdS + Vdp$

or, $dH = TdS + Vdp$ –(5), $H = U + pV$

Consider $H = H\,(S, p)$

$$dH = \left(\frac{\partial H}{\partial S}\right)_p dS + \left(\frac{\partial H}{\partial p}\right)_S dp \quad \text{............} \quad (6)$$

Comparing equation (5) and (6)

$$\left(\frac{\partial H}{\partial S}\right)_p = T \text{ and } \left(\frac{\partial H}{\partial p}\right)_S = V \quad \text{............} \quad (7)$$

with previous arguments we now write

$$\frac{\partial^2 H}{\partial p \partial S} = \frac{\partial^2 H}{\partial S \partial p}$$

or, $$\left(\frac{\partial}{\partial p}\right)_S \left(\frac{\partial H}{\partial S}\right)_p = \left(\frac{\partial}{\partial S}\right)_p \left(\frac{\partial H}{\partial p}\right)_S$$

$$\text{or,}\quad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \;\ldots\ldots\ldots\ldots\ldots\ldots (8)$$

Again from the fundamental thermodynamic relation we write

$$dU = TdS - pdV = d\,(TS) - SdT - pdV$$

$$\text{or,}\quad d\,(U - TS) = -\,SdT - pdV$$

$$\text{or,}\quad dF = -\,SdT - PdV \;\ldots\ldots\ldots\ldots\; (9) \quad F = U - TS$$

considering $F = F\,(T, V)$

$$dF = \left(\frac{\partial F}{\partial T}\right)_V dT + \left(\frac{\partial F}{\partial V}\right)_T dV \;\ldots\ldots\ldots\ldots\; (10)$$

Comparing equ (9) and equ (10)

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \quad \text{and} \quad \left(\frac{\partial F}{\partial V}\right)_T = -\,p \;\ldots\ldots\ldots\; (11)$$

Equality of cross derivatives

$$\frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V}$$

and we get as before

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \;\ldots\ldots\ldots\ldots\; (12)$$

From equ (1)

$$dU = TdS + pdV$$

$$= d\,(TS) - SdT - d(pV) + Vdp$$

$$\text{or,}\quad d\,(U - TS + pV) = -\,SdT + Vdp$$

$$\text{or,}\quad dG = -\,SdT + Vdp \;\ldots\ldots\ldots\; (13)\,; \quad G = U - TS + pV$$

Considering T and p as independent variables

$$G = G\,(T, p)$$

$$dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp \text{ .... (14)}$$

From eqn (13) and eqn (14)

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \text{ and } \left(\frac{\partial G}{\partial p}\right)_s = V \text{ .... (15)}$$

Equalily of cross derivatives

$$\frac{\partial^2 G}{\partial p \partial T} = \frac{\partial^2 G}{\partial T \partial p}$$

implies $$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \text{ .... (16)}$$

Relations (4), (8), (12) and (16) are known as Maxwell's Relations.

2.4 TdS equation

Considering the entropy of a pure substance as a function of T and V we write

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

and $$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV = dQ$$

For reversible isochoric process

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

and from Maxwell's third relation

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

$$\therefore \quad TdS = C_v dT + T\left(\frac{\partial p}{\partial T}\right)_V dV$$

The equation is known as the first TdS equation.

Considering the entropy of a pure substance as a function of T and p

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

We know $C_p = T\left(\frac{\partial S}{\partial T}\right)_p$

and from Maxwell's fourth relation

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

We get $\quad TdS = C_p\, dT - T\left(\frac{\partial V}{\partial T}\right)dp$

This equation in known as second TdS equation

2.5 Joule-Thomson effect

Joule-Thomson effect decribes the temperature change of a real gas or liquid when it is forced through a valve or porous plug while keeping it insulated so that no heat is exchanged with the environment. This procedure is called throttling process or Joule Thomson process. At room temperature, all gases except hydrogen, helium and neon cool upon expansion by Joule Thomson process when being throttled through an orifice; these three gases experience the same effect but only at lower temperatures. At room temperature are heated on throttling.

We describe porous plug experiment to demonstrate Joule Thomson effect. The experimental gas is compressed by a suitable compressor P to a high degree and forced through a poroum plug (p.p) fitting tightly in a tube A of poorly conducting material. By means of proper packing of asbestor, wool or other non conducting materials the tube A is thermally isolated so that no heat can enter or leave the system.

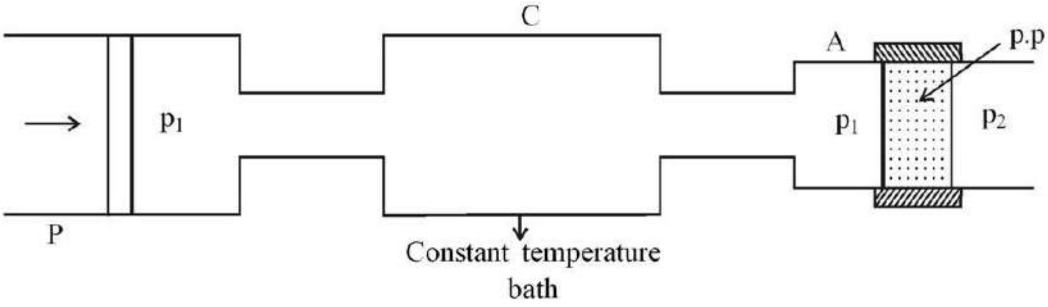


Fig. 7

Such an expansion of gas is called throttling process. The material usually used as poous plug is wool, cotton or silk having number of tiny orifices. Fluid flowing through these orifices undergoes a large droop of pressure ($p_2 << p_1$). Two platinum thermometers or thermo comples one placed at each side of the plug are placed to accurately record the temperatures T_1 and T_2 before and after throttling. Pressures p_1 and p_2 at the entry and exit are recorded by suitable guages. The gas to be cooled is first compressed and made to flow through a constant low temperature bath C to acquire a particular initial temperature. The observations of the experiment are

(i) If the initial temperature is sufficiently low all gases suffer fall of temperature. $T_2 < T_1$.

(ii) The cooling is proportional to drop of pressure.

(iii) As the initial temperature T_1 is increased the drop of temperature becomes smaller and at a particular temperature $T > T_i$ the throttled gas gets heated instead cooling. This temperature T_i is called inversion temperature and are 621K, 195K and 23.6K respectively for Nitrogen, hydrogen and helium. To get cooling effect the gas is to be taken below the inversion temperature before throttling.

Work done by the gas on the piston

$$W = \int p_2 dV_2 - \int p_1 dV_1 = p_2V_2 - p_1V_1$$

Since no heat enters and leave the system the above work has to be performed at the expense of internal energy.

$$\therefore \quad U_2 - U_1 + p_2V_2 - p_1V_1 = 0$$

$$\text{or,} \quad U_1 + p_1V_1 = U_2 + p_2V_2$$

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

$$\therefore \quad H = U + pV = \text{enthalpy} = \text{constant}$$

$$dH = dU + pdV + Vdp$$

$$= dQ + Vdp$$

$$\text{or,} \quad dH = TdS + Vdp$$

From Tds equation we know that

$$TdS = C_pdT - T\left(\frac{\partial V}{\partial T}\right)_p dp$$

$$\text{or,} \quad dH = C_pdT - T\left(\frac{\partial V}{\partial T}\right)_p dp + Vdp$$

$$\text{or,} \quad dT = \frac{1}{C_p}\left\{T\left(\frac{\partial V}{\partial T}\right)_p - V\right\}dp + \frac{1}{C_p}dH \text{ ....(1)}$$

Writing T as a function of p and H

$$dT = \left(\frac{\partial T}{\partial p}\right)_H dp + \left(\frac{\partial T}{\partial H}\right)_p dH \text{ .... (2)}$$

Comparing equation (1) and (2)

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{1}{C_p}\left\{T\left(\frac{\partial V}{\partial T}\right) - V\right\} \text{ .... (3)}$$

$\mu = \left(\frac{\partial T}{\partial p}\right)_H$ is the change in temperature per unit change of pressure under the condition of the experiment viz H = constant is known as Joule Thomson coefficient. If μ is positive the effect is cooling and if negative the effect is heating.

For Vander Waal gas

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

$$\text{or,}\quad V=\frac{RT}{p}-\frac{a}{pV}+b-\frac{ab}{pV^2}\qquad\qquad \because pV\approx RT$$

$$\text{or,}\quad V\approx\frac{RT}{p}-\frac{a}{RT}+b+\frac{abp}{R^2T^2}\ \ldots\ldots\ldots\ldots\ldots\ (4)$$

$$\left(\frac{\partial V}{\partial T}\right)_p=\frac{R}{p}+\frac{a}{RT^2}-\frac{2abp}{R^2T^3}\ \ldots\ldots\ldots\ldots\ldots\ (5)$$

$$\text{from (4)}\qquad \frac{R}{p}=\frac{V-b}{T}+\frac{a}{RT^2}-\frac{abp}{R^2T^3}$$

putting in (5) we get

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

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

$$\mu=\frac{1}{C_p}\left\{T\left(\frac{\partial V}{\partial T}\right)_p-V\right\}=\frac{1}{C_p}\left(\frac{2a}{RT}-b\right)\qquad \because \text{ab is very small}$$

(i) If intermolecular forces are strong so that $\frac{2a}{RT}>b$, $\mu>0$, cooling occurs.

(ii) If intermolecular forces are weak so that $\frac{2a}{RT}>b$, $\mu<0$, heating occurs.

(iii) If $\frac{2a}{RT}=b$ no change of temperature occurs. The temperature $T=\frac{2a}{Rb}=T_i$ (say) is known as temperature of inversion. We know the critical temperature T_c and Boyle temperature T_B are $T_c=\frac{8a}{27bR}$ and $T_B=\frac{a}{Rb}$.

$\therefore\ T_i=\frac{27}{4}\ T_c=2T_B.$

2.6 Clausius–Clapeyron equation

Clausius-Clapeyron relation is a way of characterisng a discontinuous phase transitions between two phases of matter of a single constituent. We take the entropy S for the homogeneous substance to be a function of volume V and temperature T and write.

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dv + \left(\frac{\partial S}{\partial T}\right)_V dT$$

Since during phase change temperature and pressure remain constant

$$dS = \left(\frac{\partial S}{\partial V}\right)_T dV \quad .... (1)$$

from Maxwell's third relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \quad .... (2)$$

from equation (1) and eqn (2) we write

$$dS = \left(\frac{\partial p}{\partial T}\right)_V dV$$

Since pressure and temperature remain constant, partial derivative can be replaced by total derivative and we write

$$dS = \frac{dp}{dT} dV \quad .... (3)$$

$$\text{or,} \quad \frac{dp}{dT} = \frac{dS}{dV} \quad ....(4)$$

If L be latent heat of conversion from phase 1 to phase 2 and m be the mass of substance under going phase change

$$dS = \frac{TdS}{T} = \frac{dQ}{T} = \frac{mL}{T}$$

If ν_1 and ν_2 be the specific volumes of the substance in phase 1 and phase 2 respectively.

$$dV = (\nu_2 - \nu_1)\, m$$

Putting these values of dS and dV in equation (4) we get

$$\frac{dp}{dT} = \frac{1}{T(\nu_2 - \nu_1)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

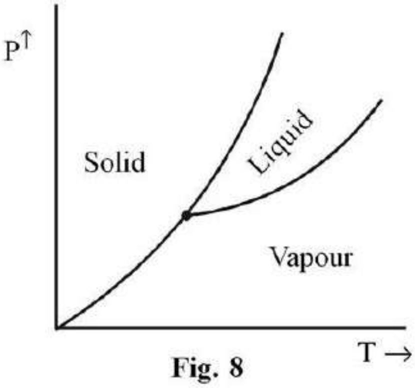


Fig. 8

On a pressure-temperature diagram the line separating two phases is known as co-existance curve. The calusius-clapeyron relation (5) gives the slope of the tangent to this curve.

