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OPEN AND DISTANCE LEARNING (ODL) PROGRAMMES

(FOR THOSE WHO JOINED THE PROGRAMMES FROM THE ACADEMIC YEAR 2023–2024)

B.Sc. Physics

Course Material

Core -III

Heat, Thermodynamics and Statistical physics

Prepared

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Tirunelveli - 12

1.CALORIMETRY:

specific heat capacity - specific heat capacity of gases C_P *and* C_V*- Meyer's relation - Joly's method for determination of Cv – Regnault's method for determination of Cp*

LOWTEMPERATURE PHYSICS:

Joule -Kelvin effect - porous plug experiment - Joule -Thomson effect-Boyle temperature - temperature of inversion - liquefaction of gas by Linde's Process - adiabatic demagnetisation.

2.THERMODYNAMICS-I:

zeroth law and first law of thermodynamics - P-V diagram- heat engine efficiency of heat engine Carnot's engine, construction, working and efficiency of petrol engine and diesel engines comparison of engines.

3.THERMODYNAMICS-II:

second law of thermodynamics - entropy of an ideal gas - entropy change in reversible and irreversible processes- T-S diagram -thermodynamical scale of temperature - Maxwell's thermodynamical relations -Clasius- Clapeyron's equation (first latent heat equation) _ third law of thermodynamics – unattainability of absolute zero-heat death.

4.HEAT TRANSFER:

modes of heat transfer: conduction, convection and radiation. Conduction: thermal conductivity – determination of thermal conductivity of a good conductor by Forbe's method - determination of thermal conductivity of a bad conductor by Lee's disc method. Radiation: black body radiation (Ferry's method) _ distribution of energy in black body radiation _ Wien's law and Rayleigh Jean's law -Planck's law of radiation_ Stefan's law - deduction of Newton's law of cooling from Stefan's law.

5.STATISTICAL MECHANICS:

definition of phase - space- micro and macro states ensembles different types of ensembles - classical and quantum Statistics _ Maxwell - Boltzmann statistics - Bose -Einstein statistics - expression for distribution function _ Fermi-Dirac statistics-expression for distribution function-comparison of three statistics.

Reference books

1. Brijlal and N. Subramaniam,2000, Heat and thermodynamics, S. Chand and Co.
2. Narayanamoorthy and krishna Rao, 1986, Heat, Triveni Publishers, Chennai.
3. V.R. Khanna and R.S. Bedi,1998 1st Edition, Text book of sound, Kedharnaath Publish and Co, Meerut.
4. Brijlal and N. Subramanyam,2001, waves and Oscillations, Vikas Publishing House, New Delhi.
5. Ghosh,1996, Text Book of Sound, S. Chand and Co.
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UNIT 1: CALORIMETRY

Specific heat capacity

Specific heat capacity, often denoted by the symbol C, is a measure of the amount of heat energy required to raise the temperature of a unit mass of a substance by one degree Celsius (or one Kelvin). It quantifies how much heat energy is needed to change the temperature of a substance.

The formula to calculate specific heat capacity is:

$$Q = mc\Delta T$$

Where:

Q is the amount of heat energy transferred,

m is the mass of the substance,

c is the specific heat capacity of the substance, and

$\Delta T$is the change in temperature.

This equation indicates that the amount of heat energy required Q is directly proportional to the mass of the substance m and the change in temperature ΔT,with c being the constant of proportionality, which is the specific heat capacity.

The specific heat capacity can be experimentally determined by measuring the heat energy transferred to a substance when its temperature changes and then calculating c using the formula above.

Different substances have different specific heat capacities due to variations in their molecular structures and interactions. For example, water has a relatively high specific heat capacity compared to many other substances, which is why it can absorb and retain large amounts of heat energy without experiencing large temperature changes.

Specific heat capacity of gases C_P and C_v

The specific heat capacities of gases are typically expressed at constant pressure C_P and constant volume C_v. These values represent the amount of heat energy required to raise the temperature of a unit mass of gas by one degree Celsius (or one Kelvin) at constant pressure or constant volume, respectively.

C_p

The change in enthalpy of a reaction taking place in solution while the atmospheric pressure is constant is measured by a constant-pressure calorimeter. A coffee-cup calorimeter is one example; it is made of two Styrofoam cups nested one inside the other, and it has a lid with two holes in it so that a stirring rod and a thermometer may be inserted. A known quantity of a solute typically water that absorbs heat from the reaction is kept in the inner cup. The outside cup acts as insulation during the process. Then

$$C_p = \frac{w\Delta H}{M\Delta T}$$

where W denotes the solute's mass, M its molecular mass, ΔH denotes the solution's enthalpy, and T is the temperature change. Cp is the specific heat at constant pressure. Since the pressure (atmospheric pressure) stays constant during the operation, measuring heat with a basic calorimeter, such as a coffee cup calorimeter, is an example of constant-pressure calorimetry. The changes in enthalpy that take place in solution are measured using constant-pressure calorimetry. In these circumstances, the heat equals the change in enthalpy ($Q=\Delta H$).

Cv

The specific heat capacity Cv is derived from the first law of thermodynamics, which states that the change in internal energy (ΔU) of a system is equal to the heat added to the system (Q) minus the work done by the system (W). For a gas undergoing a change in temperature at constant volume (V), no work is done ($W=0$), so the change in internal energy is equal to the heat added:

$$\Delta U=Q$$

The change in internal energy (ΔU) is related to the temperature change (ΔT) and the specific heat capacity (Cv) by the equation

$$\Delta U=Cv\Delta T$$

Where:

- m is the mass of the gas, and
- ΔT is the change in temperature.

Equating the expressions for ΔU, we get:

$$mCv\Delta T=Q$$

From this, we can derive the expression for the specific heat capacity at constant volume Cv:

$$Cv=\frac{Q}{m\Delta T}$$

This equation defines Cv as the heat energy Q transferred to the gas divided by the product of the mass m of the gas and the change in temperature ΔT. This is the specific heat capacity at constant volume (Cv).

Experimentally, Cv can be determined by measuring the heat energy added to a gas while keeping the volume constant and then calculating Cv using the equation above.

Meyer's relation

Let's examine a single mole of an ideal gas contained in a cylinder with an area A frictionless piston. As indicated in the picture below, let P, V, and T stand for the pressure, volume, and absolute temperature of the gas, respectively.

The gas is given dQ, the amount of heat. A little weight is positioned over the piston in order to maintain the gas's consistent volume. The gas's temperature rises to T + dT and its pressure increases to P + dP. The gas's internal energy, dU, is raised by using this heat energy, dQ. However, the gas produces no work (dW = 0).

$$dQ = du = C_V \times dT$$

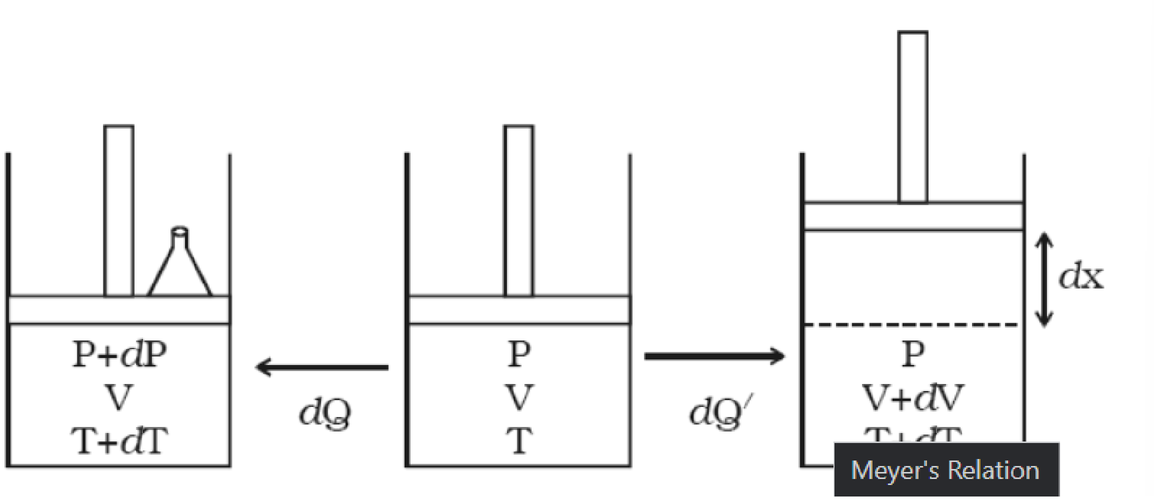
The piston is now free of the extra weight. Now, the piston rises through a distance dx, bringing the pressure inside the gas enclosure to the same level as the atmospheric pressure P. As a result of the gas expanding, its temperature drops.

The gas is now given dQ' of heat until its temperature reaches T + dT. In addition to increasing the gas's internal energy dU, this heat energy is also utilised to generate external work dW, which raises the piston.

$$dQ' = dU + dw$$

Since the expansion takes place at constant pressure,

$$dQ' = C_p \, dT + dw$$



Work done, dW = force × distance

$$dw = p \times A \times dx$$

change in volume, $dV = A \times dx$

$$dw = p \times dV$$

sub it in dQ'

$$C_P\, dT = C_V\, dT + PdV$$

The equation of state of an ideal gas is

$$PV = RT$$

Differentiate both sides and sub in previous equation we get,

$$P\, dV = C_V\, dT + R\, dT$$

$$C_P = C_V + R$$

Meyer's relation,

$$C_P - C_V = R$$

Joly's method for determination of Cv

The differential steam calorimeter, created by Joly in 1886, can be used to determine a gas's specific heat capacity at constant volume (CV).

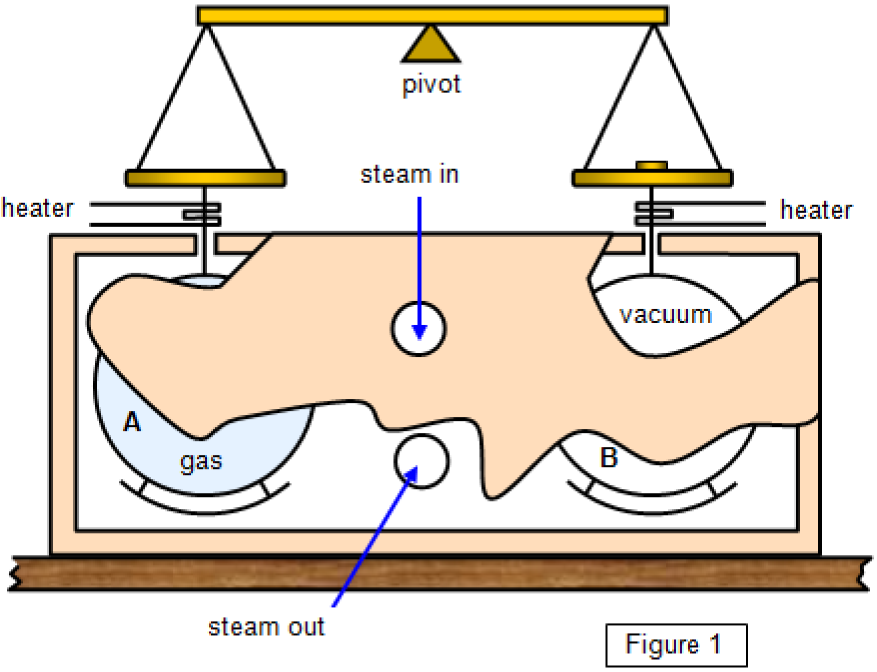


Figure 1

Two copper spheres that are hollow and have the same mass and size are suspended from a beam balance's two pans using wire. A mass of gas M at high pressure (Joly used 22 atmospheres) is contained in one of the spheres, while the other is evacuated. Steam passes via a box that encircles the spheres.

On the cold spheres, steam will condense; more steam will condense on the gas-filled sphere since it has a larger thermal capacity. After some time, the excess mass of steam that has condensed on sphere A must be balanced by adding mass m to pan B.

If θo and q1 represent the sphere's initial and final temperatures, and CV is the gas's specific heat capacity at constant volume, then:

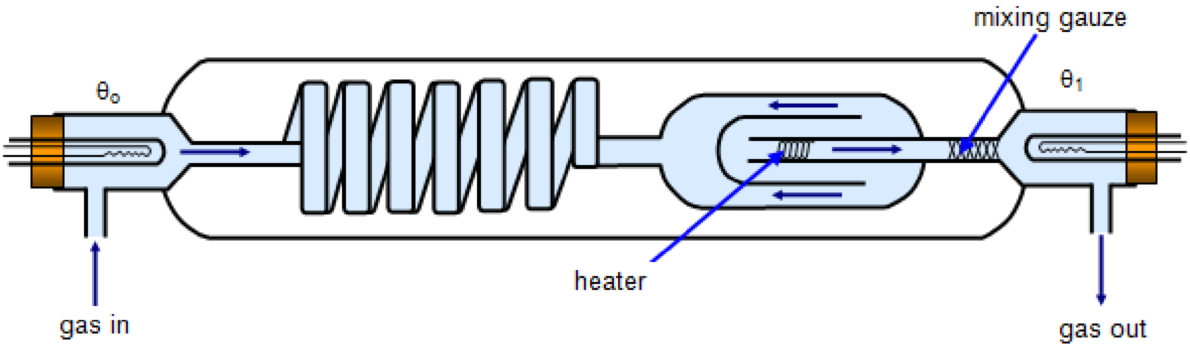
$$C_V = mL/ [M (\theta1 -\theta_o)]$$

where L is the specific heat of vaporisation of water.

There are baffles to stop water from pouring down the box's ceiling onto the spheres, and the two wires are heated to evaporate any liquid that may be accumulating on them. To measure the amount of steam condensing on the spheres when both are empty, a control experiment is conducted.

Regnault's method for determination of Cp

The continuous-flow calorimeter, developed by Regnault in 1862, can be used to determine the specific heat capacity at constant pressure (Cp). The constant-flow approach, which Swann employed for the first time in 1909, is modified by the current procedure. raised, passed by a mixing gauze, and ultimately exited at B, where its temperature is once more measured (θ1).



When steady state has been reached the temperatures are recorded, and hence C_P can be calculated from

$$VIt = M\,Cp\,(\theta 1 - \theta o) + H$$

where M is the mass of gas moving through at that moment, H is the heat lost, and VIt is the energy given to the heater in time t. As is customary in continuous-flow studies, H can be avoided by performing two observations with the same temperature differential but distinct flow rates.

Joule -Kelvin effect

If a gas is allowed to expand through a fine hole or a porous plug so that it issues from a region at a higher pressure to a region at a lower pressure there will be a fall in temperature of the gas provided the initial temperature of the gas is below is inversion temperature. This phenomenon is called Joule — Thomson effect. Joule Thomson effect proved the existence of inter molecular attraction. It is very important in the liquefaction of gases.

Consider a cylinder with non-conducting walls having a porous plug of a porous material like cotton, wool, etc. with a number of fine holes or pores in it. Consider two light frictionless pistons A and B on either side of the porous plug. Let us assume that the unit mass of high compressed gas is enclosed between the piston A and the porous plug. Let the volume of this gas be VI and the pressure be P,

Let the piston B be on the low-pressure side of the plug and be initially in constant with the plug. Due to this large pressure difference the gas flows through the pores and becomes throttle or wire drawn. That is the molecules of the gas are further drawn apart from one another. The piston A is slowly moved inward so as to keep the pressure Pl constant as the gas escapes. Similarly, the piston B will move slowly outward to keep the pressure on the other side constant at P2 Let the volume of the gas be V 2 when it has been completely expelled through the plug to the low-pressure side.

When the piston A has pushed the gas into the low-pressure Side completely.

through the plug an amount of work PIV2 has been done on the gas. When the gas enters the low-pressure Side and pushes the piston B back an amount of work p V 2 has been done by the gas.

Network done by the gas is,

$$W = P_2V_2 - P_1V_1$$

No heat energy is supplied to the gas from outside since the entire apparatus is thermally insulated. Also, the piston A is not pushed by any external agency. As thc gas in the lower part issue through the plug the piston A merely moves forward to keep the pressure P 1 constant. So, there is no supply of mechanical energy to the system from outside. Therefore, the energy required for doing the work W is drawn by the gas from its own internal energy content. If the internal energy of the gas below (Piston A side) is E1 and the above (Piston B side) is E2 we must have E2 < E1 so that the decrease (El — E2) in the internal energy is equal to the energy used by the gas for doing the work W.

$$W = E_1 - E_2$$

$$W = P_2V_2 - P_1V_1$$

$$E_1 + P_1V_1 = E_2 + P_2V_2$$

$$E + PV = constant$$

The quantity E + PV is called the total heat or the enthalpy of unit mass of the gas. In the porous plug experiment the enthalpy of the gas remains constants so that the expansion of the gas is an isenthalpic process.

Boyle's temperature

Case 1:

For perfect gas which obeys Boyle's law,

$$P_2V_2 = P_1V_1$$

Further there are no intermolecular forces in a perfect gas so that

(PE.)2 - (PE)1 = 0

Therefore,

(K.E.)1- (K.E)2 = 0

There will be no change of temperature or no cooling effect.

Case 2:

For a real gas, in which there are intermolecular attractive forces, the potential energy increases when the molecules are pulled apart to greater distances during the expansion of the gas through the porous plug.

$$P_2V_2 > P_1V_1$$

(K.E.)1>(K.E)2

Above the Boyle temperature of the gas PV decreases as P

decreases so that P2V2< P 1V1

(K.E.)1 + (K.E.)2=$P_2V_2 - P_1V_1$+[(P.E.)1-(P.E.)2]

Since (P1V1 — P2 V2) is positive, the cooling produced due to decrease of

kinetic energy becomes less.

Joule Thomson effect

The Joule-Thomson effect, also known as the Joule-Kelvin effect, describes the temperature change that occurs when a gas or liquid undergoes throttling or expansion without external work or heat exchange. This effect is named after James Prescott Joule and William Thomson (Lord Kelvin), who independently studied and formulated its principles in the mid-19th century.

When a gas or liquid flows through a valve or porous plug from a region of high pressure to a region of low pressure, it experiences a drop in pressure. According to the ideal gas law, a decrease in pressure without any corresponding increase in volume results in a decrease in temperature, while an increase in pressure without any corresponding decrease in volume results in an increase in temperature. This is due to the work done by or on the gas molecules during the expansion or compression.

The Joule-Thomson coefficient (μ) quantifies the rate of change of temperature with respect to pressure at constant enthalpy. It is given by the formula:

$$\mu = (dT/dP)\ H$$

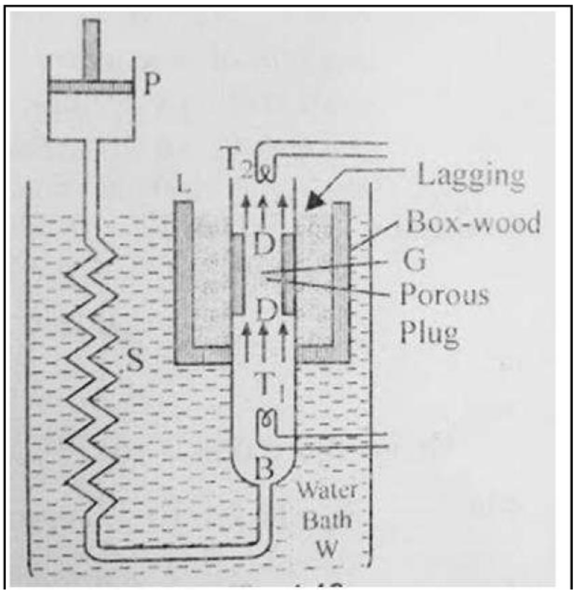
Where:

- μ is the Joule-Thomson coefficient,
- dT/dP is the change in temperature with respect to pressure, and
- H is the enthalpy.

Depending on the initial temperature and pressure conditions, a gas or liquid undergoing Joule-Thomson expansion can experience either cooling (temperature decreases) or heating (temperature increases). This effect has various practical applications, including in refrigeration systems, natural gas processing, and cryogenics.

Porous plug experiment

The experiment set up used in this experiment is shown and it consists of a porous plug K placed between two perforated brass discs D1, D. the plug is kept in wooden tube to provide thermal insulation. Wooden tube W is surrounded by cotton wool contained in a brass vessel B to give the perfect thermal insulation.



Porous plug setup

The wooden tube is connected with conducting cooper tube L&M on either side. The lower conducting cooper tube M is connected to a cylinder fitter with the piston P through a spiral tube S. the temperature of gas before & after passing through porous plug is measured with help of two platinum resistance thermometers R1 and R2 respectively.

The Pressure of gas in tube ss is measured with the help of a pressure gauge. To ensure the constant temperature for the entire apparatus is kept in water bath.

There is any heating of the gas due to its compression then this heat is removed by water circulating in water bath.

The compressed gas allowed to pass through porous plug K restricts the velocity of gas on passing through the porous plug. In order to obtain a steady state, the gases allowed to flow for an hour or so the temperature indicated by R1 and R2 are noted joule Thomson repeated this experiment with different gases at different temperature ranges.

The results obtain by them are as follows

1. At sufficiently low temperatures all gases show cooling effect

2. At ordinary temperatures most gases show cooling effect, H &He shows heating effect.
3. The fall in the temperature of gas through the porous plug is proportional to pressure difference on two sides of the porous plug.

Temperature inversion

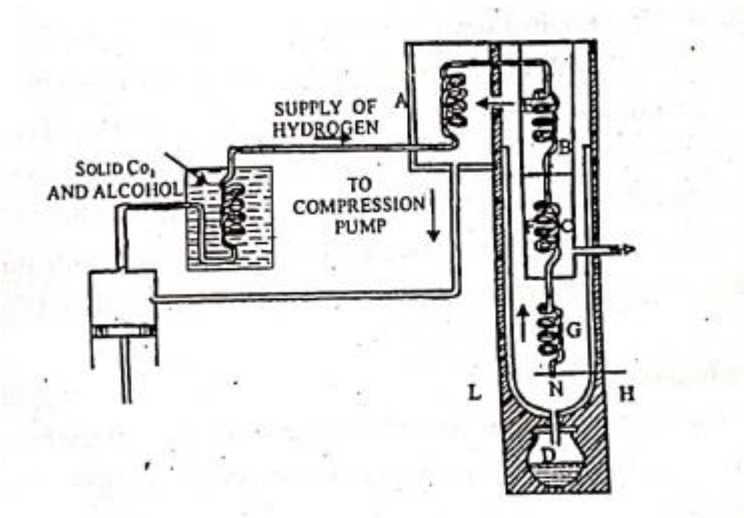
The temperature of inversion is the point at which the Joule-Thomson effect changes sign, turning the cooling effect into the heating effect. (Ti). It is neither heating nor cooling at this temperature (Ti).

Liquification of gases

Linde’s process:

Air was long believed to persist in its gaseous condition at all temperatures. Permanent gases included nitrogen, oxygen, hydrogen, and helium, among others. Under extreme pressure, a freezing mixture has the ability to liquefy substances such as ammonia, hydrogen sulphide, chlorine, and sulphur dioxide. Andrew's C02 experiment from 1862 demonstrated that a gas may be made liquefiable below the critical temperature with just the application of pressure, but that no amount of pressure can make a gas liquefiable above the critical temperature. A gas is referred to as a vapour below the critical temperature and as a gas above it.

Pictet liquefied using the Cascade technique in 1877. By using the Joule-Kelvin effect, Linde was able to liquefy air in 1896. applying the Joule-Kelvin effect theory. Additionally, helium and hydrogen were liquefied.



The Cascade process is unable to liquefy hydrogen due to its critical temperature of -240 ^{0}C. Since hydrogen has a temperature inversion of -83 ^{0}C, Linde's standard equipment for liquefying air cannot be utilised for hydrogen. For the Joule-Kelvin effect to cause cooling, the gas must first be cooled to a temperature below the inversion temperature.

Dewar (1898) created the first device, which was later enhanced by Travers, Olszewski, Nernst, and others. The entire device is housed in an exterior Dewar flask L for total insulation.

A coil submerged in solid CO_2 and alcohol is filled with hydrogen at a pressure of 200 atmospheres. It moves into chamber A's coil, where the escaping hydrogen cools it even further. Hydrogen in the coil E is cooled by liquid air in chamber B.