2.7 Heat Capacities

Heat capacity equations

Equating the first and second TdS equations

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

Solving from above relation

$$dT = \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_p - C_v} dV + \frac{T\left(\frac{\partial V}{\partial T}\right)_p}{C_p - C_v} dp \quad \ldots\ldots\ldots\ldots (1)$$

Writing T as a function of V and P

$$dT = \left(\frac{\partial T}{\partial V}\right)_p dV + \left(\frac{\partial T}{\partial p}\right)_V dp \text{ .... (2)}$$

Comparing equation (1) and (2) we get

$$\left(\frac{\partial T}{\partial V}\right)_p = \frac{T\left(\frac{\partial p}{\partial T}\right)_V}{C_p - C_v}$$

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

From either of the above relation

$$C_p - C_v = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial T}\right)_V \text{ .... (3)}$$

Using simple theorem of partial differential calculus viz

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

We have $$\left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T \text{ .... (4)}$$

From (3) and (4)

$$C_p - C_v = - \, -T\left(\frac{\partial V}{\partial T}\right)_p^2 \left(\frac{\partial p}{\partial V}\right)_T \text{ .... (5)}$$

Equation (5) is an important equation in thermodynamics and it shows that

(i) Since $\left(\frac{\partial p}{\partial V}\right)_T$ is always negative for all known substances $C_p \geq C_v$

(ii) As $T \rightarrow 0$ $C_p \rightarrow C_v$; at absolute zero two heat capacities are equal.

(iii) $C_p - C_v$ when $\left(\frac{\partial V}{\partial T}\right)_p = 0$. (at 4°c of water)

We know that the volume expansivity and isothermal compressibility are respectively defined as

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p \text{ and } K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$$

In terms these quantities eqn (5) becomes $C_p - C_v = \frac{TV\beta^2}{K}$

2.8 Problems

Solved Problems

1. Calculate Joule-Thomson cooling of oxygen at NTP. Given, $a = 1.86 \times 10^6$, $b = 32$ cc and $C_p = 7.03$ cal mol^{-1} K^{-1}.

$$\frac{\Delta T}{\Delta P} = \frac{1}{C_P}\left(\frac{2a}{RT} - b\right)$$

$$= \frac{1}{4.18 \times 10^7 \times 7.03}\left(\frac{2 \times 1.86 \times 10^6 \times 76 \times 981 \times 13.6}{8.3 \times 10^7 \times 273} - 32\right)$$

$$= \frac{134.46}{4.18 \times 10^7 \times 7.03} \text{ degree dyne}^{-1} \text{ cm}^{-2}$$

$$= \frac{134.46 \times 76 \times 13.6 \times 981}{4.18 \times 10^7 \times 7.03} \text{ °c atoms}^{-1}$$

$$= 0.45 \text{ °c atoms}^{-1}$$

2. Calculate the temperature of inversion of hydrogen. Given T_c for hydrogen is 29.5 K.

Temperature of inversion $T_i = \frac{27}{4} \times T_c$

$$= \frac{27}{4} \times 29.5 \ = 199.1 \text{ K}$$

$$= 73.9°\text{c}.$$

Problems

1. Calculate the temperature of inversion for helium. Give T_c for helium is 5.26K.
2. Assuming oxygen as a Vander Waal's gas having a = 1.36×10^6 atm – cm^2, b = 32 cc and C_p - 7.03 cal. Calculate J – T coefficient for oxygen.
3. Helium gas suffers J – T effect of –173°c. The pressure difference on two sides of the plug is 20 atm. What is the change of temperature? Given a = 0.3341 $litre^2$ atm. mol^{-2}, b = 0.0237 litre mol^{-1} R = 8.3 JK^{-1}

2.9 Questions

1. Describe porous plug experiment of Joule Thomson.
2. What is Joule Thomson effect ? Obtain an expression for the change in temperature during porous plug experiment.

Unit - 3 ❑ Kinetic theory of Gases

Structure

3.0 Objectives

In this section you will learn the randem motion of gas molecules & its velocity distribution in different temperature. Also you gather knowledge about transport phenomenon of gas & its distribution of energy is different direction.

3.1 Introduction

The concept of molecular constituent of gas and their motion as heat are two main pullars of kinetic theory of gases. Even without experimental proof of existance of molecules and their motion the subject was developed mathematically sucessfully. Later on however, Brownian motion discovered by Robert Brown showed that the basic concepts of kinetic theory were very much correct.

3.2 Assumptions of kinetic theory of gases

Assumptions of kenetic theory of gases.

1. The gas consists of large number of identical particles moving ceaselessly having velocities with all possible direction and magnitude.
2. The size of a particle is very small compared to average interparticle separation.
3. The particles obey Newton's laws of motion.
4. The particles do not interact except during collision.
5. The particles undergo perfectly elastic collision with each other and with the walls of the container.
6. The volume occupied by the particles is small compared to the volume of the container of the gas.
7. The gas if left to itself for a sufficient time becomes homogeneous and isotropic.

3.3 Pressure of an Ideal gas

We consider an ideal gas having N particles in a cubical container of edge L. Let one corner of the container is the origin O of our cartesian coordinate system with axes parallel to the edges of the cube.

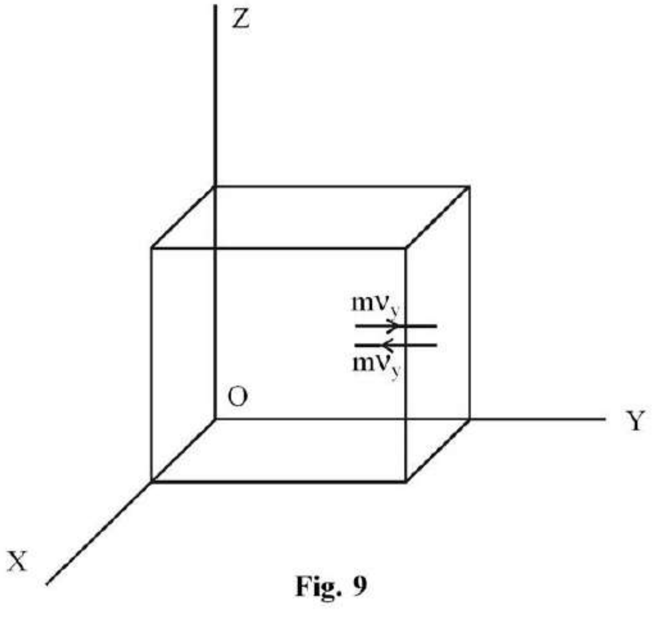


Fig. 9

Suppose a particle having velocity v (v_x, v_y, v_z) moves and collides on the right XY-plane and rebound. The Y-momentum of the particle is mv_y both before and after willision with opposite direction. The change of momentum for this impact is $2mv_y$, where m is the mass of the particle. Such impacts will occur at time intervals of $\frac{2L}{v_y}$.

Therefore the momentum imparted to the wall in question per second is

$$\frac{2mv_y}{2L/v_y} = \frac{m}{L}v_y^2$$

This is nothing but the force exerted by the particle.

The total force on the wall due to all the particles is there force.

$$F = \sum \frac{m}{L} v_y^2$$

Now, since all the directions are equally probable

$$\sum v_y^2 = \sum v_x^2 = \sum v_z^2 = \frac{1}{3}\sum v_x^2 + v_y^2 + v_z^2$$

$$= \frac{1}{3}\sum v^2$$

$$\therefore \quad F = \frac{1}{3}\frac{m}{L}\sum v^2 = \frac{1}{3}\frac{mN}{L}\frac{\sum v^2}{N}$$

$$\therefore \quad \text{pressure } p = \frac{F}{L^2} = \frac{1}{3}\frac{mN}{L^3}\frac{\sum v^2}{N}$$

$$\text{or,} \quad p = \frac{1}{3}\rho c^2$$

where $\rho = \frac{mN}{L^3}$ = densily of the gas.

$\frac{\sum v^2}{N} = \frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N} = C^2$, is the mean square velocity and C is root mean square or rms velocity.

$$\therefore \quad \text{RMS velocity} = C = \sqrt{\frac{3p}{\rho}}$$

From ideal gas relation

$$pV = RT$$

$$\text{or,} \quad \frac{p}{\rho} = \frac{RT}{M} \qquad (M = V\rho)$$

$$\therefore \quad C = \sqrt{\frac{3RT}{M}}$$

again $p = \frac{1}{3}\rho c^2 = \frac{2}{3} \times \frac{1}{2}\rho c^2$

or, $p = \frac{2}{3}E$, where $E = \frac{1}{2}\rho c^2$ is the kinetic energy per unit volume of the gas.

3.4 Kinetic energy and temperature

Once mole of gas contains N, (Avogadro's number) molecules. Let each molecule has a mass m and the velocities of the molecules are c_1, c_2, c_3 .....c_N. The kinetic energy of 1 mole of gas is therefore.

$$E = \frac{1}{2}mc_1^2 + \frac{1}{2}mc_2^2 + \frac{1}{2}mc_3^2 + \cdots + \frac{1}{2}mc_N^2$$

$$= \frac{1}{2}m\left(c_1^2 + c_2^2 + c_3^2 + \cdots c_N^2\right)$$

$$= \frac{1}{2}mNc^2, \text{ where } c^2 = \frac{c_1^2 + c_2^2 + c_3^2 + \cdots c_N^2}{N} = \text{Mean squre velocity}$$

$$\text{or,} \quad E = \frac{1}{2}MC^2$$

$$\text{or,} \quad E = \frac{1}{2}M \times \frac{3RT}{M} = \frac{3}{2}RT; \; R = \text{Universal gas constant}$$

or, $\overline{E}$ = Average kinetic energy

$$= \frac{E}{N} = \frac{3}{2}\frac{R}{N}T = \frac{3}{2}KT; \quad K = \text{Bollzman constant}$$

3.5 Boyle's Law

$$p = \frac{1}{3}\rho c^2$$

or, $pV = \frac{1}{3}V\rho c^2 = \frac{1}{3}MC^2$, M = mass of certain quantity of gas.

At constant temperature RMS velocity C is constant hence.

$$pV = \text{constant at constant temperature}$$

or, $p \propto \frac{1}{V}$ at constant temperature.

Charle's law

$$pv = \frac{1}{3}MC^2 = \frac{1}{3}M\frac{3RT}{M} = RT$$

$\therefore$ at contant pressure $V \propto T$

3.6 Maxwell's Law of distribution of velocities

We consider an ideal gas having N particles per unit volume each of mass m. We are to find how the particles of the gas possess different velocities or more clearly how the velocities are distributed among the particles.

The number of particles dN in unit volume having velocity in the interval c and c + dc must be proportional to the interval i.e.

$$dN \propto dc$$

or, $dN = adc$ [a is the constant of proportionality]

Over and above dN must depend on the velocity itself. We write $a = f(c)$ and finally dN will be proportional to N.

Thus $dN = N\, f(c)\, dc$.

if dc = 1, $f(c) = \frac{dN}{N}$, is called the distribution function and is the fraction of particles whose velocities are within unit inverval of velocity at c. It is also the probability that a particle in unit volume having velocity within the unit interval near c. This distribution function is also called probability density.

If u, v and w are the components of c along three co-ordinate axes,

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

$$\text{or,} \quad udu + vdv + wdw = 0 \text{ .... } (1)$$

The probability that a particle selected at random has velocity between u and u + du is f (u) du and similary it has velocity between v and v + dv and than between w and w + dw are f(v) dv and f(w) dw.

The probability that a particle has velocity components lying between u and u + du, v and v + dv and w and w + dw is

$$f(u)\, f(v)\, f(w)\, du\, dv\, dw$$

of N particles if dN be number in the above range of velocities

$$dN_v = N\, f(u)\, f(v)\, f(w)\, du\, dv\, dw$$

We write $\rho = \frac{dN}{du\,dv\,dw} = N\, f(u)\, f(v)\, f(w)$

which represents the number of particles of the specified type per unit volume in the volume space.