Liquid air is let to boil in chamber C at a decreased pressure of 10 cm of Hg, while hydrogen in coil F is cooled to a temperature of -200^{0}C. This cooled hydrogen went via the nozzle N and the regeneration coil G. The Joule-Kelvin effect causes hydrogen to cool even further. As seen in figure, the cooled hydrogen from nozzle N is permitted to return to the pump. After a while, the regenerative cooling process continues, liquefying the hydrogen and collecting it in the Dewar flask D.

Adiabatic demagnetisation

A paramagnetic material undergoes external work when it becomes magnetised, which raises its temperature. The material does work when it becomes demagnetized. Therefore, the substance's temperature decreases if it demagnetizes adiabatically. We refer to this as adiabatic demagnetization. Low starting temperatures and the application of a high magnetic field can result in maximum cooling.

Inside glass bulb B is suspended a paramagnetic salt. Dewar flasks D1 and D2, which hold liquid hydrogen and helium, respectively, are encircling bulb B. As seen, the entire apparatus is positioned in between the pole components of a powerful magnetic.

1. The specimen becomes magnetised when the magnetic field is turned on.
2. A high vacuum pump is used to remove the heat caused by magnetization by first pumping hydrogen gas into B. D1 and D2 are now thermally isolated from the cold magnetised specimen.
3. The magnetic field has now been turned off.

Let χ_1 and χ_2 be the susceptibilities of the specimen salt at the initial and final T1 and T2.

According to Curie’s law,

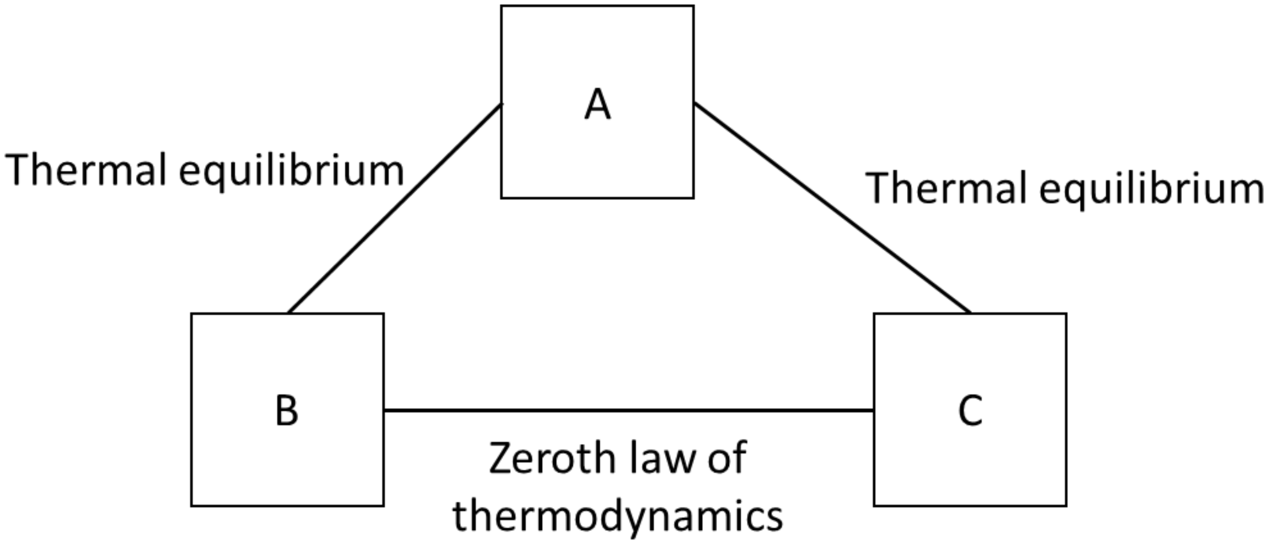
$$T_2 = {}^{\chi 1}/_{\chi 2}\ .T1$$

The specimen experiences adiabatic demagnetization, resulting in a drop in temperature. Using a solenoid coil CC, the susceptibility of the substance is measured at the start and finish of the experiment to estimate the final temperature of the specimen (T1).

UNIT2 - THERMODYNAMICS-I:

zeroth law and first law of thermodynamics

According to the Zeroth Law of Thermodynamics, two bodies A and B are in thermal equilibrium with each other if they are independently in thermal equilibrium with a third body C, as demonstrated.

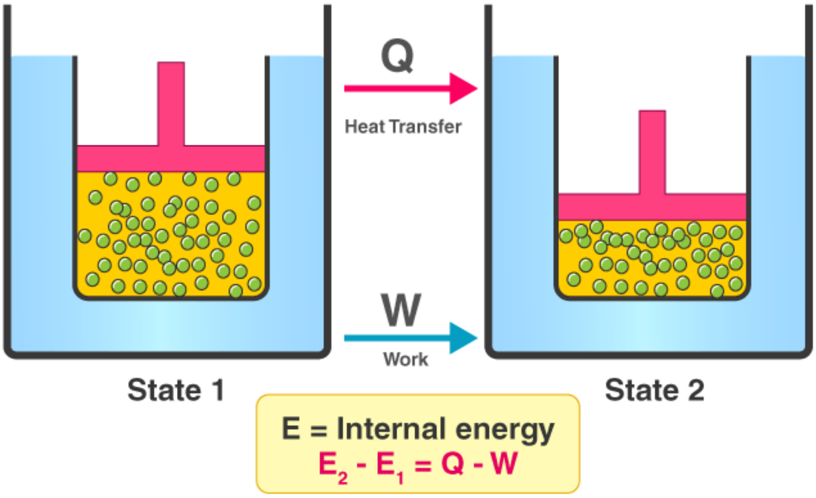


First law of thermodynamics

A system that undergoes external work W to transition from state 1 to state 2 requires a particular quantity of heat Q, and that amount of heat is equal to the sum of the system's increased internal energy and its external work.

The formula for the law,

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

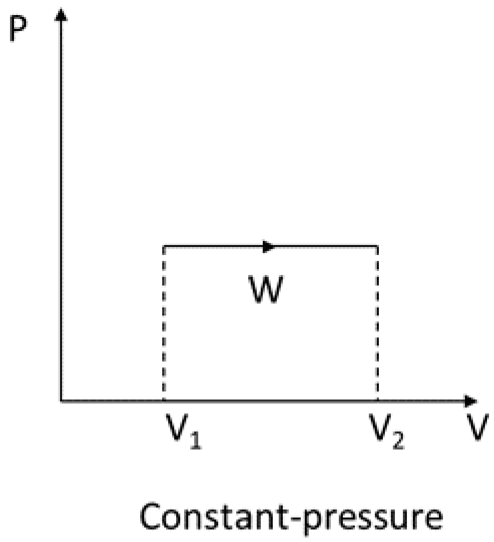


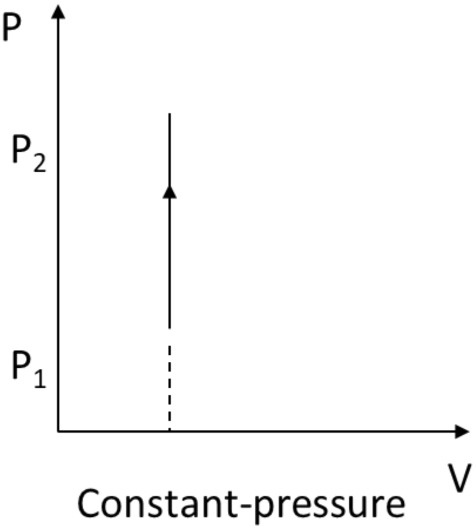
P-v diagrams

A pressure-volume diagram, also known as an indicator diagram is used to show changes to the pressure and volume in thermodynamic cycles. The area under a p-V curve represents the work done on or by a gas.

Constant pressure and constant volume

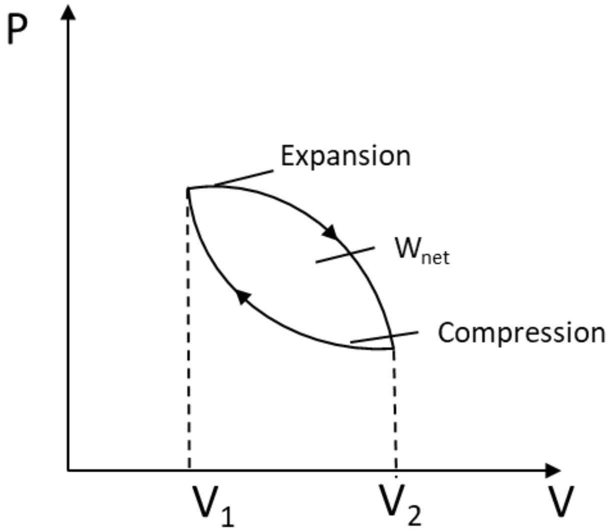
A constant pressure process is represented as a horizontal line. The work done is the area under this line. If the volume is increasing through expansion, the work is done by the gas. If the arrow is reversed and the volume is decreasing, work is done on the gas. A constant volume process is represented as a vertical line. As in a constant volume process no work can be done, the area under this curve is zero.





Thermodynamic cycle

p-V diagrams can be used to show closed thermodynamic cycles whereby a system is taken back to its original state.

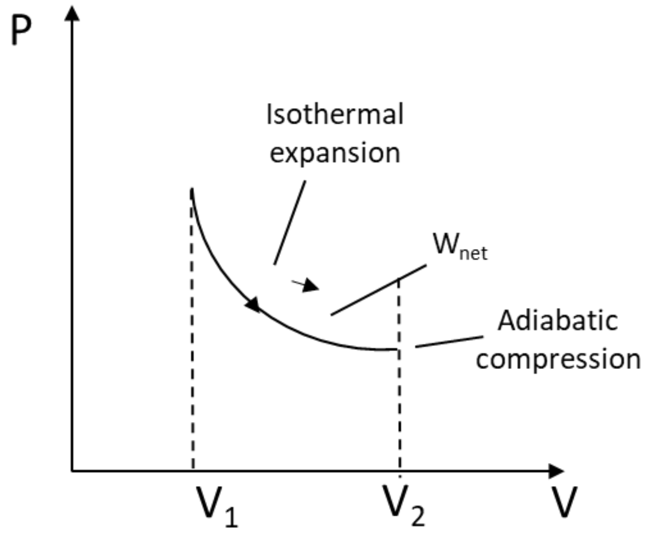


- From the high pressure to high volume, the gas expands so the area under the curve is the work done by the gas.
- From the high volume to high pressure, the gas is compressed so the area under the curve is the work done on the gas.

Since the area under the expansion curve is greater than the area under the compression curve, the net work done by the gas is positive and is represented by the area between the curves.

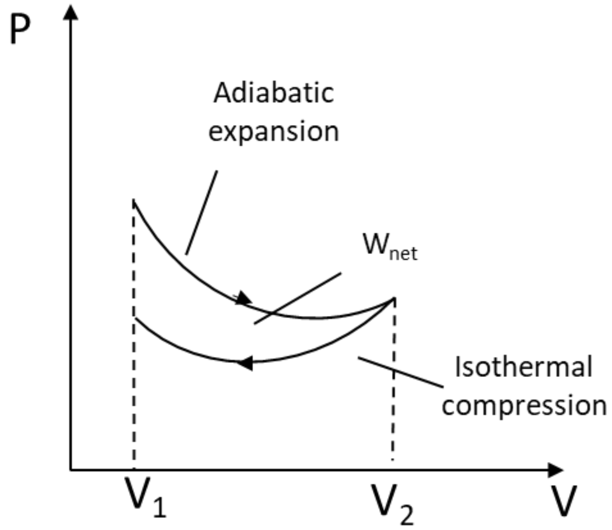
Isothermal and adiabatic expansions

In an adiabatic process no heat transfer can occur as $\Delta U=0$, whereas in an isothermal process the temperature is constant. During an isothermal expansion, heat can be transferred to the gas which increases the pressure. This results in the adiabatic expansion having a steeper curve.



Adiabatic expansion with isothermal compression

This p-V diagram shows a gas that has been expanded adiabatically then compressed isothermally to its original volume. The area between the curves is the net work done by the gas.