In steady state

$$d\rho = d\,[f(u)\, f(v)\, f(w)] = 0$$

$$\text{or,} \quad f'(u)\, f(v)\, f(w)\, du + f(u)\, f'(v)\, f(w)\, dv + f(u)\, f(v)\, f'(w)\, dw = 0$$

$$\text{or,} \quad \frac{f'(u)}{f(u)}du + \frac{f'(v)}{f(v)}dv + \frac{f'(w)}{f(w)}dw = 0 \text{ .... } (2)$$

multiplying (1) with Lagrange's undeterminant multiplier α and adding with (2) we get

$$\left(\frac{f'(u)}{f(u)} + \alpha u\right)du + \left(\frac{f'(v)}{f(v)} + \alpha v\right)dv + \left(\frac{f(w)}{f(w)} + \alpha w\right)dw = 0$$

The above relation is true only if

$$\frac{f'(u)}{f(u)}+\alpha u=0,\ \frac{f'(v)}{f(v)}+\alpha v=0;\ \frac{f'(w)}{f(w)}+\alpha w=0$$

Integrating above,

$$f(u)=Ae^{\frac{-\alpha u^2}{2}},f(v)=Ae^{\frac{-\alpha v^2}{2}},\ w=Ae^{\frac{-\alpha w^2}{2}}$$

$$\therefore\ dN = NA^3e^{-\frac{\alpha}{2}(u^2+v^2+w^2)}du\,dv\,dw$$

$$\text{and } \rho = NA^3e^{-bc^2};\ \text{where } b=\frac{\alpha}{2}$$

$$\int\int_{-\infty}^{\infty}\int NA^3e^{-b(u^2+v^2+w^2)}du\,dv\,dw=N$$

$$I = \int_{-\infty}^{\infty} e^{-bu^2}du=\int_{-\infty}^{\infty} e^{-bv^2}dv=\int_{-\infty}^{\infty} e^{-bw^2} =\frac{1}{A}=\sqrt{\frac{\pi}{b}}$$

again pressure

$$p = 2mn\int_0^{\infty} f(u)u^2du=2mNA\int_0^{\infty} e^{-bu^2}u^2du$$

$$= 2mNA\ \frac{1}{4}\sqrt{\frac{\pi}{b^3}}$$

Equating this with NKT and taking $A = \sqrt{\frac{b}{A}}$, we get

$$b = \frac{m}{2KT}\ \text{and } A = \sqrt{\frac{m}{2\pi KT}}$$

$\therefore$ Number of particles dN_c having velocity lying between c and c + dc is ρ times the volume between two spheres (spherical cell) of radii c and c + dc is

$$dN_c = \rho \times 4\pi c^2dc = 4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2}e^{\frac{-mc^2}{2KT}}c^2dc$$

$$\text{or, }\ \frac{dNc}{N} = F\ dc;\ F = 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2}e^{-\frac{mc^2}{2KT}}c^2$$

In the diagram F, the Maxwell speed distribution function is plotted against the speed (c)

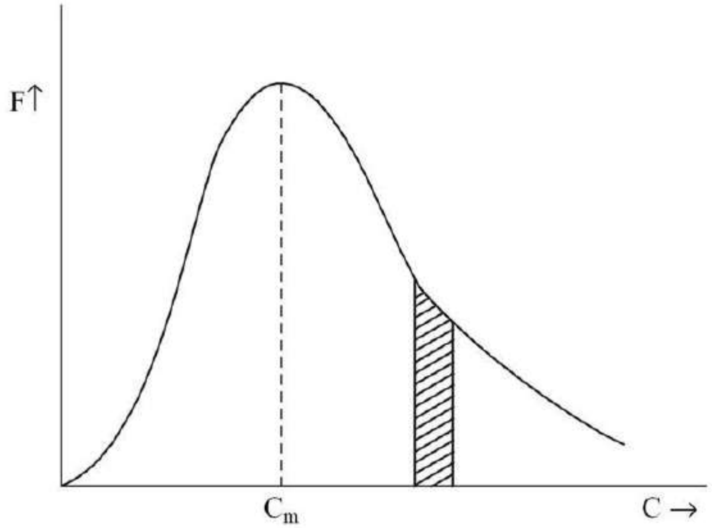


Fig. 10

F = 0 for c = 0 and c = ∞ Maximum number of particles possess the velocity c_m, known as most probable velocity. Area of the strip with width dc gives the number of particles having velocity lying between c and c + dc. The area below the

curve $\int_0^\infty F dc = 1$

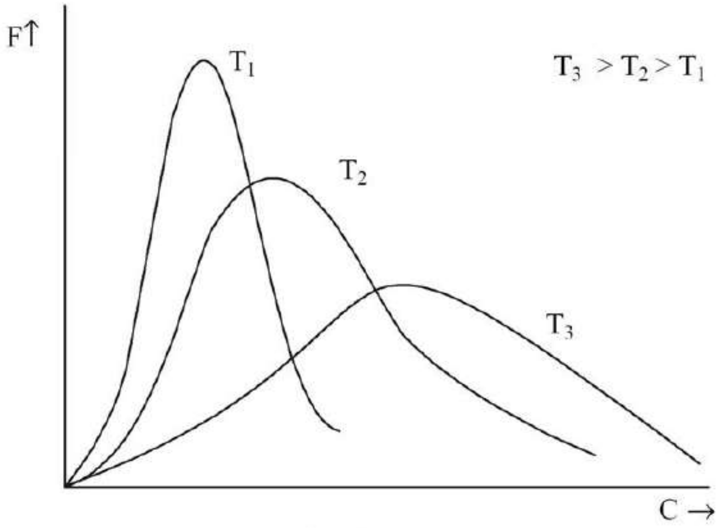


Fig. 11

Figure-2 shows the function for three different temperatures. The higher the temperature, wider is the spread of values of the speed. Area under each curve is 1. Lower is the temperature greater is the fraction of fast moving particles.

3.7 Most probable velocity, average velocity and RMS velocity

We have $dN_c = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{\frac{-mc^2}{KT}} c^2 dc$

$$\frac{dN_c}{dc} = 4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2$$

It the temperature is kept constant.

$$\frac{dN_c}{dc} = Ac^2 e^{-\frac{mc^2}{2KT}}; A = 4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2}$$

differentiating and equating to zero

$$\therefore \quad d\left(\frac{dN_c}{dc}\right) = A\frac{d}{dc}\left(c^2 e^{-\frac{mc^2}{2KT}}\right) = 0$$

$$\text{or,} \quad 2ce^{-\frac{mc^2}{2KT}} + c^2 \times \frac{-2mc}{2KT} e^{-\frac{mc^2}{2KT}} = 0$$

$$\text{or,} \quad 2ce^{-\frac{mc^2}{2KT}}\left(1 - \frac{mc^2}{2KT}\right) = 0$$

whereform (i) $c = 0$, (ii) $c = \infty$ or, $1 - \frac{mc^2}{2KT} = 0$

at $c = 0$ and at $c = \infty$ $dN_c = 0$

$\therefore$ dN_c is maximum for $1 - \frac{mc^2}{2KT} = 0$

This provides the most probable velocity c_m from $1 - \frac{mc_m^2}{2KT} = 0$

$$Cm = \sqrt{\frac{2KT}{m}} = \sqrt{\frac{2RT}{M}}$$

Average velocity

The average velocity say C_a is given by

$$C_a = \frac{1}{N}\int_0^\infty c\,dN_c = \frac{1}{N}\int_0^\infty c.4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2} c^2\, e^{-\frac{mc^2}{2KT}}\,dc$$

$$= 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2}\int_0^\infty c^3 e^{-bc^2}\,dc \qquad \therefore\; b = \frac{m}{2KT}$$

$$= 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2} \frac{1}{2b^2}$$

$$= 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2} \times \frac{1}{2}\left(\frac{2KT}{m}\right)^2$$

$$= \sqrt{\frac{8KT}{m\pi}} = \sqrt{\frac{8RT}{M\pi}}$$

RMS velocity

The RMS velocity C is given by

$$C^2 = \frac{1}{N}\int_0^\infty c^2 dN_c = \frac{1}{N}\int_0^\infty c^2\, 4\pi N\left(\frac{m}{2\pi KT}\right)^{3/2} c^2\, e^{-\frac{mc^2}{KT}}\,dc$$

$$= 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2}\int_0^\infty c^4 e^{-bc^2}\,dc;\; b = \frac{m}{2KT}$$

$$= 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2} \frac{3}{8}\sqrt{\frac{\pi}{b^5}}$$

$$= 4\pi\left(\frac{m}{2\pi KT}\right)^{3/2} \frac{3\sqrt{\pi}}{8}\left(\frac{2KT}{m}\right)^{5/2}$$

$$= \frac{3KT}{m}$$

$$\therefore \; C = \sqrt{\frac{3KT}{m}} = \sqrt{\frac{3RT}{M}}$$

$$\text{Thus } C_m : C_a : C = \sqrt{\frac{2KT}{m}} : \sqrt{\frac{8KT}{m\pi}} : \sqrt{\frac{3KT}{m}}$$

$$= \sqrt{2} : \sqrt{\frac{8}{\pi}} : \sqrt{3}$$

$$= 1 : 1.128 : 1.224$$

We show them in the velocity distribution curve below

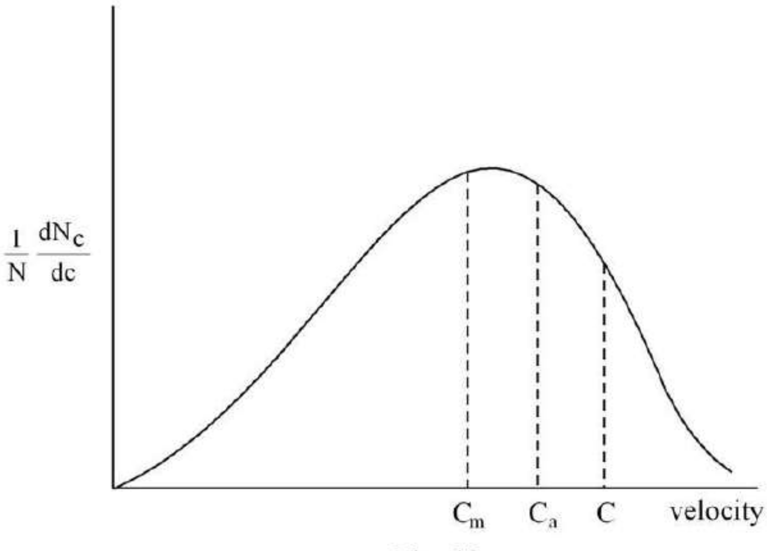


Fig. 12

3.8 Experimental verification of Maxwell's velocity distribution law

From an electirc oven cesium atoms come out and pass through the slit S_0. Most of these atoms are stopped by the diaphram D_1 and those who goes through S_1 constitute a narrow, almost horizontal beam.

The slit S_2, called collimating slit is in between the diaphram D_1 and detector

D_2. The detector consists of a hot tungsten wire with which almost all cesium atoms of the beam strike and get ionised leaving the tungsten wire as positively charged ion. These positively charged ions are collected by a negatively charged plate. The plate current measure the number of cesium atom striking the detector per unit time. An analysis of the parabolic path of the atoms due to gravity that strike D_2 at a distance S gives a relation between the deflection 'S' and the speed ν.