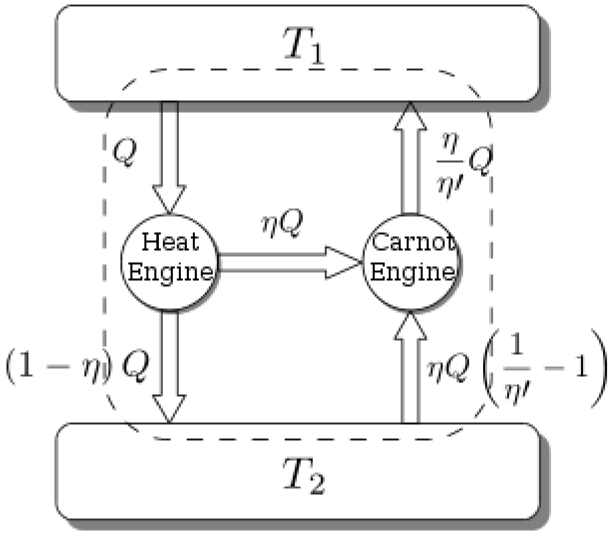
Carnot’s engine

Carnot's engine is a theoretical engine that operates on the principles of thermodynamics, named after the French physicist Sadi Carnot. While no practical Carnot engine can be built due to idealizations and limitations, it serves as a useful theoretical construct for understanding the maximum efficiency of heat engines.

Construction:

The Carnot engine consists of four main components:

- A heat source (usually a high-temperature reservoir) where the working substance absorbs heat.
- A working substance (often an ideal gas) that undergoes a thermodynamic cycle.
- A heat sink (usually a low-temperature reservoir) where the working substance releases heat.
- A reversible engine cycle that allows the working substance to convert heat into work with maximum efficiency.



Working:

The Carnot cycle consists of four reversible processes:

- Isothermal Expansion: The working substance absorbs heat from the high-temperature reservoir while expanding isothermally (at a constant temperature). During this process, it does work on the surroundings.
- Adiabatic Expansion: The working substance continues to expand adiabatically (without heat exchange with the surroundings) and undergoes a drop in temperature.
- Isothermal Compression: The working substance is placed in contact with the low-temperature reservoir and compressed isothermally, releasing heat to the surroundings.
- Adiabatic Compression: The working substance continues to be compressed adiabatically, increasing its temperature back to the initial state.

Efficiency of a Carnot's engine

The efficiency (η) of a Carnot engine is defined as the ratio of the work output to the heat input at the high-temperature reservoir:

$$\eta = \frac{w}{Q_1}$$

$$\eta = \frac{(S - S_1)(T_1 - T_2)}{T_1(s_2 - s_1)}$$

$$\eta = \frac{T_1 - T_2}{T_1}$$

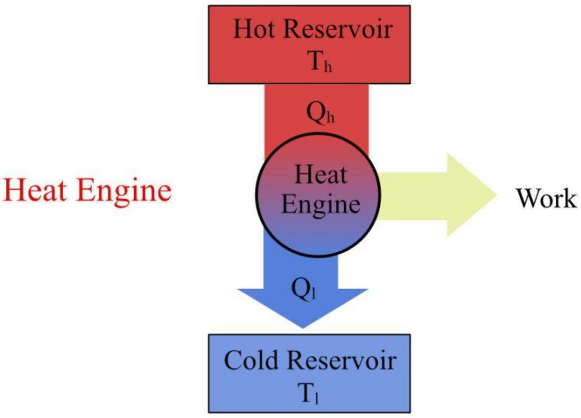
$$\eta = 1 - \frac{T_2}{T_1}$$

or

$$\eta = 1 - (Tc / Th)$$

Where:

- η is the efficiency,
- Tc is the temperature of the cold reservoir (in Kelvin),
- Th is the temperature of the hot reservoir (in Kelvin).



This equation demonstrates that the efficiency of a Carnot engine depends only on the temperatures of the heat reservoirs. It indicates that the efficiency increases with an increase in the temperature of the high-temperature reservoir or a decrease in the temperature of the low-temperature reservoir. However, it also establishes that no engine can have an efficiency greater than that of a Carnot engine operating between the same two reservoirs.

Carnot's engine is a theoretical construct, it provides insight into the maximum efficiency that any heat engine can achieve, given the temperatures of the heat reservoirs involved.

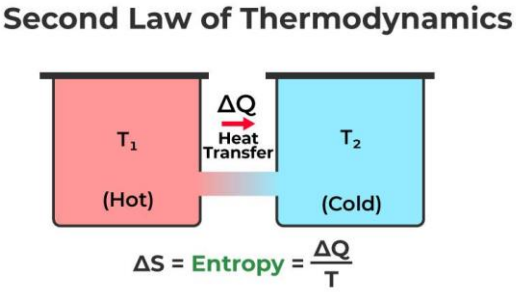
Comparison between the petrol and diesel engine

Aspect	**Petrol Engine**	**Diesel Engine**
Working Cycle	Typically operates on the Otto cycle	Operates on the Diesel cycle
Fuel Types	Combustion occurs via spark ignition	Runs on diesel fuel
Combustion Process	Combustion occurs via spark ignition	Combustion occurs due to high compression without spark ignition
Efficiency	Lower thermal efficiency, typically 20% to 30%	Higher thermal efficiency, typically 30% to 40%
Emissions	Lower NOx and particulate matter, higher CO and HC	Historically higher NOx and particulate matter, lower CO and HC

UNIT 3. THERMODYNAMICS-II:

Second law of thermodynamics

Entropy is an isolated system that is not in equilibrium will tend to increase over time until it reaches a maximum equilibrium level. If you keep the door open between two adjoining rooms of different temperature the cooler room will become warmer and the warmer room will cool down until they both reach the same final temperature.



Second law of thermodynamics,

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

Where,

$\Delta s =$ Change in entropy.

ΔQ = Heat energy.

T = Temperature.

Entropy of an Ideal Gas

The Sackur-Tetrode equation is a well-known formula that expresses the entropy S of a monoatomic ideal gas.

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

- where N denotes the atom count.
- Boltzmann's constant, k =
- V stands for volume.
- U stands for internal energy.
- h is the Planck constant.

This equation allows for the direct determination of several parameters, including the change in entropy during an isothermal expansion in which N and U are constant (implying Q=W). By applying log combination rules to the entropy expression for V_f and Vi, we may get

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

It is helpful to expand the entropy formulation and separate the U and V dependency using the logarithm of products in order to determine other functions.

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

Next, applying the entropy-based definition of temperature:

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

This provides a term for internal energy that makes sense given the energy's equilibrium.

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

with kT/2 of energy for every atom's degree of freedom.

The relationship can be used to calculate the change in entropy for processes involving an ideal gas.

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

This can be expressed using the nature of system work and the first rule of thermodynamics.

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

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

If the temperatures and volumes are known, this is a helpful calculating form; nonetheless, it is better to have it expressed in those terms if you are working on a PV diagram. Using the law of ideal gas

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

Then,

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

.

However, since CP = CV + R relates particular temperatures,

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

These equations can be used to any two points that can be plotted on a normal graph, as entropy is a state variable that only depends on the initial and final states.

Entropy changes in reversible and irreversible processes

Reversible:

When a change can be undone by making an equally tiny adjustment to the initial conditions, it is said to occur reversibly when it can be carried out in a succession of minuscule stages.

Reversing any step will return the system and its surroundings to their initial state. For instance, lowering the external pressure in a series of minuscule increments can cause a gas to expand reversibly.

This is discussed under two criteria:

Isothermal

Consider an isothermal reversible process. In this process system absorbs heat Q from surroundings at temperature T. Heat dQ enters the system from the surroundings.

Consequently, the surrounding environment's entropy will decrease by

$$\Delta_{surrounding}\, S = -\frac{dQ}{T}$$

And the entropy of the system will increase by,

$$\Delta s\ system = \frac{+Q}{T}$$

$$\Delta s + \Delta s = {}^{Q}/_{T} + \left[\frac{-Q}{T}\right]$$

$$\Delta s = 0$$

Change of entropy in isothermal reversible process is zero.

Adiabatic

Isolated is the name given to a system with the rigid boundary with ideal heat insulation The ideal heat insulation prevents any heat exchange between the system and the surroundings dQ = 0

$$\Delta s\ \ system\ \ = \frac{Q}{T} = 0$$

$$\Delta s\ \ surrounding\ \ = \frac{Q}{T} = 0$$

$$\Delta s\ \ system + \Delta s\ \ system = 0$$

Change in entropy of an adiabatic process is zero.

Irreversible

Think about the environment and the system at various temperatures and T, respectively, where T1> T2. There will be heat transmission between the environment and the system. If there is a heat flux (dQ) from the system to the environment. As a result, the system's entropy will decrease.

Decrease in entropy of system = - $\frac{Q}{T_1}$

Increase in entropy of the surroundings = $\frac{Q}{T_2}$

Net entropy changes of process = ∇ S $_{\text{surroundings}}$+ ∇ S $_{\text{system}}$

$$\Delta S_{Process} = \frac{-Q}{T_1} + \frac{Q}{T_2} = Q$$

Since,

$$T_2 < T_1$$

We have

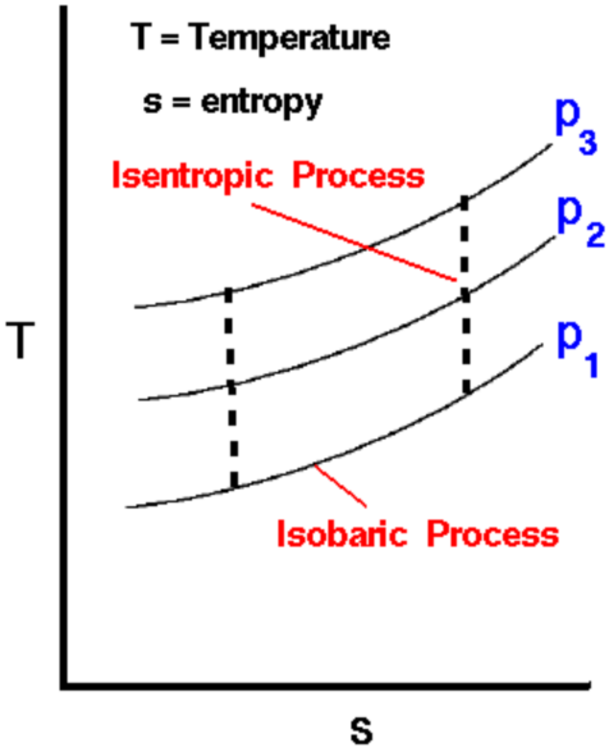
$$\Delta s_{Process} = positive$$

An irreversible process results in an increase in the entropy of an isolated sytem.

Natural processes in universe are irreversible, so the entropy of the universe increasing

$$\Delta S \ \ universe \rangle 0$$

T-S diagram

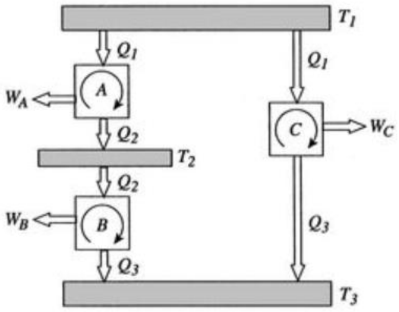


A propulsion system's working fluid is a gas. Gas pressure (p), temperature (T), mass (M), and volume (V) are among the qualities of gases that we can perceive with our senses. The values of these attributes determine the condition of the gas, and careful, scientific observation has shown that these variables are connected to one another. Two other variables that can be used to characterise the state of a gas are enthalpy and entropy S, which are defined by the first and second laws of thermodynamics. A thermodynamic process modifies the state variables in a predetermined way, such heating or compressing the gas. The starting and final states of the gas, as well as the method employed to alter the state, determine the total work and heat imparted to the gas.

Plotting a gas's state changes as it goes through a thermodynamic process is helpful. Two different kinds of plots that are used to depict state transitions are depicted in the figure. A p-V diagram, which shows the pressure vs volume, is depicted on the left. Lines of constant temperature curve from upper left to lower right on a p-V diagram. An isothermal process is one that is carried out at a steady temperature. The dotted line illustrates how the temperature, pressure, and volume of the gas change during an adiabatic operation, but no heat is delivered to the gas. The area under a process curve on a p-V diagram, as shown on the work slide, is equal to the gas. We have plotted the temperature versus the gas's entropy on the right side of the picture. We refer to this plot as a T-s diagram. On a T-s diagram, lines of constant pressure curve from lower left to upper right. An isobaric process, which operates at constant pressure, takes place in a gas turbine engine's combustor. An isentropic process is reversible and does not result in a change in the system's entropy. On a T-s diagram, an isentropic process is represented by a vertical line. The quantity of heat transmitted to the gas is indicated by the area under a process curve on a T-s diagram.