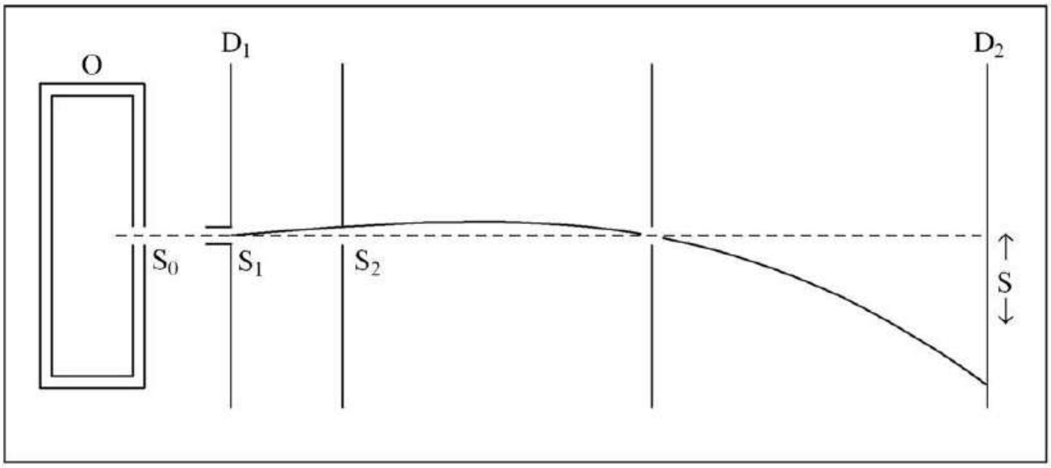


Fig. 13

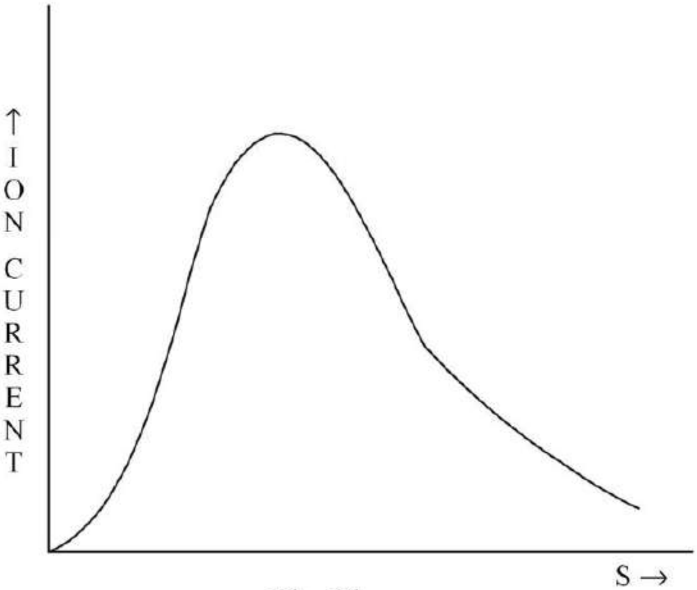


Fig. 14

The experimental results are shown in the figure 2 where the smooth curve is a plat of Maxwell function and dots are experimental point.

3.9 Mean free path

According to the assumption of kinetic theory gas molecules always collide with each other and with the walls of the container. They travel in straight line with constant velocity between two successive collisions. After a collision the magnitude and direction of velocity change. The distance traveled by a molecule between two successive collision is known as free path. When a molecule under goes a number of collisions the path will differ in length and form an irregular zig-zag motion as shown below.

The mean value of these straight paths is called the mean free path and is the average distance travelled by a molecule between two successive collision and can be expressed simply as

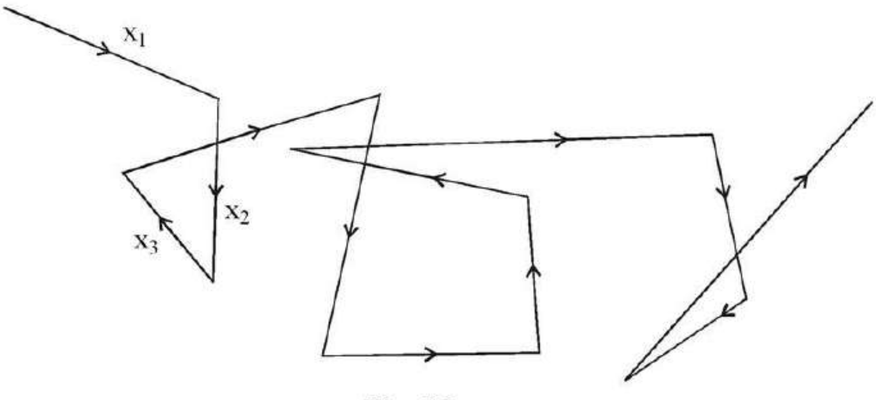


Fig. 15

$$l = \frac{x_1+x_2+x_3+\cdots}{n}$$

We assume a gas containing 'n' molecules per unit volume and 'd' is the diameter of each of the molecule. For the purpose of an easy method we consider that only one molecule is moving and all others are at rest. Let v the veolcity of the molecule. This molecule will collide with the molecules which are at distance d from its centre. The space traversed per second by the molecule is a cylinder of base area πd^2 and length v ie of volume πd^2 v, containing $n\pi d^2 v$ other molecules. Thus in the

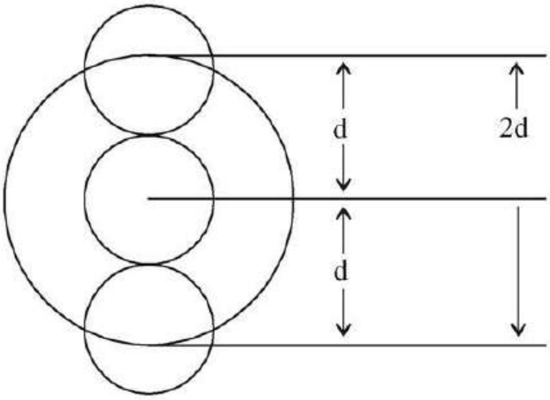


Fig. 16

path length v if will have $n\pi d^2 v$ collision. Therefore the mean free path is

$$\lambda = \frac{v}{n\pi d^2 v} = \frac{1}{n\pi d^2}$$

Bollzmann deduced and expression for λ assuring all the molecules are moving with same average velocity and obtained $\lambda = \frac{3}{4\pi d^2 n}$. Maxwell using velocity distribution law deduced.

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

3.10 Transport phenomenon

In equilibrium state of a gas the mass motion, temperature and number of particles per unit volume are same at every part of the gas.

Suppose the equilibrium of the gas is violated by flow velocity (mass motion) being imparted to one of its parts that differs the flow velocity of adjucent parts. So there will be a relative motion between the layers of the gas. If the gas so disturbed is left to itself equlibrium is found to be restored after some time. The velocity of the entire gas will again become identical in all parts. It is the thermal motion of the gas particles that level out the flow velocity by transport of momentum from the faster moving parts of the gas to slower moving ones. This process gives rise to the phenomenon of internal friction or viscosity.

Consider next the equilibrium of the gas is violated by heating a part of it. In equilibrium condition the temperature of the gas is same everywhere. So by heating process temperature inequality among its parts has been injected. Here too if the gas is left to itself equilibrium is restored after some time. Temperature again become identical through out. This leveling of temperature is due to continuous motion of the particles. There are more fast particles in the heated part, but due to molecular motion they rush to region where their number is smaller till they get equally distributed throughtout. Molecules at the same time also move to the heated parts so the densily of moloecules does not change either in heated or in other parts. The only thing occur is the transport of thermal energy form the region of higher temperature to the regoin of lower temperature. This process is called thermal conductivity.

Finally let the equilibrium is disturbed by adding small amount of the same gas filling a certain volume. So that with identical pressure and volume throughout, the concentration of one part will be greater than that in other parts. Here too after certain time the added gas gets distributed through out the entire volume and the concentration becomes uniform. Such leveling out of concentration is entirely due to the motion of molecules from the region of higher concentration to the region of lower concentration. Moleculer at the same time move to the region of higher concentration so that the pressure remain constant. Only the transport of mass of the added gas occurs. This phenomenon is called diffusion.

Thus if the gas is not in equilibrium state there will be either transport of momentum or thermal energy or mass from one region to another inside the gas giving rise to the phenomenon called viscosity, thermal conductivity or diffusion. Therefore these pheonomena are known as transport phenomena.

3.11 Law of Equipation of energy

We assume the molecules of a gas as hard tiny sphere. The energy of each molecule may be written as

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 \quad \ldots\ldots\ldots\ldots\ (1)$$

where 'm' is the mass of the molecule and v_x, v_y and v_z are the components of velocity v along three cartisean co-ordinate axes. There are three terms in the expression and each may be treated independently. Monatonic gas molecules behave similarly and such a molecule is said to have three degrees of freedom. The molecules of diatomic gases some what looks like dumbbel. Two tiny masses at the end of a rigid rod. The centre of mass of the diatomic molecule can change three co-ordinates indepently the translational kinetic energy is similar to equation. Over and above the translational motion the molecule may have two rotational motions. If x be the line joing the two atoms the molecule can rotate about y and z axis. The rotational kinetic energy may written as

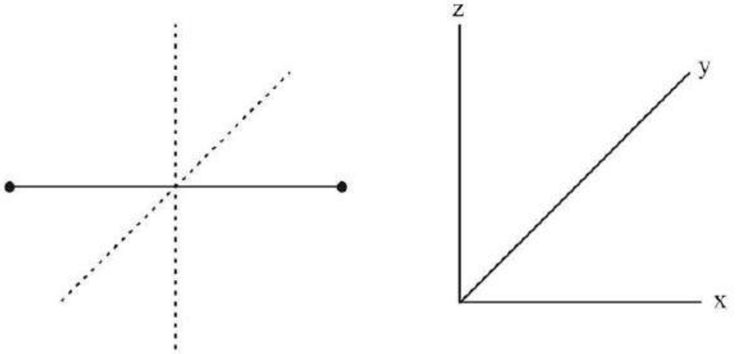


Fig. 17

$$\frac{1}{2}I_y w_y^2 + \frac{1}{2}I_Z w_Z^2 \quad \ldots\ldots\ldots\ldots\ldots\ (2)$$

I_z and I_y are the moment of inertia and w_z and w_y are the angular velocity of rotation about the z and y-axis respectively of the molecule.

The total kinetic energy is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mz^2 + \frac{1}{2}I_y w_y^2 + \frac{1}{2}I_z w_z^2$$

The molecule has five degrees of freedom. If the distance between two atoms of the molecule is not rigid but can change, the molecule can vibrate along z-axis. There is kinetic energy due to such vibration given by $\frac{1}{2}\mu v^2$ and a potential energy of the pair of the atoms equal to $\frac{1}{2}kz^2$. The total energy in this case is

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_y w_y^2 + \frac{1}{2}I_z w_z^2 + \frac{1}{2}\mu v^2 + \frac{1}{2}kz^2$$

There are seven independent terms and the gas is said to have seven degrees of freedom.

According to the principle of equipartition of energy the average energy of a molecue in a gas associated with each degree of freedom is $\frac{1}{2}KT$ where K is the Boltzman constant and T is the absolite temperature.

If we consider n moles of monatonic gas. The energy is

$$E = nN_A \times \frac{3}{2}KT = n\frac{3}{2}RT$$

The molar heat capacity at constant volume is

$$C_v = \frac{1}{n}\frac{dE}{dT} = \frac{3}{2}R$$

The molar heat capacity at constant pressure is

$$C_p = C_v + R = \frac{5}{2}R$$

$$\gamma = \frac{C_p}{C_v} = \frac{5}{3} = 1.67$$

For a diatomic gas having no vibrational energy

$$E = n\frac{5}{2}RT \quad \text{and } C_v = \frac{5}{2}R$$

and $$C_p = \frac{7}{2}R; \quad \gamma = \frac{7}{5} = 1.40$$

For diatomic gas taking vibrational energy into consideration

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{9}{2}R}{\frac{7}{2}R} = \frac{9}{7} = 1.29$$

Relation between degrees of freedom and γ.

Let the number of degrees of freedom of each molecule of gas is f. The kinetic energy of one mole of gas is

$$E = \frac{1}{2}kT \times f \times N = \frac{1}{2} f RT$$

∴ The molar specific heat at constant volume

$$C_v = \frac{dE}{dT} = \frac{1}{2} f R$$

The molar specific heat at constant pressure is therefore.

$$C_p = C_v + R = \frac{1}{2} f R + R = R\left(1+\frac{f}{2}\right)$$

$$\gamma = \frac{C_p}{C_v} = \frac{1+\frac{f}{2}}{\frac{f}{2}} = 1+\frac{2}{f}$$

3.12 Problems

Solved Prolems

1. Calculate the root mean square velocity of air molecules at N.T.P. given that the density of air is 1.293 Kg m^{-3}.

Solution

We know the RMS velocity is given by

$$C_{rms} = \sqrt{\frac{3P}{\rho}} = \sqrt{\frac{3\times1.013\times10^5}{1.293}} = 4.85 \times 10^2 \text{ ms}^{-1}$$

2. The average kinetic energy of a molecule of hydrogen at 0°c is 5.64×10^{-21} J. The molar gas constant R = 8.32 JK^{-1}. Calculate the Avogardo number.