Thermodynamical scale of temperature

The working medium has not been discussed in the Carnot cycle concerns in this section. As a result, they hold for Carnot cycles in any medium and are not restricted to an ideal gas. The temperature specification used in the ideal gas equation was not necessary to support the thermodynamic reasons when we previously obtained the Carnot efficiency using an ideal gas as a medium. We can establish a thermodynamic temperature scale that is not reliant on the working medium more precisely. Examine the scenario below, which consists of three reversible cycles, to understand this. At T1 and T3, there are heat reservoirs with high and low temperatures, respectively. The ratio of the amounts of heat rejected and absorbed in a Carnot cycle has the same value for all systems for any two temperatures, T1 and T2.



We choose the cycles so Q1 is the same for A and C. Also, Q3 is the same for B and C. For a Carnot cycle,

$$\eta = 1 + \frac{Q_L}{Q_H} = F(T_L, T_H)$$

η is only a function of temperature.

$$\frac{Q_1}{Q_2} = F(T_1, T_2)$$

$$\frac{Q_2}{Q_3} = F(T_2, T_3)$$

$$\frac{Q_1}{Q_3} = F(T_1, T_3)$$

$$\frac{Q_1}{Q_3} = \frac{Q_1}{Q_2}\frac{Q_2}{Q_3}$$

$$F(T_1, T_3) not\ a\ function\ of\ T2$$

$$= F(T_1, T_2) \times F(T_2, T_3) cannot\ \ be\ a\ function\ of\ T2$$

We thus conclude that $F(T_1, T_3)$ has the form f(T1)/f(T2) and similarly

$F(T_2, T_3) =$ (T2)/f(T3)

$$\frac{Q_1}{Q_3} = F(T_1, T_3)$$

$$= \frac{f(T_1)}{f(T_3)}$$

$$\frac{Q_H}{Q_L} = \frac{f(T_H)}{f(T_L)}$$

Thermodynamic scale of temperature,

$$\frac{Q_H}{Q_L} = \frac{(T_H)}{(T_L)}$$

Maxwell's thermodynamical relations

From thermodynamics,

$$dU = T\,ds - P\,dV$$

Where,

T is the temperature

S is the entropy

P is the pressure

V is the volume

U is the internal energy

H is the entropy

G is the Gibbs free energy

F is the Helmholtz free energy

Total differential from

$$dU = \left(\frac{\partial z}{\partial x}\right) y \;\; dx + \left(\frac{\partial z}{\partial y}\right) x \;\; dy$$

$$dz = M\,dx + N\,dy$$

$$M = \left(\frac{\partial z}{\partial x}\right) y \; and \; N = \left(\frac{\partial z}{\partial x}\right) \; x$$

From $dU = T\,ds - P\,dV$,

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

$$\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right) V = \frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right) x = \frac{\partial 2Z}{\partial y \partial x} = \frac{\partial 2Z}{\partial x \partial y}$$

$$\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) \; V = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right) \; S$$

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

With respect to pressure and particle number, enthalpy and Maxwell’s relation can be written as:

$$\left(\frac{\partial\mu}{\partial P}\right) S, \mathrm{N} = \left(\frac{\partial V}{\partial N}\right) S, P = \left(\frac{\partial 2H}{\partial P \partial N}\right)$$

Clapeyron's equation first latent heat equation

The Clausius-Clapeyron equation relates the latent heat (heat of transformation) of vaporization or condensation to the rate of change of vapour pressure with temperature. Or, in the case of a solid-liquid transformation, it relates the latent heat of fusion or solidification to the rate of change of melting point with pressure.

Let us imagine a vapour in equilibrium with its liquid held in a cylinder by a piston, at a constant temperature – namely the temperature at which the liquid and vapour are in equilibrium – that is to say, the boiling (or condensation) point for that pressure. We imagine the piston to be pulled out, at constant temperature; liquid evaporates and the pressure remains constant. If the piston is pushed in, vapour condenses, at constant temperature and pressure. During this process the pressure and temperature remain constant, so the Gibbs free energy of the system is constant.

Let G1 be the specific Gibbs free energy for the liquid and G2 be the specific Gibbs free energy for the vapour.

Suppose that a mass dm of the liquid vaporizes, so that the Gibbs free energy for the liquid decreases by G1dm and the Gibbs free energy for the vapour increases by G2dm. But the Gibbs free energy for the system is constant. This therefore shows that, when we have a liquid in equilibrium with its vapour (i.e. at its boiling point) the specific Gibbs free energies of liquid and vapour are equal. (The same is true, of course, for the molar Gibbs free energies.) That is:

$$H_1-TS_1=H_2-TS_2$$

Or

$$T(S_2-S_1) = H_2-H_1$$

In which the enthalpy and entropy are specific. The left-hand side is the specific latent heat of vaporization, and we already knew from Chapter 9 that this was equal to the difference in the specific enthalpies of liquid and vapour.

The equality of the specific Gibbs free energies of liquid and vapour can also be written as

$$U_1-TS_1+PV_1=U_2-TS_2+PV_2,$$

Or

$$T(S_2-S_1) = (U_2-U_1) + P(V_2-V_1)$$

This shows that the latent heat of vaporization goes into two things: To increase the internal energy upon vaporization (especially the increase of potential energy as the molecules are pulled apart from each other) and the PdV work done against the external pressure as the volume increases. Thus, we could divide the latent heat into an internal latent heat and an external latent heat.

In the foregoing, we imagined that some liquid vaporized as we withdrew the piston. Now let us imagine that we cause some liquid to vaporize as we add some heat at constant volume. The specific Gibbs free energies of liquid and vapour both increases, but they increase by the same amount because, as we have seen, when a liquid and its vapour are in equilibrium at the boiling point, their specific Gibbs free energies are equal. Thus

$$-S_1dT+V_1dP = -S_2dT+V_2dP$$

Or

$$dP/dT=S2-S1/V2-V1$$

The left-hand side is the rate of increase of vapour pressure with temperature, while S2 – S1 is equal to L/T, where L Is the specific latent heat of vaporization. Thus, we arrive at the Clausius-Clapeyron equation:

$$dP/dT = L/T\ (V2-VL)$$

Third law of thermodynamics

As the temperature of a system approaches absolute zero, the entropy of the system approaches a minimum value, typically zero.

$$S - S_0 = k_B \ln\boldsymbol{\Omega}$$

Where,

- S is the entropy of the system.
- S0 is the initial entropy.
- kB denotes the Boltzmann constant.
- **Ω** refers to the total number of microstates that are consistent with the system’s macroscopic configuration.

Unattainability of absolute zero:

One most statement of the third law of thermodynamics is that the lowering of the temperature of a material body to the absolute zero is impossible in the finite number of steps. To understand this claim, recall the concept of Carnot refrigerator first. A Carnot refrigerator is basically just the reverse of the Carnot heat engine. i.e. Carnot heat engine working in reverse cycle. Since a Carnot heat engine provides work through reversible isothermal adiabatic compressions and expansions a net amount of work must be done in Carnot refrigerator making lit electricity consumer.

Let q1 be the amount of heat absorbed by a Carnot refrigerator form a body at lower temperature T1 and q2 as the amount of heat rejected by the same refrigerator to a body at higher temperature T2. The coefficient of performance (β) of the reversible Carnot refrigerator can be given by the following relation.

$$\beta=1/\left(q_2/q_1^{-1}\right) \quad \text{-------------------} \quad (1)$$

Since for Carnot cycle, we know that

$$q_1/T_1 = q_2/T_2 \quad \text{---------------------} \ (2)$$

After using the value q2/q1 from equation (2) in equation (1), we get

$$\beta=1/\left(T_2/T_1^{-1}\right) \ \text{-----------------}(3)$$

Furthermore, we also know that the coefficient of performance of an ideal Carnot refrigerator is simply the ratio of the cooling effect to the work done i.e.

$$\beta= q_1/w \ \text{----------------}(4)$$

Which means that how much is removed from the body at lower temperature per unit of work done. Now from equation (3), (4) we have

$$q_1/w=1/\left(T_2/T_1^{-1}\right)$$

$$q_1/w=T_1/\left(T_2-T_1\right)$$

Taking reciprocal of the above result, we get

$$w/q_1 = \left(T_2-T_1\right)/T_1$$

Thus, it is obvious from the above equation that as the lower temperature T_1 approaches zero, more and more work will be needed to remove the same amount of heat (w is inversely proportional to T_1), which is the unattainability of the absolute zero.

UNIT 4. HEAT TRANSFER:

Modes of Heat Transfer

The mode of heat transfer refers to the specific way in which heat energy is transferred from one object or substance to another. There are three main modes of heat transfer:

- Conduction,
- Convection
- Radiation.

Conduction:

Conduction is the transfer of heat through direct contact between two objects or substances. When objects are in contact, heat energy flows from the hotter object to the cooler one. This transfer occurs due to the collision of particles within the objects, causing the faster-moving particles to transfer their energy to the slower-moving particles.

Example: When you touch a hot metal spoon, heat is transferred from the spoon to your hand through conduction. The molecules in the spoon vibrate rapidly due to the heat, and this energy is transferred to the molecules in your hand as they come into contact.

Convection:

Convection involves the transfer of heat through the movement of fluids or gases. When a fluid or gas is heated, it becomes less dense and rises, while the cooler, denser fluid or gas sinks. This creates a circulation pattern known as convection currents, which transfer heat from one place to another.

Example: A classic example of convection is the heating of a room by a radiator. The hot air near the radiator rises, creating a convection current. As the hot air rises, it transfers heat to the cooler air in the room. The cooler air then sinks and gets heated in turn, creating a continuous circulation of warm air.

Radiation:

Radiation is the transfer of heat through electromagnetic waves. Unlike conduction and convection, radiation does not require a medium to transfer heat. Heat energy is emitted in the form of electromagnetic waves, which can travel through empty space. Examples of radiation include the heat we receive from the sun or the warmth we feel when standing near a fire.

Example: An example of radiation is the heat we receive from the sun. The sun emits electromagnetic waves, including infrared radiation, which travels through space and reaches the Earth. When these waves come into contact with objects on Earth, they are absorbed, and their energy is converted into heat.

Thermal conductivity

Thermal conductivity is a property that quantifies the ability of a material to conduct heat. It is defined as the rate at which heat flows through a unit area of a material per unit temperature gradient. Essentially, it measures how efficiently a material can transfer heat from one point to another. The higher the thermal conductivity, the better the material is at conducting heat.

The formula for thermal conductivity (k) is

$$k = \left(\frac{Q\times l}{(A\times \Delta t}\right)$$

Where:

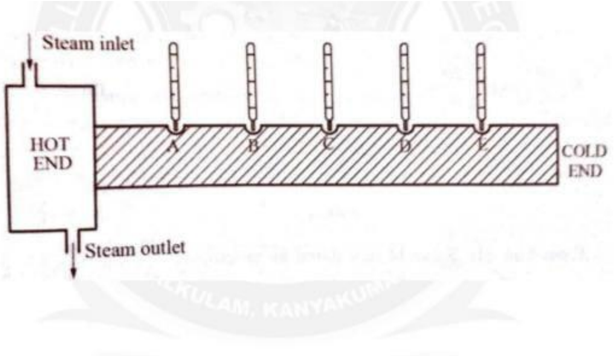
- Q is the amount of heat transferred
- l is the distance or thickness of the material
- A is the cross-sectional area of the material

- Δt is the temperature difference across the material

Thermal conductivity of good conductor Forbe's method

Metals are good conductors of both heat and electricity. To account for their heat conductor capacity, a quantity called "Thermal conductivity" is defined; higher the value of thermal conductivity more is the heat conduction.

One of the oldest methods of determining the thermal conductivity of metals is being Forbes. In this method, a long rod of a metal with uniform cross section is heated at one of its ends. The entire length of the rod is left exposed to the surrounding air at the ambient room temperature. As the rod gets heated up, it starts losing the acquired heat from its exposed surface to the surroundings. After a certain period, a steady state is reached in, which the entire heat supplied to the rod is lost to the surroundings. Let us consider cross section of the rod along its length at a distance 'x' from the heated end.