The average kinetic energy of a molecule is

$$E = \frac{3}{2} kT, \text{ where } K = \frac{R}{N} \text{ is the Boltzman constant}$$

$$\therefore \; N = \frac{3RT}{2E} = \frac{3 \times 8.32 \times 273}{2 \times 5,64 \times 10^{-21}} = 6 \times 10^{23}$$

3. 2 moles of hydrogen gas at 30°c is mixed with one mole of helium gas at 60°c. Find the temperature of the mixture.

Solution

The kinetic energy (Average) of a mole of gas = $\frac{3}{2}KN \times N$ K = Baltzmann constant

Kinetic energy of 2 moles of hydrogen of 30°c is N = Avogardo number

$$E_1 = z\frac{3}{2} \times k\,(30 + 273) \times N \times 2$$

$$= 3K \times 303 \times N$$

Kinetic energy of 1 mole of helium is

$$E_2 = \frac{3}{2} \times k \times (60 + 273) \times N \times 1$$

$$= \frac{3}{2}\,k \times 333 \times N$$

Let the mixture of 3N molecules has temperature TK, and kinetic energy

$$E_3 = \frac{3}{2}\,k \times T \times 3N$$

$$\therefore \; E_3 = E_1 + E_2$$

$$\frac{3}{2}\,KT \times 3N = 3K \times 303 \times N + \frac{3}{2}\,K \times 333 \times N$$

$$3T = 2 \times 303 + 333$$

$$T = \frac{606 + 333}{3} = 313K \quad = 313 - 273 = 40°c$$

4. Assuming Maxwell's distribution find the most probable, average and RMS speed of nitrogen at 27°c. Given that molecular mass of nitrogen is [illegible]$^{-3}$ kg and gas constant is 8.314 J $mol^{-1}\,k^{-1}$.

Solution

The must probable velocity

$$C_m = \sqrt{\frac{2KT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2\times 8.314\times 300}{28\times 10^{-3}}}$$

$$= 4.22 \times 10^2 \text{ ms}^{-1} \qquad (27 + 273 = 300)$$

The average velocity

$$C_a = \sqrt{\frac{8KT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8\times 8.314\times 300}{3.14\times 28\times 10^{-3}}}$$

$$= 4.76 \times 10^2 \text{ ms}^{-1}$$

Rms velocity

$$C_{rms} = \sqrt{\frac{3KT}{m}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times 8.314\times 300}{28\times 10^{-3}}}$$

$$= 5.17 \times 10^2 \text{ ms}^{-1}$$

Problems

1. Find the ratio of most probable velocity of oxygen to that of helium.
2. Calculate the molecular kinetic energy of 1 g of hydrogen at 50°c. Molecular mass of hydrogen = 2, R = 8.3 $\text{Joule}^{-1}\ \text{k}^{-1}$.
3. γ for diatomic and polyatomic gases are 1.4 and 1.33 respectively. Find the degrees of freedom of the molecules.
4. At what temperature will the rms veolcity of nitrogen molecule be double its value at N.T.P. Pressure remaning constant.

3.13 Questions

(i) What are the basic assumption of kinetic theory of gases. Are all of them justified.

(ii) Obtain a relation between pressure, volume and temperature of gas according to kinetic theory.

(iii) What do you mean by degrees of freedom. Show $\gamma = 1+\frac{2}{f}$

Unit - 4 ❑ Theory of Radiation

Structure

4.0 Objectives

In this unit thermal radiation & its distribution of energy will be discussed. You will learn different laws related to radiation & its application in different thermal system.

4.1 Introduction

Radiation

The process of emission of energy or matter from a body and its transmission like wave or particle is called radiation. The radiant energy or particle is also known as radiation. We come across the following types of radiation in our daily life.

1. Eelectromagnetic Radiation like radio waves, micro waves, infrared, vissible light, ultra violet, x-ray and g-ray.
2. Particles like α, β and neutron.
3. Accoustic radiation like sound, ultrasound and seismic waves.
4. Gravitation.

4.2 Black Body Radiation

A body that absorbs all incident electromagnetic radiation regardless of frequency and angle of incidence and emit maximum amount of thermal radiation at all wavelength at any specified temperature is known as black body.

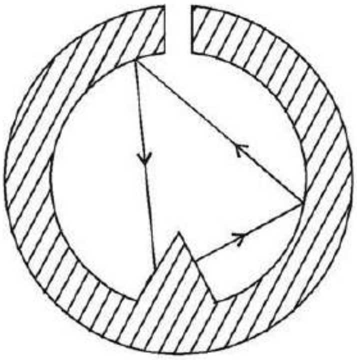


Fig. 18

A cavity with a small hole and inside wall blackened may play the role of a black body.

4.3 Absorptivity, Reflectivity and Transmitivity

When a radiation say R_i (Wm^{-1}) is incident on a body, a part R_r (say) is reflected , a part R_t (say) is transmitted and a part R_a say is absorbed. So that

$$R_i = R_r + R_t + R_a$$

$$\text{or,} \quad \frac{R_r}{R_i} + \frac{R_t}{R_i} + \frac{R_a}{R_i} = 1$$

$$\text{a} \quad \rho + \tau + \alpha = 1$$

Where $\rho = \frac{R_r}{R_i}$ = fraction reflected known as reflectivity or reflection co-efficient

$\tau = \frac{R_t}{R_i}$ = fraction transmitted known as transmitivity or transmission co-efficient

and $\alpha = \frac{R_a}{R_i}$ = fraction absorbed known as absorptivity or absorption co-efficient.

ror black body $\rho = 0, \tau = 0, \alpha = 1$

for opaque body $\tau = 0, \rho + \alpha = 1$

for white body $\rho = 1, \tau = 0, \alpha = 0$

4.4 Prevost theory and Kirchhoff's law

A body constantly exchanges heat with its sunounding, radiating an amount of energy which is independent of its surrounding. The temperature of the body increases or decreases depending on whether it absorbs more radiation than it emits or vice-versa.

Kirchhoff's law of radiation

The ratio of spectral emissive power to the spectral obsorptive power for any wavelength for any substance at the same temperature is same and is equal to the spectral imessive power for the same wavelength for a black body at the same temperature.

$$\frac{E_\lambda}{a_\lambda} = \text{constant} = E_{\lambda b} \quad \because \quad a_{\lambda b} = 1$$

4.5 Spectral distribution

A function expressing analytically or graphically the relation between radiant flex per wavelength (or frequency) interval against the wavelength (or frequency) is called spectral distribution.

Black body spectrum

Black body spectral distribution at three different temperatures are shown in the figure. The radiation is a characteristic continuous spectrum. In each case $E_\lambda \to 0$ as either $\lambda \to 0$ or $\lambda \to \infty$.

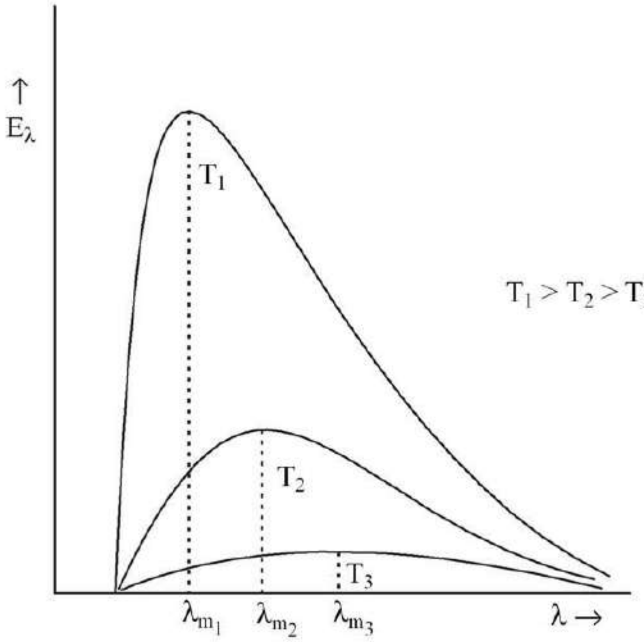


Fig. 19

In between them for a particular of λ (λ_m) E_λ is maximum. Higher is the temperature lower is the value of λ_m. In fact $\lambda_m T$ = constant. The area under the curve gives the total radiant energy of the black body at the respective temperature.

An analysis of the above graphs provides the following facts.

(i) Energy associated with the radiation of a given wavelength increases with increase in temperature of the black body.

(ii) The energy E_m emitted corresponding to the wavelength of maximum emission (λ_m) increases with fifth power of the absolute temperature of the black body.

(iii) The area under each curve represents the total energy emitted for the complete spectrum at a particular temperature and is proportional to fourth power of the temperature.

(iv) At a particular temperature of the black body, energy associated with the radiation initially increases with wavelength, becomes maximum at wavelength λ_m and then decreases.

(v) The wavelength for maximum emission λ_m shifts toward lower wavelength as the temperature of the black body increases.

4.6 Concept of energy density

Radiation energy density can be defined as Radiant energy per unit volume. From Planck's law we know that the energy density at frequency υ is given by

$$U_\upsilon = \frac{8\pi h}{c^3} \frac{\upsilon^3}{e^{\frac{h\upsilon}{kT}} - 1}$$

here u_υ is the spectral energy density at frequency υ and $u_\upsilon d_\upsilon$ is the energy density of radiation of frequency between υ and $\upsilon + d\upsilon$. When integrated over entire frequency range from zero to ∞ we get the rediation energy density as.

$$u = \int_0^\infty u_\upsilon d_\upsilon = \frac{8\pi^5 k^4}{15c^3h^3} T^4$$

The unit of u is Jm^{-3}.

The total energy emitted per unit area per second at temperature T is given by Stefan's law as.

$$E = \sigma T^4 \qquad \sigma = \text{Stefan's constant. Unit of E is } Jm^{-2}s^{-1}.$$

E and u can be shown to be related as

$$u = \frac{4E}{c}$$

According to special theory of relativily the momentum of a photon is $\frac{h\upsilon}{c}$. The radiation pressure (p) is the momentum transferred on irradiant surface of unit area per sec is given by

$$p = \frac{\sum h\upsilon}{c} = \frac{E}{c} = \frac{u}{4}$$

4.7 Derivation of Planck's Law

In order to explain the black body radiation and the distribution of energy among wavelength Planck introduced the concept of atomic oscillator. He assumed that

(i) Cavity radiation comes from the atomic oscillators in the cavity walls of the black body.

(ii) The energy of an oscillator can have only certain discrete values given by $E_n = nh\upsilon$; (υ = frequency, h = Planck's constant) and n is a positive integer called quantum no.

(iii) The oscillator emit or absorb energy when making a transition from one quantum state to another. The entire energy difference between the initial and final states in the transition is emitted or absorbed as a single quantum of radiation.

Now it is to be considered that al modes (and photons) are to be in thermal equilibrium at temperature T. In order to establish equilibrium there must be ways of exchanging energy between the modes (and photons) and this can occur through interaction with any particle or oscilator within the volume or with the walls of the enclosure.

We use Boltzman distribution to determine the excepted occupancy of the modes in thermal equilibrium. The probability that a single mode has energy $E_n = nh\upsilon$ is given by Boltzman law is

$$p(n) \quad = \frac{\exp(-E_n/kT)}{\sum \exp(-E_n/kT)}$$

The mean energy of the mode of frequency υ is

$$\bar{E}_\upsilon \quad = \sum_0^\infty E_n p(n) = \frac{\sum_0^\infty E_n \exp(-E_n/kT)}{\sum_0^\infty \exp(-E_n/kT)}$$

$$= \frac{\sum_0^\infty nh\upsilon \exp(-nh\upsilon/kT)}{\sum_0^\infty \exp(-nh\upsilon/kT)}$$

$$= n\upsilon \frac{\sum\limits_{0}^{\infty} nx^n}{\sum\limits_{0}^{\infty} x^n}; \quad \text{where } x = e^{\frac{-h\upsilon}{KT}}$$

$$= h\upsilon \; \frac{x + 2x^2 + 3x^3 + \cdots\cdots\infty}{1 + x + x^2 + \cdots\cdots\infty}$$

$$= h\upsilon x \; \frac{1 + 2x + 3x^2 + \cdots\infty}{1 + x + x^2 + \cdots\infty}$$

$$\text{or, } \bar{E}_\upsilon = h\upsilon x \frac{(1-x)^{-2}}{(1-x)^{-1}} = \frac{h\upsilon x}{1-x}$$

$$\text{or, } \bar{E}_\upsilon = \frac{h\upsilon}{x^{-1}-1} = \frac{h\upsilon}{e^{\frac{h\upsilon}{kT}}-1}$$

We know that the number of modes in frequency interval υ and $\upsilon + d\upsilon$ is $\frac{8\pi\upsilon^2}{c^3}d\upsilon$ per unit volume.

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

$$\text{or, } u(\upsilon)\, d\upsilon = \frac{8\pi h\upsilon^3}{c^3} \frac{d\upsilon}{e^{\frac{h\upsilon}{kT}}-1} \quad \ldots\ldots\ldots\ldots\ldots (1)$$

putting $\upsilon = \frac{c}{\lambda}$ in equation (1) we write for the energy density of radiation in the wavelength range λ and $\lambda + d\lambda$ as

$$u(\lambda)\, d\lambda = \frac{8\pi ch}{\lambda^5} \frac{d\lambda}{e^{\frac{hc}{\lambda kT}}-1} \quad \ldots\ldots\ldots\ldots\ldots (2)$$

Either of the expressions (1) and (2) may be taken as Planck's distribution function.

4.8 Wien's distribution law from Planck's Law

The Planck's distribution law can be written in terms of wavelength λ as

$$E_\lambda d_\lambda = \frac{8\pi ch}{\lambda^5} \frac{d\lambda}{e^{\frac{hc}{\lambda kT}} - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

For short wavelength $e^{\frac{hc}{\lambda kT}} > 1$

we write equation (2) as.

$$E_\lambda d_\lambda = \frac{8\pi ch}{\lambda^5} \cdot \frac{d\lambda}{e^{\frac{d\lambda}{\lambda kT}}}$$

$$\text{or, } E_\lambda d_\lambda = c_1 \lambda^{-5}\ e^{-\frac{c_2}{\lambda T}} d\lambda \quad \ldots\ldots\ldots\ldots\ldots (3)$$

where $c_1 = 8\pi ch$ and $c_2 = \frac{hc}{k}$ are constants. Equation (3) is the Wien's distribution law.

4.9 Rayleigh Jeans Law from Planck's Law

We write Planck's law in terms of wavelength λ as.

$$E_\lambda d_\lambda = \frac{8\pi ch}{\lambda^5} \frac{d\lambda}{e^{\frac{hc}{\lambda kT}} - 1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

For large wavelength $e^{\frac{hc}{\lambda kT}} \square 1$

Neglecting higher order of expansion we write

$$e^{\frac{hc}{\lambda kT}} = 1 + \frac{hc}{\lambda kT}$$

Equation (1) becomes

$$_{\lambda}d\lambda = \frac{8\pi ch}{\lambda^5} \frac{1}{1 + \frac{hc}{\lambda kT} - 1}$$

$$= \frac{8\pi ch}{\lambda^5} \times \frac{\lambda kT}{hc}$$

$$\text{or } E_{\lambda}d\lambda = \frac{8\pi kT}{\lambda^4} \quad \text{.............} \ (4)$$

Equation (4) is the Rayleigh Jeans distribution law.

4.10 Stefans Boltzmann Law from Planck's Law

Stefans Boltzmann Law states that the total energy emitted by a unit area of ablack body per second is directly proportional to the fourth power of its absolute temperature. Thus we write for total energy of all wavelength emitted per unit area per second E as.

$$E = \sigma T^4 \ \text{.........} \ (5)$$

Where σ is a constant unknon as Stefan's constant and has a value 5.67×10^{-8} $Wm^{-2} K^{-4}$.

This law can be obtained from Planck's distribution law.

We write Planck's distribution law as

$$u(\upsilon)\, d\upsilon = \frac{8\pi h}{c^3} \frac{\upsilon^3 d\upsilon}{e^{\frac{h\upsilon}{kT}} - 1} \quad \text{..................} \ (1)$$

To obtain the total energy density we integrate equation for frequenicy from 0 to ∞ i.e.

$$u = \int_0^\infty u(\upsilon)d\upsilon = \frac{8\pi h}{c^3}\int_0^\infty \frac{\upsilon^3 d\upsilon}{e^{\frac{h\upsilon}{kT}} - 1}$$

$$= \frac{8\pi h}{c^3}\int_0^\infty \frac{x^3k^3T^3}{h^3}\ \frac{kTdx}{h(e^x - 1)} \quad [\text{Let } x = \frac{h\upsilon}{kT}, \upsilon = \frac{xkT}{h}\ d\upsilon = \frac{kTd\upsilon}{h}]$$

$$= \frac{8\pi k^4T^4}{c^3h^3}\int_0^\infty \frac{x^3dx}{e^x - 1}$$

$$= \frac{8\pi k^4T^4}{c^3h^3}\cdot\frac{\pi^4}{15}\ [\int_0^\infty \frac{x^3dx}{e^x - 1} \text{ is a standard integral whose value is } \frac{\pi^5}{15}]$$

$$\text{or, } u = AT^4 \text{ .... (5) } A = \text{constant} = \frac{8\pi^5k^4}{15c^3h^3}$$

The total energy E per unit area per sec. is related with u as

$$E = \frac{uc}{4} = \frac{Ac}{4}T^4$$

$$\text{or, } E = \sigma T^4 \text{ .... (6); } \sigma = \frac{Ac}{4}$$

which is the Stefan's law.

Stefan's law can be extended to include the net loss of energy by a body after exchange of heat with the surroundings. If a body at temperature T is kept in an enclosure at a lower temperature T_0, the body loses heat by emission of radiation and gains heat from the enclosure. The net loss of heat per unit area per second is

$$E = \sigma (T^4 - T_0^4) \text{ .... (7)}$$

Newton's laws of cooling from Stefan's law.

When the temperature of the hot body T and that of surroundings to differ by small amount, Newton's law of cooling states that the rate of cooling is proportional to the tempeature difference $(T - T_0)$

From equation (7)

$$
\begin{aligned}
E &= \sigma\,(T^4 - T_0^4) \\
&= \sigma\,(T^2 + T_0^2)\,(T + T_0)\,(T - T_0) \\
&= \sigma \times 2T_0^2 \times 2T_0\,(T - T_0) \qquad Q\ T_1 \approx T_0. \\
&= 4\sigma\, T_0^3\,(T - T_0) \\
&= K\,(T - T_0)\ .....(8),\ K = \text{constant}
\end{aligned}
$$

4.11 Wien's displacement law from Planck's Law

Wien's displacement law states that the product of the waveleng λ_m corresponding to maximum energy emission and the absolute temperature T of a black body is constant. Mathematically

$$\lambda_m T = \text{const}$$

We write Planck's distribution law as.

$$u_\lambda = \frac{8\pi ch}{\lambda^5}\,\frac{1}{e^{\frac{hc}{\lambda kT}} - 1} \ .... (5)$$

In order to find the value of λ for which u_λ is maximum we must differentiate equation (5) w.r.t. λ and equate to zero. We rewrite equation (5) as

$$u_\lambda = 8\pi ch\,\frac{\lambda^{-5}}{e^{\frac{hc}{\lambda kT}} - 1}$$

differentiating

$$\frac{du_\lambda}{d\lambda} = 8\pi ch\,\frac{d}{d\lambda}\left(\frac{\lambda^{-5}}{e^{\frac{hc}{\lambda kT}} - 1}\right)$$

$$\text{Thus } -5\,\lambda^{-6}\left(e^{\frac{hc}{\lambda kT}} - 1\right)^{-1} + \lambda^{-5}\left(e^{\frac{hc}{\lambda kT}} - 1\right)^{-2} e^{\frac{hc}{\lambda kT}} \times \frac{hc\lambda^{-2}}{kT} = 0$$

$$\text{or,}\quad -5 + \left(e^{\frac{hc}{\lambda kT}} - 1\right)^{-1} e^{\frac{hc}{\lambda kT}} \times \frac{hc}{\lambda kT} = 0$$

$$\text{or,}\quad \frac{\frac{hc}{\lambda kT}e^{\frac{hc}{\lambda kT}}}{e^{\frac{hc}{\lambda kT}}-1} = 5 \text{ : putting } x = \frac{hc}{\lambda kT}$$

$$\text{or,}\quad \frac{xe^{x}}{e^{x}-1} = 5 \quad \text{................} \quad (6)$$

Equation (6) is a trancendental equation and must be solved numerically. The result is

$$x = 4.965$$

$$\text{or,}\quad \frac{hc}{\lambda kT} = 4.965,$$

[This λ corresponds to the max^{m} energy hence equals to λ_m]

$$\text{or,}\quad \lambda_m T = \frac{hc}{4.965k}$$

$$\text{or,}\quad \lambda_m T = 2.898 \times 10^{-3}\ \text{mK} = \text{constant.}$$

4.12 Problems

Solved Problems

1. A black body at temperature 1373°c has a wavelength corresponding to the maximum emission is 1.78 micron. Determine the temperature of the moon if the wavelength corresponding to the maximum emission is 10 micron.

According to wein's displacement law $\lambda_m T$ = constant.

For the 1st case $\lambda_m = 1.78$ micron

and temperature $T = 1373^\circ + 273 = 1646$ K

For moon $\lambda_m = 10$ micron

$$T = ?$$

$$14 \times T = 1.78 \times 1646$$

$$T = \frac{1.78 \times 1646}{10} = 292.99\ \text{K} = 19.99^\circ\text{c}$$

2. Two identical black bodies A and B at temperature 227°c and 327°c respectively are separately placed in two evacuted enclosures at temperature 27°c. Compare their rate of heat loss.

From Stefan Boltzman Law.

$$E = s\,(T^4 - T_0{}^4)$$

For A $\quad T = 227 + 273 = 500\text{ K}$

$$T_0 = 27 + 274 = 300\text{K}$$

$$E_A = \sigma\,(500^4 - 300^4)$$

$$= \sigma \times 544 \times 10^8$$

For B $\quad T = 327 + 273 = 600\text{K}$

$$T_0 = 300\text{K}$$

$$E_B = \sigma\,(600^4 - 300^4)$$

$$= \sigma \times 1215 \times 10^8$$

$$\frac{E_A}{E_B} = \frac{544}{1215}$$

3. The wavelength corresponding to maximum energy in the lunar spectrum is found to be 14.46×10^{-4}cm. If the value of Wein's constant be 0.293 cm K, Find the effective lunar temperature.

From Wein's Law $\lambda_m T = 0.293$

$$T = \frac{0.293}{14.46 \times 10^{-4}} = 200\text{K}$$

4.13 Questions

1. A platinium ball of radius 1 cm at temperature 927°c is suspended in an enclosure at 27°c. Determine the rate of loss of heat by the ball. Given $s = 1.36 \times 10^{-12}$ cal cm^{-2} s^{-1}K^{-4}.
2. The wavelength of maximum energy of the spectrum of an unknown star is 20×10^{-4} cm. If the Wein constant is 3×10^{-1} cm K find the temperature of the star.
3. What is meant by black body ? How can it the realised in practice? Draw the distribution curve of energy against wavelength of the spectrum of the black body of a particular temperature.
4. Obtain Stefan's law from the Planck's distribution law.