Theory

Before steady state is reached, the amount of heat conducted through a particular point say B, per second can be written as,

$$Q_1 = KA(d\theta / dx)_B \text{--------------}(1)$$

Here K is the thermal conductivity of the material.

A is the area of cross section of the material

$(\theta\ dx)B$ is the change in temperature per unit length of the rod at B

The total heat lost from the point B to E is,

$$Q_2 = \rho SA \int_E^B d\theta/\ d\ \ dx$$

S – Specific heat capacity,

ρ – Density

In a steady state condition, $Q_1 = Q_2$

$$K\ (d\theta\ /dx)\ B = \rho SA\int_E^B d\theta\ /dt\ dx$$

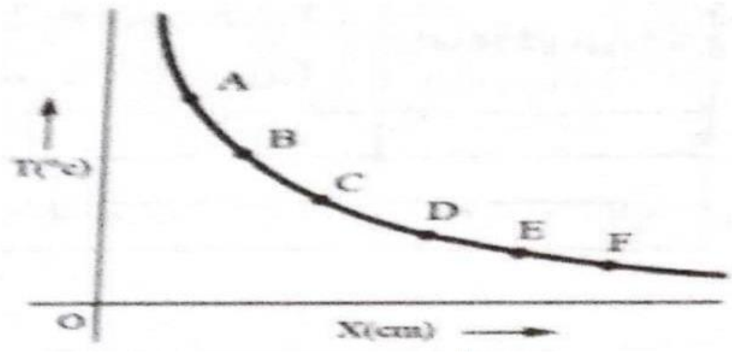
Thermal conductivity

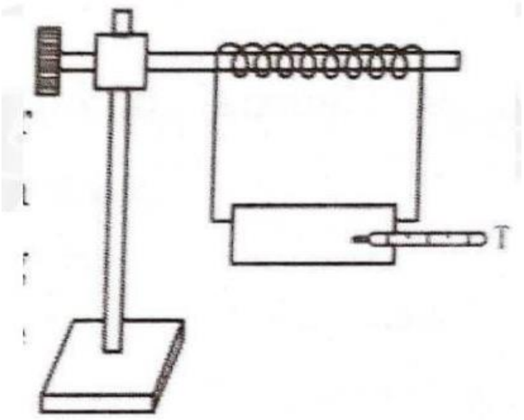
$$K = \rho SA\int_E^B d\theta/dt\ dx/\ K\ (d\theta\ /dx)\ B$$

From equation (4), K can be calculated by measuring $d\theta/\ dx$ and $d\theta\ /dt$

To find ($\boldsymbol{\theta/dx}$) $\boldsymbol{B}$:

Position	Distance from the hot end	Temperature θ

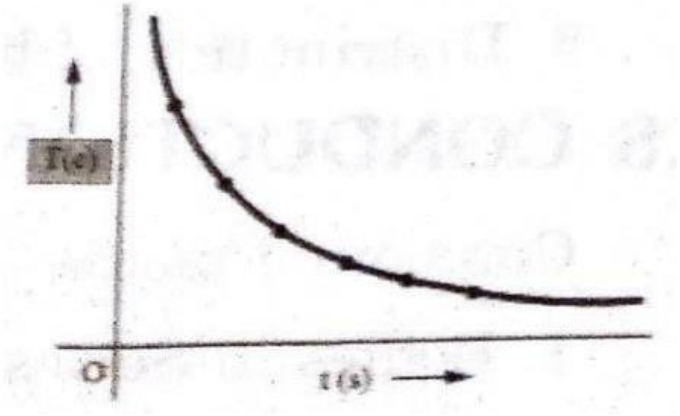




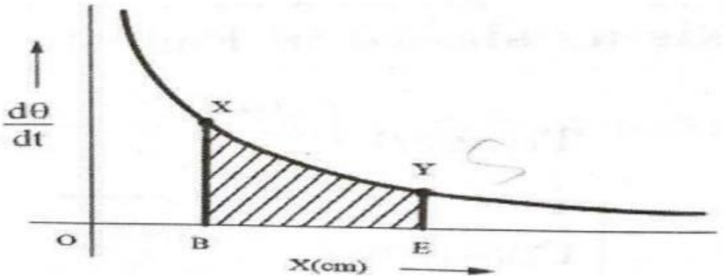
Temperature vs time setup

To find $d\theta/dt$

Sl.No	Time	Temperature θ



Graph to find $d\theta/dt$



Find the slopes $d\theta\ dt$ at the points A, B, C, D etc. from the figure

Now a graph is plotted by taking $d\theta\ dt$ along y-axis and distance along x-axis as

Mark two points x and y on the graph corresponding to the position B and E.

Determine the area under the curve X, Y. BXYE in figure.

$$\text{Area of } BXYE = \int_E^B d\theta/dt \, dx \text{ -----------------------(5)}$$

Thermal conductivity K can be calculated using equation (4) and (5).

$$K = \rho S \text{Area of BXYE} / (d\theta/dx)\, B \text{ --------------------(6)}$$

Note that instead of B and E, any two pair of points can be taken and accordingly the equation (6) can be modified.

Determination of thermal conductivity of a bad conductor by Lee's disc method.

Thermal conductivity, k, is the property of a material that indicates its ability to conduct heat. Conduction will take place if there exists a temperature gradient in a solid (or stationary fluid) medium. Energy is transferred from more energetic to less energetic molecules when neighbouring molecules collide. Conductive heat flow occurs in direction of the decreasing temperature because higher temperature is associated with higher molecular energy. Fourier’s Law expresses conductive heat transfer as

The thermal conductivity of bad conductivity,

$$k = \frac{MS\left(\frac{d\theta}{dt}\right)d(r+2h)}{\pi r^2(\theta_1-\theta_2)(2r+2h)} wm^{-1}k^{-1}$$

Where,

M - Mass of the metallic disc in kg.

S - Specific heat capacity of the material of the disc in Jkg -1K-1.

$(\frac{d\theta}{dt})$ - Rate of cooling at steady temperature in K/s.

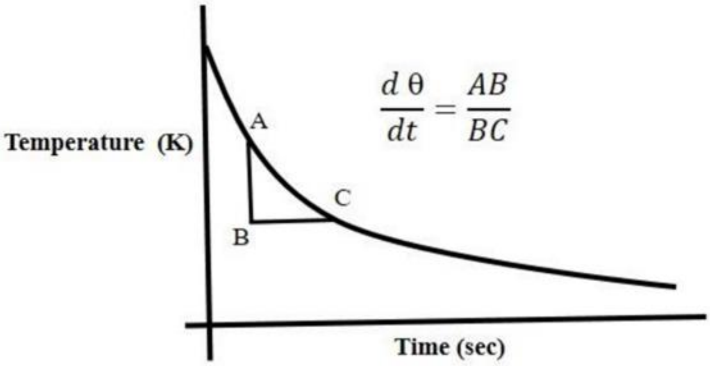
θ1 - Steady temperature of a steam chamber K.

θ2 - Steady temperature of the metallic disc K.

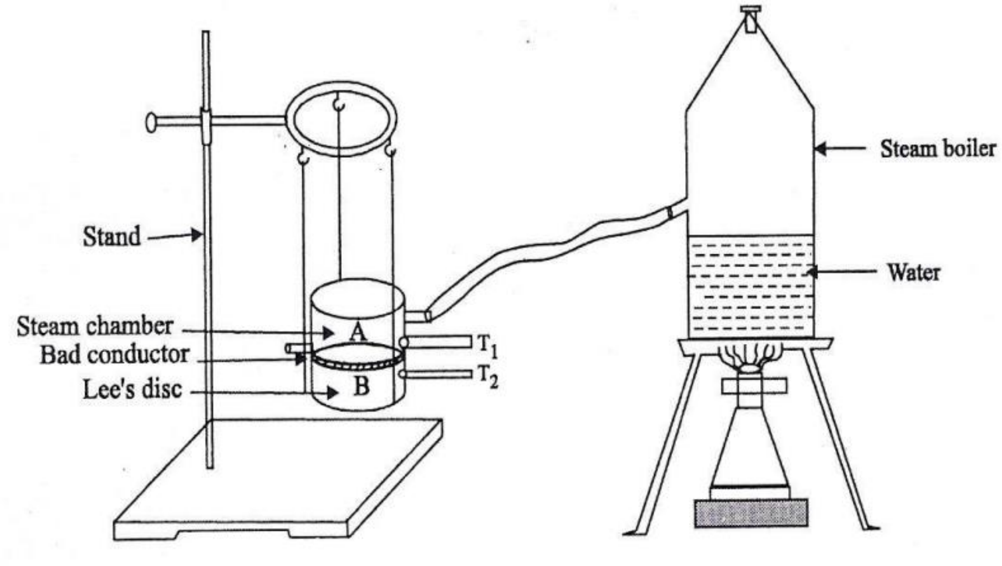
r - Radius of the metallic disc m.

h - Thickness of the metallic disc m.

d - Thickness of the bad conductor m.



From graph, $\left(\frac{d\theta}{dt}\right)$ = 0.036 K/s



Experimental setup of lee’s disc apparatus

Procedure:

1. Allow the steam to pass through the inlet of the vessel B and it escapes out through the outlet. The temperature indicated by the two thermometers will start rising.
2. After the steady state is reached (there will be no change in the temperature with time), the temperatures in both the thermometers are noted as θ1and θ2respectively. This is the static part of the experiment.

3. The bad conductor is removed by gently lifting the upper steam chamber. Now the lower metallic disc is allowed to be directly in contact with the steam chamber.

4. When the temperature of the lower disc attains a value of about 10o C more than its steady state temperature (θ2), the steam chamber is then removed and the lower metallic disc is allowed to cool down on its own.

5. A stop watch is started when the temperature is 5ºC above the steady temperature θ2 and time is noted for every 1ºC fall in temperature until the metallic disc attains 5ºC below θ2.
6. A graph between temperature and time is drawn. Rate of cooling dθ/dt at θ2 is calculated from the graph.

The mass of the disc (M) is found using rough balance and the thickness (d) of the bad conductor and thickness of the metallic disc (h) are measured using screw gauge.

To determine the rate of cooling of disc at θ

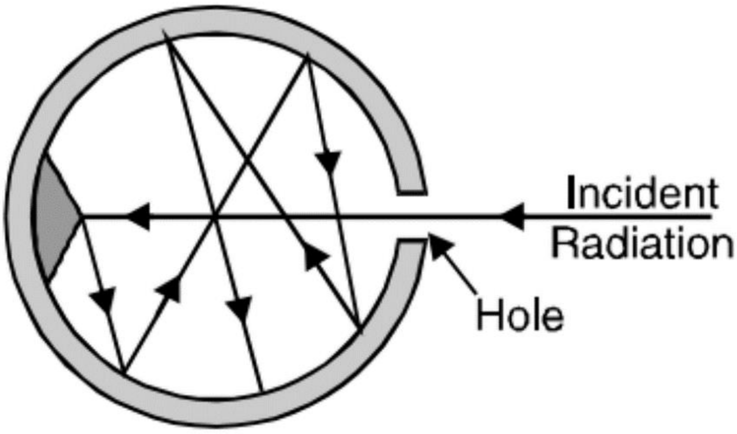
S. No.	Temperature in K	Time in Sec
1		
2		
3		
4		
5		
6		
7		

8		
9		
10		

Ferry's Black body radiation method.

Several nineteenth-century physicists tried to create a body that was completely black. Ferry proposed the simplest design for the flawlessly black body. Below is a description of the same.

Ferry's black body is made out of a metallic spherical with two hollow walls and a little aperture on one side, as seen.



The enclosure's inner wall has a black paint job. A conical projection P with a sharp edge is placed directly across from the opening O. This makes sure that no light beam that may impact ordinarily at the surface directly opposite the opening O can travel back in the same direction.