Unit - 5 ❑ Statistical Mechanics

Structure

5.0 Objectives

The entire privious knowledge of any thermal system will change by reading this unit. A modern statistical approach is adopted to eastablish thermal laws as well as some new phenomear is discussed by this new method.

5.1 Introduction

Classical mechanics based mainly on Newton's laws describes the motion of a system in time and space in terms of displacement, velocity, energy etc of the individual particles. The results are nice so far the system contains small number of particles. But when the system contains a large number of particles it is not possible to apply the laws of dynamics to describe the behaviour of the system. Statistical method must he applied in such cases. The statistical mechanics provides a frame work relating the microcopic properties of individual particles to the macrocopie bulk properties of material. It is said sometimes that statistical mechanics is not a science but a pure mathematics which explains the natural phenomenon so nicely.

The statistical mechanics is divided into classical statistics governing the distinguishable particles known as Maxwell-Boltzman statistics and Quantum statistics governing indistinguishable particles known as Bose-Einstein statistics and Fermi-Dirac statistics.

5.2 Phase space

Statistical Machanics

To describe the state of motion of a point particle, it is custormary to set up a six diamensional hypothetical space, called phase space, in which six coordinates x, y, z, p_x, p_y and p_z are marked along six mutually perpendicular axes. The first three x, y, z are three position co-ordinate and the second three p_x, p_y and p_z on the momentum co-ordinates representing the component of linear momentum along three space axes. This phase space for a single particle is also known as μ-space.

To describe the state of motion of system of N point particles it is customary to set up a 6N diamential hypothetical space in which 6N co-ordinates, (x_1, x_2, x_3 .... x_{3N-1}, x_{3N}, p_1, p_2, p_3......p_{3N-1}, p_{3N}) are marked along 6N mutually perpenducular axes. The first three x_1, x_2 and x_3 are three position co-ordinates of the first particle, x_4, x_5 and x_6 are three position co-ordinates of second particle and so on, while p_1, p_2 and p_3 are three momentum co-ordinates of the first particle, p_4, p_5 and p_6 are three momentum co-ordinates of the second particle and so on. This phase space for a system of particle is known as Γ–space.

5.3 Macrostate and microstate

Microstate : A description of a system of particles that specifies the properties of each individual particle is a microscopie description and the state is referred as microstate. Position, momentum etc of particles are the properties used for such description.

Macrostate : A more generalised description can be in terms of macroscopic quantities such as pressure, volume etc or in can be interms of the number of particles whose properties fall within a given range.

We consider a system of four molecues (A, B, C and D) and we have two compartments to accomodate the molecules.

(i) We can placed all the molecules in compartment 1 and keep compartment 2 empty.

(ii) We can place 3 molecules in compartment 1 and one moloculecule in compartment 2.

(iii) We can place 2 molecules in compartment 1 and 2 molecutes in compartment 2.

(iv) We can place one molecule in compartment 1 and 3 moleccules in compartment 2.

(v) We can place all the molocules in compartment 2 and keep the compartment 1 empty.

Thus we have 5 choies. These are the five macrostates.

Now we describe with more details the macrostate (i) as $\boxed{ABCD|O}$ only.

The macrostate (ii) as

$\boxed{ABC|D}$, $\boxed{BCD|A}$, $\boxed{CDA|B}$, $\boxed{DAB|C}$ four microstate

The macrostate (iii) as

$\boxed{AB|CD}$, $\boxed{BC|DA}$, $\boxed{CD|AB}$, $\boxed{DA|BC}$, $\boxed{AC|BD}$, $\boxed{BD|AC}$

There are six microstate.

The macrostate (iv) as

$\boxed{A|BCD}$, $\boxed{B|CDA}$, $\boxed{C|DAB}$, $\boxed{D|ABC}$

There are four microstates.

The macrostate (v) as $\boxed{O|ABCD}$ only

Thus corresponding to 5 macrostate we have $1 + 4 + 6 + 4 + 1 = 16$ microstates.

5.4 Entropy and thermodynamic Probability

According to Boltzmann the entropy S of a state is a function of thermodynamic probability (W) of the state. We write

$$S = f(w) \text{ .... } (1)$$

We consider two system of entropies S_1 and S_2 and the thermodynamic probabilities w_1 and w_2.

$$\therefore \; S_1 = f(w_1) \text{ and } S_2 = f(w_2)$$

If the two systems are mixed the entropy is $S = S_1 + S_2$ and the probability is $w = w_1 \times w_2$

$$\therefore \; S_1 + S_2 = f(w_1 \times w_2)$$

$$\text{or, } f(w_1) + f(w_2) = f(w_1 \times w_2) \text{ .... } (2)$$

Differentiating above relation w.r.t. w_1 keeping w_2 constant we get

$$f'(w_1) = f'(w_1 \times w_2) \times w_2$$

$$\text{or, } \frac{f'(w_1)}{w_2} = f'(w_1 \times w_2) \text{ .... } (3)$$

Similarly, differentiating (2) w.r.t. w_2 and keeping w_1 constant we get

$$\frac{f'(w_2)}{w_1} = f'(w_1 \times w_2) \text{ .... } (4)$$

From equation (3) and (4) we get

$$\frac{f'(w_1)}{w_2} = \frac{f'(w_2)}{w_1}$$

$$\text{or, } w_1 f'(w_1) = w_2 f'(w_2) = wf'(w) = c_1 = \text{constant}$$

$$\text{or, } f'(w)\, dw = c_1 \frac{dw}{w}$$

$$\text{or, } f(w) = c \ln w + c_2, \; c_2 = \text{constant}$$

$$\text{or, } S = c \ln w + c_2 \text{ .... } (5)$$

Planck showed that $c_2 = 0$. For pure crystal $w = 1$ and $S = 0$, putting these in equation 5 we get $c_2 = 0$.

For an isothermal expansion of one mole of ideal gas from volume V to V′ we know

$$\frac{w'}{w} = \left(\frac{V'}{V}\right)^N \quad ; \ N = \text{Avogadro number}$$

If S′ and S are the entropies after and before expansion

$$S' - S = c_1 \ln w' - c_1 \ln w$$

$$\text{or,}\ \ S' - S = c_1 \ln \frac{w'}{w} \ \ = c_1 N \frac{V'}{V} \ \ldots\ldots\ldots (6)$$

Again change of entropy for the isothamal expansion is given by

$$S' - S = R \ln \frac{V'}{V} \ \ldots\ldots\ldots\ldots (7) \ ; \ \ R = \text{gas constant}$$

From equation (6) and (7)

$$c_1 N = R$$

$$\text{or,}\ \ c_1 = \frac{R}{N} = K \ = \text{Boltzman constant}$$

Thus the relation between the entropy and thermodynamic probability, one of the most popular relation is physics is given by

$$S = K \ln w.$$

5.5 Maxwell-Baltzmann Law

In statistical mechanics Maxwell—Boltzmann law describes the average distribution of non-inracting material particles over various energy states in thermal equilibrium and is applicable when temperature is high enough or particle density is low enough to render quantum effect negligible.

The basic pestulates

1. The particles are identical but distinguishable.
2. The total number of particles is constant.
3. The total energy of the system is constant.
4. The particles are spinless and do not obey Pauli's exclusion principle and Heisenberg's uncertainity principle.

Suppose there are N number of particles of which N_1 are in the energy state E_1, N_2 are in the energy state E_2 .... N_n are in the energy state E_n.

Total number of particles

$$N_1 + N_2 + \dots\dots\dots + N_n = N = \text{constant} \dots\dots\dots (1)$$

Total energy

$$N_1E_1 + N_2E_2 + \dots\dots + N_nE_n = E = \text{constant} \dots\dots\dots (2)$$

The number of ways in which the groups of particles could he chosen from N particles is

$$W_1 = \frac{N!}{N_1 1\, N_2 !\cdots N_n !}$$

$$\text{or, } W_1 = \frac{N!}{\prod_i^n N_i !} \dots\dots\dots\dots\dots\dots (3)$$

If g_i is the number of quantum state, corresponding to the energy E_i, the possible arrangement of N_i particles in g_i states is $g_i^{N_i}$. Thus the possible arrangement of N_1 particles in g_1 states, N_2 particles in g_2 states .... N_n particles in g_n states is

$$W_2 = \prod_i^n g_i^{N_i} \dots\dots\dots\dots\dots\dots (4)$$

Therefore the total number of ways (W) in which all the N particles are distributed among the quantum states is

$$W = W_1W_2 = \frac{N!}{\prod_i^n N_i !} \prod_i^n g_i^{N_i} \dots\dots\dots\dots\dots\dots (5)$$

$$\text{or, } \ln W = \ln N! + \sum_i^n N_i \ln g_i - \sum \ln N_i !$$

Taking the help of stirling formula ln x! = x ln x – x, the above relation becomes.

$$\ln W = N \ln N - N + \sum_1^n N_i \ln g_i - \sum_1^n (N_i \ln N_i - N_i)$$

$$\text{or, } \ln W = N \ln n + \sum_1^n N_i \ln g_i - \sum_1^n N_i \ln N_i \dots\dots\dots\dots (6)$$

The statistical equilibrium corresponds to the most favourable distribution ie $\delta w = 0$ or $\delta \ln W = 0$

From equation (6)

$$\delta \ln W = \sum_{1}^{n} dng_i \delta N_i - \sum_{1}^{n} \ln N_i \delta N_i$$

$\therefore$ For statistical equilibrium

$$\sum_{1}^{n} \left[\ln N_i - \ln g_i\right] \delta N_i = 0 \quad \ldots\ldots\ldots\ldots (7)$$

from equation (1) we have

$$\sum_{1}^{n} \delta N_i 1 = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

And from equation (2) we have

$$\sum_{i=1}^{n} E_i \, \delta N_i = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots (9)$$

multipying equation (8) and α and equation (9) by β, where α and β are known as Lagrange's undermined multiplier and adding with equation (7) we get

$$(\ln N! - \ln gi + \alpha + \beta E_i) \, \delta N_i = 0$$

whereform

$$\ln \frac{N_i}{g_i} + \alpha + \beta E_{i = 0}$$

$$\frac{N_i}{g_i} = \frac{1}{e^{\alpha} e^{\beta E_i}} = f_{MB}(E_i)$$

where $f_{MB}(E_i) = \frac{1}{e^{\alpha} e^{\beta E_i}}$ is known Maxwell Boaltzmann distribution function.

5.6 Distribution of velocity

We write Maxwell Boltzmann distribution function as number of particles N_i with energy E_i.

$$Ni = \frac{g_i}{e^{\alpha} e^{\beta E_i}} \ \ldots\ldots\ldots\ldots\ldots \ (1)$$

where g_i is the number quantum state with energy E_i,

It can be shown that

$$e^{\alpha} = \frac{N}{V}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}, \quad \beta = \frac{1}{KT}$$

Maxell–Boltzmann is a classical statistics. For continuous Energy spread we may write equation (1) as the number of particles with energy between E and E + dE

$$N(E)\, dE = g(E)\, dE\, e^{-\alpha} e^{-\beta E} \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots \ (2)$$

where g(E) is called the density of states of a system describing the number of state, that are occupied by the system at energy level E.

The equation (2) therefore becomes, on inserting the value of g(E)

$$N(E)\, dE = \frac{4\pi V\sqrt{2E}}{h^3}\, m^{3/2}\, dE\, \frac{N}{V}\left(\frac{h^2}{2\pi mKT}\right)^{3/2} e^{-\frac{E}{KT}}$$

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

For number of particles with velocity lying between c and c, we put $E = \frac{1}{2}mc^2$ and dE = mcdc putting in equation 3 we get

$$N(c)dc = 4\pi N \left(\frac{m}{2\pi KT}\right)^{3/2} e^{-\frac{mc^2}{2KT}} c^2\, dc$$

5.7 Fermi–Dirac distribution Law

In quantum statistical mechanics Fermi-Divac law describes the average distribution of electrons, protons, neutrons and all hyperons over various energy states in thermal equlibrium. Particles obeying Fermi-Dirac statistics are called fermions.

The basic postulates

1. The particles are indentical and indistingushable.
2. The total number of particles is constant.
3. The total energy of the system is constant.
4. The particles have spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ etc. in units of $\hbar$. They obey Pauli's exclusion principle and Heisenberg's uncertainity principle.
5. The wave function is antisymmetric under the positional exchange of any two particles.

We consider a system of N non-interacting particles of which N_1 are in the energy state E_1, N_2 are in the energy state E_2, ...N_n are in the energy state E_n. Such that the total number of particles

$$N_1 + N_2 + \text{..........} N_n = N = \text{constant} \text{ ....(1)}$$

and total energy

$$N_1E_1 + N_2E_2 + \text{......}N_nE_n = E = \text{constant} \text{ .... (2)}$$

Let g_i is the number of quantum states corresponding to the energy E_i. Since N_i particles are to be distributed among g_i degenerate state, $(g_i \geq N_i)$ having energy E_i, N_i states will be filled up and $(g_i - N_i)$ states will remain vacant. Now g_i states can be arranged in $g_i!$ possible ways. But since the particles and quantum states are indistinguishable we have deduct $N_i!$ ways and $(g_i - N_i)!$ways from the all possible ways to get effective number of arrangements.

Thus total number of possbble ways of arrangement for the ith state is

$$W_i = \frac{g_i!}{N_i(gi - Ni)!}$$

And total number of possible ways of arrangements for all the states is

$$W = \prod_{i=1}^{n} \frac{g_i\,!}{N_i\,!(g_i - N_i)!} \quad \text{..................} \ (1)$$

$$\text{or } \ln W = \sum_{i=1}^{n} \ln g_i\,! - \ln N_i\,! - \ln (g_i - N_i)!$$

using Stirling formula.

$$\ln W = \sum_{i=1}^{n} \left[g_i \ln g_i - g_i - N_i \ln N_i + N_i - (g_i - N_i) \ln(g_i - N_i) + g_i - N_i \right]$$

$$\text{or, } \ln W = \sum \left[g_i \ln g_i - N_i \ln N_i - (g_i - N_i) \ln(g_i - N_i) \right]$$

taking the differential

$$\delta \ln W = \sum_{1}^{n} \left[-\delta N_i \ln N_i - N_i \frac{\delta N_i}{N_i} + \delta N_i \ln(g_i - N_i) + (g_i - N_i) \frac{\delta N_i}{g_i - N_i} \right]$$

$$\text{or, } \delta \ln W = \sum_{1}^{n} \left[-\ln N_i + \ln (g_i - N_i) \right] \delta N_i$$

The statistical equilibrium corresponds to the most favourable distribution is

$$\delta W = 0 \quad \text{or, } \ \delta \ln W = 0$$

$$\text{or, } \sum_{i=1}^{n} \left[-\ln N_i + \ln (g_i - N_i) \right] \delta N_i = 0 \quad \text{..........} \ (2)$$

Since total number of particle is constant

$$\sum_{i=1}^{n} \delta N_i = 0 \quad \text{....................} \ (3)$$

Since total energy is constant

$$\sum_{i=1}^{n} E_i \delta N_i = 0 \quad \text{.....................} \ (4)$$

multiplying equation (3) by $-\alpha$ and equation (4) by $-\beta$, where α and β are lagranges undermined constants and adding with equation (2) we get

$$\sum\left(-\ln N_i + \ln(g_i - N_i) - \alpha - \beta E_i\right)\delta N_i = 0.$$

where from

$$-\ln N_i + \ln(g_i - N_i) - \alpha - \beta E_i = 0$$

$$\text{or, } \ln\left(\frac{g_i - N_i}{N_i}\right) = a + bE_i$$

$$\text{or, } \frac{g_i - N_i}{N_i} = e^{\alpha} e^{\beta E_i}$$

$$\text{or, } \frac{g_i}{N_i} = e^{\alpha} e^{\beta E_i} + 1$$

$$\text{or, } \frac{N_i}{g_i} = \frac{1}{e^{\alpha} e^{\beta E_i} + 1} = f_{FD}^{(E_i)}$$

where $f_{FD}^{(E_i)} = \dfrac{1}{e^{\alpha} e^{\beta E_i} + 1}$ is known as Fermi-Driac distribution function.

5.8 Electron gas

Electrons are part of family of particles known as fermions. Fermions have spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ ..... in units of $\hbar$ and follow Fermi-Dirac statistics. A gas like collection of electrons which have many of the properties of conversional gas like hydrogen or neon including pressure, temperature volume etc is called electron gas or more generally free electron gas. This concept is very successful in explaining the electrical and thermal conductivity, the thermionic and field emission of electrons in metals. In an atom of a metal, the valency electron is loosely bound with the atom.

If a large number of metalic atoms are closely arranged in metal the binding of the valence electrons becomes very very small and become almost free. They are confined within the boundary of the metal. These free electrons more within the metal in between the ionic core like molecules of gas as assumed in the kinetic theory. The ions at the lattice ponits becomes less important only provide the electrical neutrality. In this theory following assumptions are considered.

1. Electrons move at random in all direction with different velocities in metal in between the ionic cores.
2. The electrons undergoes collisions with each other. he collision with the ionic core may be neglected.
3. The mean time between two successive collision is called the mean free time, which is independent of position and velocity of the electrons.
4. Electrons exchange energy during collision and equilibrium state is reached.
5. There are no other interaction with electrons except that during collision.

5.9 Bose–Einstein distribution Law

In statistical mechanics Bose–Einstein Law describes the average distribution of photons, phonons, mesons and material partiles having integral spin over various energy states in thermal equilibrium. Particles obeying Bose-Einstein statistics are called bosons.

The basic pastulates

1. The particles are identical and indistenguishable.
2. The total number of particles is constant.
3. The total energy of the system is constant.
4. The particles have zero or integral apin. They do not obey Pauli's exclusion principal but obey Heisenberg uncertainigy principle.
5. The wavefunction is symmetric under the positional exchange of any two particles.

Suppose there are N number of particles of which N_1 are in the state of energy E_1, N_2 are in the state of energy E_2...........N_n are in the state of energy E_n. Leg g_i is the number of quantum states corresponding to energy E_i. N_i particles are to be distributed among g_i quantum states each having energy E_i. So that the ith energy level have $(N_i + g_i)$ objects. Keeping the first quantum state fixed the remaining $(N_i + g_i - 1)$ objects can be permuted in $(N_i + g_i - 1)!$ possible ways. But since the partilces and quantum states are indistinguslable we deduct N! ways and $(gi - 1)!$ ways from the all possible ways to get the effective number of arrangement. Thus the total number of possible ways of arrangement for the ith state is

$$\frac{(g_i + N_i - 1)!}{N_i!(g_i - 1)!}$$

and total number of possible ways of arrangement of all the particles in all the energy states is

$$W = \prod_{i}^{n} \frac{(g_i + N_i - 1)!}{N_i!\,(g_i - 1)!}$$

$$\text{or } W = \prod_{i=1}^{n} \frac{(g_i + N_i)!}{g_i!\,N_i!} \quad \text{................(1) ; neglecting 1}$$

$$\text{or } \ln W = \sum_{i=1}^{n} \ln\,(g_i + N_i)! - \sum_{1}^{n} g_i! - \sum_{1}^{n} N_i!$$

using stirling formula, we get

$$\ln W = \sum_{1}^{n} \left[(g_i + N_i)\ln\left(g_i + N_i\right) - g_i - N_i - g_i \ln g_i + g_i - N_i \ln N_i + N_i \right]$$

$$= \sum_{1}^{n} \left[(g_i + N_i)\ln(g_i + N_i) - g_i \ln g_i - N_i \ln N_i \right]$$

$$\text{or } \delta \ln W = \sum_{1}^{n} \left[\ln(g_i + N_i)\delta N_i + (g_i + N_i)\frac{\delta N_i}{g_i + N_i} - \delta N_i \ln N_i - N_i \frac{\delta N_i}{N_i} \right]$$

$$\text{or } \delta \ln W = \sum_{1}^{W} \left[\ln(g_i + N_i) - \ln N_i \right] \delta N_i$$

The statistical equilibrium corresponds to the most favourable distribution i.e.

$$\delta W = 0, \quad \text{or,} \quad \delta \ln W = 0$$

$$\text{or,} \quad \sum\left[\ln(g_i + N_i) - \ln N_i\right]\delta N_i = 0 \quad \text{............} \ (2)$$

Since total number of particles is constant

$$N_1 + N_2 + \text{............} + N_n = N = \text{constant}$$

$$\text{or,} \quad \sum_1^n \delta N_i = 0 \quad \text{......................} \ (3)$$

Since total energy is constant

$$E_1N_1 + E_2N_2 + \text{...........}E_nE_n = E = \text{constant}$$

$$\text{or,} \quad \sum_1^1 E_i\delta N_i = 0 \quad \text{...................} \ (4)$$

Multiplying equation (3) by —α and equation (4) by—β, where α and β are Lagrange's undermined multipliers and adding with equation (2) we get

$$\sum_1^w \left(\ln\left(g_i + N_i\right) - \ln N_i - \alpha - \beta E_i\right)\delta N_i = 0$$

$$\text{or,} \quad \ln\left(\frac{g_i}{N_i} + 1\right) - \alpha - \beta E_i = 0$$

$$\text{or,} \quad \frac{g_i}{N_i} + 1 = e^{\alpha} + \beta E_i$$

$$\text{or,} \quad \frac{g_i}{N_i} = e^{\alpha}e^{\beta E_i} - 1$$

$$\text{or,} \quad \frac{N_i}{g_i} = \frac{1}{e^{\alpha}e^{\beta E_i} - 1} = f_{BE}(E_i)$$

where $f_{BE}(E_i) = \frac{1}{e^{\alpha}e^{\beta E_i} - 1}$

is known as Bose-Einstein distribution function.

5.10 Photon gas

Photons are part of family of particles known as bosons. Basons have spin 0, 1, 2, ... in units of $\hbar$ and follow Bose-Einstein Statistics. The other members of this family one phonons, mesons and material particles with integral spin.

A gas like collection of photons which has many of the properties of convensional gas like hydrogen or neon including pressure, tempeature etc. The most common example of photon gas is black body radiation. The important properties, of photon gas very different from convensional gas or electron gas are.

1. The photon number is not conserved.
2. There is no collision between photons.
3. Photon interact with material particles in the cavity or in the walls of the enclosure.
4. During such interactions photons are born when material particles go to lower energy state from higher energy state and are lost when from lower energy state to higher energy state.
5. The exchange of energy between material particles and photons helps to attain equilibrium condition.

5.11 Comparison of three statistics

Comparison of M-B, B-E and F-D statistics

Quantity	M-B	B-E	F-D
1. Nature of particles	Distinguishable gas molecules	Indistunguishable called boson. Photons, phonons etc.	Indistinguishable called fermions electron, photons, neutrons etc.

Quantity	M-B	B-E	F-D
2. Spin	Spinless	0, 1, 2, ...	$\frac{1}{2}, \frac{3}{2}, \frac{5}{2}$ ......
3. Wave function	—	Symmetric	Antisymmetric
4. Number particles per quantum state	No upper limit	No upper limit Bosons obey Heisenberg principle but do not obey Pauli's exclusion principle	One particle per quantum state. Fermions obey Heisenberg principle and Pauli's exclusion principle.
5. Distribution function f(E)	$\frac{1}{e^{\alpha}e^{\beta E}}$	$\frac{1}{e^{\alpha}e^{\beta E}-1}$	$\frac{1}{e^{\alpha}e^{\beta E}+1}$

5.12 Questions

1. State the basic postulates of (i) M-B statistics (ii) B-E statistics and (iii) F-D statistics.
2. What is meant by phase space?
3. Obtain Bose-Einstein distribution law.
4. Compare between (i) M-B statistics (ii) B-E statistics and (iii) F-D statistics.

5.13 Suggested Readings

1. Head & thermodynamics & statistical physics — Brijlal (S. Chand)
2. Heat & thermodynamics — Zemonsky
3. Thermal Physics — C. K. Ghosh & S. C. Gang