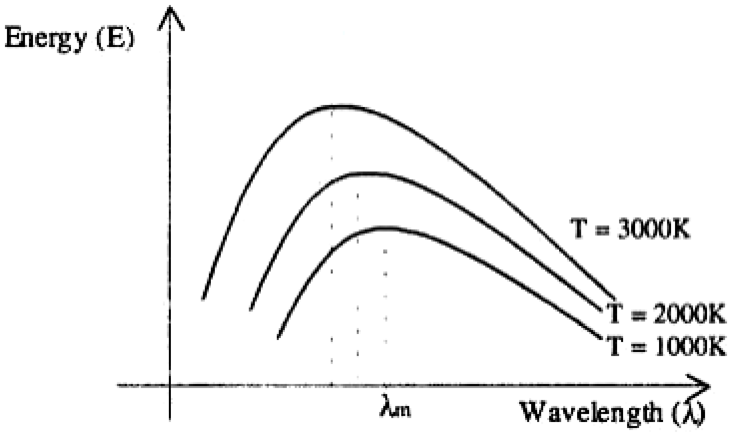
A radiation beam experiences several reflections when it enters the enclosure through opening O, as depicted in Fig. Roughly 97% of the incident beam is absorbed with each reflection, and eventually the entire ray is absorbed. The wavelength of the incident light has no bearing on the aforementioned absorption process. As a result, the enclosure's absorptive power is 1 since all radiations coming through opening O are totally absorbed. It is discovered that the radiations within an enclosure with a constant temperature are homogenous, isotropic, and solely temperature-dependent. They are also known as temperature radiations for this reason.

In the event of a Ferry's black body, radiations emitted from the enclosure's walls may now escape, and the radiations that do so will retain all of the properties of the radiations contained within.

In other words, radiation characteristics will be determined by the enclosure's temperature rather than by the type, form, colour, etc. of the walls.

Distribution of energy in black body

An idealised physical form known as a "black body" is one that absorbs all incoming electromagnetic radiation. At any temperature higher than absolute zero, the body's internal thermal energy pool produces energy that is transformed electrodynamically and released as thermal radiation from a black body. With a frequency distribution that features a maximum radiative power frequency that changes to higher frequencies as temperature rises, this radiation is known as blackbody radiation.



Wien's Displacement Law:

Wein's displacement law states that the black-body radiation curve for different temperatures will peak at different wavelength that are inversely proportional to the temperature.

Wien's Displacement law is expressed mathematically as follows:

$$\lambda_{max} T = b$$

where,

λ_{max} = wavelength at which the blackbody dominantly radiates

b = Wien's constant (2.897×10^{-3}mK)

T = temperature in kelvin.

Rayleigh Jeans Law:

The law states that the intensity of the radiation emitted by a black-body is directly proportional to the temperature and inversely proportional to the wavelength raised to a power of four.

Rayleigh jeans law is expressed mathematically as follows:

$$B_{\lambda}(T) = \frac{2ckBT}{\lambda 4}$$

where,

$B_{\lambda}(T)$ = the spectral radiance (energy density) at wavelength λ and temperature T.

c = the speed of light.

k_B = Boltzmann constant.

T = temperature in Kelvin

λ = wavelength of the radiation.

Stefan's law

According to Stefan's law, the radiation emitted from a body per unit area and unit time is directly proportional to the temperature's fourth power.

Assume that E represents the radiation emitted from a body per unit area and per unit time.

Let T be the kelvin temperature of it. Next, in line with Stefan's law

$$E\alpha T^4$$

$$E = \sigma T^4$$

where σ is called Stefan's constant. Its value is 5.67×10^{-8} Wm^{-2} K^{-4}

Then the rate of emission of radiations from the body is given by A σ T4 .

Newton's law of cooling from Stefan's law

According to Newton's rule of cooling, as long as there is little temperature differential between a body and its surroundings, the rate of heat loss per unit surface area of a body is exactly proportional to that temperature difference.

Assume that the body's temperature is T and the ambient temperature is T0.
Then, based on the cooling law of Newton.

The body's rate of heat loss is exactly proportional to $T - T_0$

Unit 5 - STATISTICAL MECHANICS:

Phase space:

A space which combines the three coordinates of position space and three coordinates of momentum space is called the phase space. It just means the combined 'space' of position and momentum. Provides a graphical representation of all possible states of a dynamic system. It tells us the system's characteristics such as position, momentum and other parameters defining its state at any given time. Each point represents a state of the system. In a gas of N point particles, each particle has three positional coordinates and three corresponding momentum coordinates, so that the phase space has 6N-dimensions.

Ensemble:

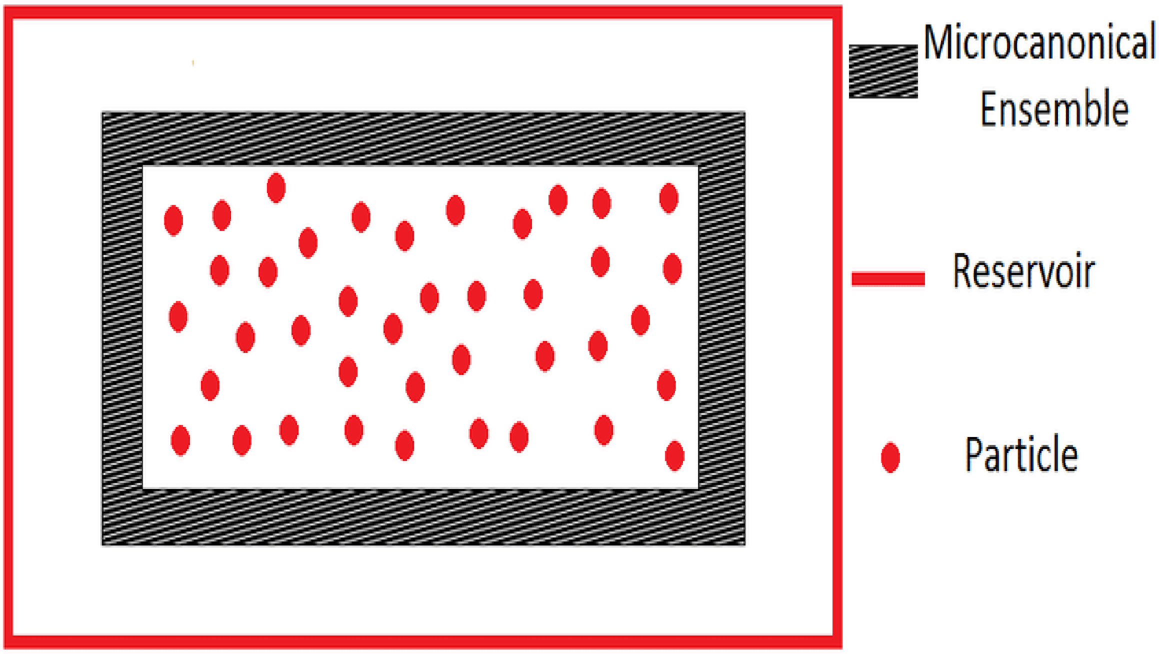
A collection of number of macroscopically identical but essentially independent systems. The term macroscopically identical means, each of the systems constituting an ensemble satisfies the same macroscopic conditions, like Volume, Energy, Pressure, Temperature and total number of particles etc.,

Types:

- Micro canonical ensemble
- Canonical ensemble
- Grand canonical ensemble

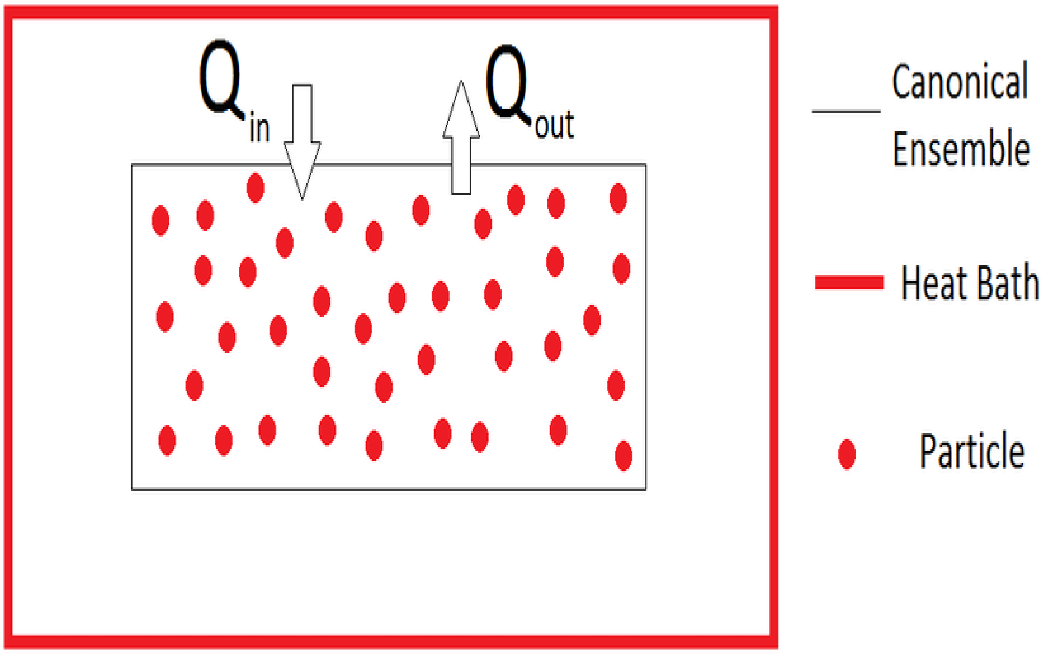
Micro canonical ensemble:

A collection of systems with exactly the same number of particles and with the same volume. The system is assumed to be isolated that it cannot exchange energy or particles with its environment, so that the energy of the system does not change.



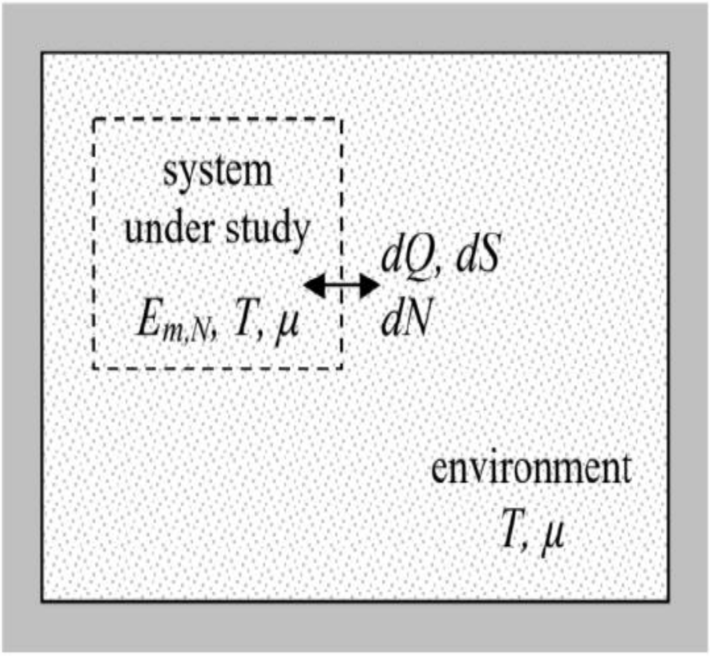
Canonical ensemble:

A canonical ensemble is a collection of systems characteristics of systems characterised by the same values of N, V and T. It is the sum of microcanonical ensemble.



Grand Canonical ensemble:

An ensemble with constant chemical potential μk of all components, and constant volume V that is at thermal equilibrium with a heat bath at constant temperature T and in chemical equilibrium with its environment is called a grand canonical ensemble. It is the sum of Canonical ensemble.



Microstate:

Microstate is a term that describes the microscopic properties of a thermodynamic system. Changes in quantum states.

Macrostate:

Macrostate is a term that describes the macroscopic properties of a thermodynamic system. Changes in Temperature, pressure, volume, and density.

Classical and quantum statistics

Classical Statistics:

- Classical statistics, also known as classical thermodynamics or classical statistical mechanics, is based on classical mechanics, which describes the behaviour of macroscopic objects according to Newton's laws of motion.

- In classical statistics, particles are treated as distinguishable entities, meaning that one can always track the individual motion and properties of each particle.
- Classical statistics is appropriate for systems where particles have well-defined positions and momenta and do not exhibit quantum mechanical effects.
- The most common framework in classical statistics is the Maxwell-Boltzmann distribution, which describes the distribution of speeds of particles in a gas at a given temperature.

Quantum Statistics:

- Quantum statistics, on the other hand, applies the principles of quantum mechanics to systems of particles. It's essential when dealing with particles like atoms, electrons, or photons, where quantum effects are significant.
- In quantum statistics, particles are often indistinguishable, meaning that one cannot track individual particles' identities due to phenomena like quantum entanglement and the indistinguishability of particles of the same type.
- There are two main types of quantum statistics: Bose-Einstein statistics and Fermi-Dirac statistics, which describe the behaviour of bosons and fermions, respectively.
- Bose-Einstein statistics apply to particles with integer spin (bosons), such as photons, while Fermi-Dirac statistics apply to particles with half-integer spin (fermions), such as electrons.
- Quantum statistics plays a crucial role in understanding phenomena like superconductivity, superfluidity, and the behaviour of particles in extremely cold conditions (e.g., Bose-Einstein condensation).

Maxwell - Boltzmann statistics

Consider an ideal case in closed in a vessel of Volume V forming an isolated system hence total energy "u" of all the molecules of the gas remains constant. let n be the number of molecules in the gas. we are interested to find energy wise distribution of these n molecules having total energy "u" enclosed in a volume V in the equilibrium state are most probable state.

We can divide energy u into k intervals $u_1, u_2, \ldots\ldots.., u_k$. Let $g_1, g_2, \ldots\ldots., g_k$ be the number of cells in energy intervals $u_1, u_2, \ldots\ldots.., u_k$respectively. Let $n_1, n_2, \ldots\ldots, n_k$be the number of particles in cells $g_1, g_2, \ldots\ldots., g_k$respectively. then thermodynamical probability of Macrostate $(n_1, n_2, \ldots\ldots, n_k)$ is given by

$$w = n!\,(g_1)^{n_1}(g_2)^{n_2} \ldots\ldots..(g_k)^{n_k}$$

Consider an ideal gas in close in the vessel of Volume V. Forming an isolated system. Hence, total energy u of all the molecules of the gas remains constant. Let N be the number of molecules in the gas. We are interested to find NHY distribution of this en molecules having total energy u enclosed in a volume in the equilibrium state are most probable state.

Weekend debate energy u into k intervals$u_1, u_2, \ldots\ldots.., u_k. at\ g_1, g_2, \ldots\ldots., g_k$Be there number of cells in energy intervals$u_1, u_2, \ldots\ldots.., u_k$respectively. Let $n_1, n_2, \ldots\ldots, n_k$Be the number of Particles in cells$g_1, g_2, \ldots\ldots., g_k$ respectively. The thermodynamics killed probability of Macrostate $n_1, n_2, \ldots\ldots, n_k$is given by

$$w = \frac{n!\,(g_1)^{n_1}(g_2)^{n_2} \ldots\ldots..(g_k)^{n_k}}{n_1!\,n_2! \ldots\ldots\ldots\ldots..n_k!}$$

Taking log on both sides,

$$log\,w = \log\left[\frac{n!\,(g_1)^{n_1}(g_2)^{n_2}\ldots\ldots..(g_k)^{n_k}}{n_1!\,n_2!\ldots\ldots\ldots\ldots..n_k!}\right]$$

$$log\,w = logn! + log(g_1)^{n_1} + log(g_2)^{n_2} + \cdots + log(g_k)^{n_k}$$
$$- \log[n_1!\,n_2!\ldots\ldots\ldots\ldots..n_k!]$$

$$log\,w = logn! + [n_1\log(g_1) + n_2\log(g_2) + \cdots + n_k\log(g_k)] - [\log n_1! + \log n_2! + \cdots + \log n_k!]$$

$$log\,w = logn! + \sum_{i=1}^{k} n_i\log(g_i) - \sum_{i=1}^{k}\log n_i! \rightarrow 1$$

From Stirling formula,

$$log\,n! = \log n - x \rightarrow 2$$

Using 2 in 1 we get,

$$log\,w = (n\log n - n) + \sum_{i=1}^{k} n_i\log(g_i) - \sum_{i=1}^{k}(\mathrm{nlog}\,n - n)$$

$$log\,w = (n\log n - n) + \sum_{i=1}^{k} n_i\log(g_i) - \sum_{i=1}^{k} n_i\log g_i$$

$$-\sum_{i=1}^{k} n_i\log x_i + \sum_{i=1}^{k} n_i$$

$$log\,w = (n\log n - n) + \sum_{i=1}^{k} n_i\log(g_i) - \sum_{i=1}^{k} n_i\log g_i - \sum_{i=1}^{k} n_i\log n_i + n$$

$$log\, w = n\log n + \sum_{i=1}^{k} n_i \log(g_i) - \sum_{i=1}^{k} n_i \log n_i$$

Differentiating both sides

$$d(log\, w) = 0 + \sum_{i=1}^{k} dx_i \log g_i - \sum_{i=1}^{k} \log n_i d\, n_i + n_i \frac{1}{n_i} dn_i$$

$$d(log\, w) = \sum_{i=1}^{k} dx_i \log g_i - \sum_{i=1}^{k} \log n_i d\, n_i - \sum_{i=1}^{k} dn_i$$

now as

$$\sum_{i=1}^{k} n_i = x = constant$$

so

$$\sum_{i=1}^{k} dn_i = 0 \rightarrow 4$$

Also, most probable state is that state for which thermodynamical probability w is maximum.

Using 4&5 in 3 we get,

$$0 = \sum_{i=1}^{k} dx_i \log g_i \sum_{i=1}^{k} \log x_i d\, n_i - 0$$

$$0 = \sum_{i=1}^{k} (\log g_i - \log n_i) dx_i \rightarrow 6$$

From 4 $\sum_{i=1}^{k} dn_i = 0$

Multiply both sides by α

$$0 = \sum_{i=1}^{k} \alpha dx_i \rightarrow 7$$

Also $\sum_{i=1}^{k} n_i\, u_i = u = constant$

Differentiating on both sides

$$\sum_{i=1}^{k} (n_i\, dx_i + n_i du_i) = 0$$

Multiply both sides by β

$$\sum_{i=1}^{k} \beta u_i dx_i = 0 \rightarrow 8$$

Subtracting 7 and 8 from 6 we get

$$0 = \sum_{i=1}^{k} (\log g_i - \log n_i) dx_i - \sum_{i=1}^{k} \alpha dx_i - \sum_{i=1}^{k} \beta u_i dx_i$$

$$0 = \sum_{i=1}^{k} \left(\log \frac{g_i}{n_i} - \alpha - \beta u_i\right) dn_i = 0$$

$$\log \frac{g_i}{n_i} - \alpha - \beta u_i = 0$$

$$\log \frac{g_i}{n_i} = \alpha + \beta u_i$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta u_i}$$

$$\frac{n_i}{g_i} = e^{-\alpha - \beta u_i}$$

This is called Maxwell-Boltzmann energy distribution law.

Bose einstein energy distribution law

Bose Einstein is applied to the indistinguishable and identical particles having integral spin. These particles like photons, mesons etc are called bosons. Any number of particles can occupy a single cell i.e. Bosons don't obey Pauli's exclusion principle. Let us consider an isolated system of 'n' bosons obeying B.E statistics with volume 'v'. Let the system be divided into k-compartments such that $n_1, n_2, \ldots n_k$ are the no of particles with mean energy values $u_1, u_2, \ldots u_k$ in compartments 1,2,3,……k respectively. Let $g_1, g_2, \ldots, g_k$ be the no of elementary cells in compartments 1,2,3,….k respectively.

The Thermodynamical probability (w) for the Macrostate $(n_1, n_2, \ldots n_k)$ is given by :-

$$w = \frac{(n_1 + g_1 - 1)!}{n_1!\,(g_1 - 1)!} \times \frac{(n_2 + g_2 - 1)!}{n_2!\,(g_2 - 1)!} \times \ldots \ldots \times \frac{(n_k + g_k - 1)!}{n_k!\,(g_k - 1)!}$$

$$w = \prod_{i=1} \frac{(n_1 + g_1 - 1)!}{n_1!\,(g_1 - 1)!}$$

Since $n_i \& g_i$ are very large so $n_i + g_i - 1 \approx n_i + g_i \& \ g_i - 1 \ \approx g_i$

$$w = \prod_{i=1} \frac{(n_i + g_i)!}{n_i!\,(g_i)!}$$

Taking log on both sides

$$logw = \sum_{i=1}^{k} log(n_i + g_i)! - logn_i! - \log g_i \rightarrow 1$$

According to Stirling's formula

$$log\,n! = \log n - n \rightarrow 2$$

So

$$log(n_i + g_i) = (n_i + g_i)log(n_i + g_i) - (n_i + g_i) \rightarrow 3$$

$$logn_i! = \ n_i logn_i - n_i \rightarrow 4$$

$$logg_i! = \ g_i logg_i - g_i \rightarrow 5$$

Using 3,4&5 in 1 we get

$$logw = \sum_{i=1}^{k}[(ni + gi)log(ni + gi) - (ni + gi)] - (ni\ log\ ni - ni) - (gi\ log\ gi - gi)$$

$$logw = \sum_{i=1}^{k}(ni + gi)log(ni + gi) - (ni\ log\ ni)] - (gi\ log\ gi) \rightarrow 6$$

Differentiating both sides, we get

$$\mathrm{d}[\log w] = \sum_{i=1}^{k}[(n_i + g_i) \times \frac{1}{n_i + g_i}(dx_i + 0) + \log(n_i + g_i)(dx_i + 0)] - (n_i \times \frac{1}{n_i}dx_i + \log n_i\,dn_i) - 0$$

$$\mathrm{d}[\log w] = \sum_{i=1}^{k} log(n_i + g_i)dni - (log\ n_i dn_i) \rightarrow 7$$

The equilibrium state of most probable state is that for which thermodynamical probability (w) is max i.e. d[w]=0

$$\mathrm{d}[\log w] = 0 \rightarrow 8$$

Using 8 in 7 we get

$$0 = \sum_{i=1}^{k} [log(\frac{n_i + g_i}{n_i})]dn_i \rightarrow 9$$

In isolated system, total no of particles n is constant & total energy of particles remains constant i.e. $n_1+n_2 + \ldots\ldots n_k$= constant

$$\sum_{i=1}^{k} n_i = constant$$

$$\sum_{i=1}^{k} dn_i = 0$$

$$\sum_{i=1}^{k} \propto dn_i = constant \rightarrow 10$$

n1k1+n2k2 +…..$n_k u_k$= constant

$$\sum_{i=1}^{k} dn_i u_i = constant$$

$$\sum_{i=1}^{k} dn_i u_i = 0$$

$$\sum_{i=1}^{k} \beta\, u_i\, dn_i = 0 \rightarrow 11$$

Subtracting 10&11 from 9 we get

$$0 = \sum_{i=1}^{k} [log(\frac{n_i + g_i}{n_i})]dn_i - \sum_{i=1}^{k} \propto dn_i - \sum_{i=1}^{k} \beta\, u_i\, dn_i$$

$$0 = \sum_{i=1}^{k} [log(\frac{n_i + g_i}{n_i}) - \propto - \beta\, u_i]dn_i$$

$$\sum_{i=1}^{k} [log(\frac{n_i + g_i}{n_i}) - \propto - \beta\, u_i] = 0$$

$$log\left(\frac{n_i + g_i}{n_i}\right) = \propto + \beta\, u_i$$

$$\left(\frac{n_i + g_i}{n_i}\right) = e^{\propto + \beta\, u_i}$$

$$\frac{g_i}{n_i} = e^{\propto + \beta\, u_i - 1}$$

$$\frac{n_i}{g_i} = \frac{1}{e^{\propto + \beta\, u_i - 1}}$$

This is called Bose- Einstein energy distribution law.

Fermi dirac energy distribution law

Fermi Dirac statistics is applied to the indistinguishable particles which obey Pauli’s exclusion principle. These particles have half integral spin like electrons, protons, neutrons etc. Only one particle can occupy a single cell.

Let us consider an isolated system of ‘n’ fermions obeying Fermi Dirac statistics with volume V. Let the system be divided into k compartments such that n_1, n_2, n_k,…….,n_k are the number of particles with mean energy values u1, u_2,……u_k in compartments 1,2, 3,…..,k respectively. Let g_1, g_2,….g_k be the number of elementary cells in compartments 1,2,3,…..,k. As each cell can contain either zero or one particles according to Pauli's exclusion principle so the number of cells should be more than or equal to the number of particles in each compartment.

Thermodynamical probability of microstate ($n_1,n_2,\ldots,n_k$) is given by ,

$$w = g_1c_{n_1} \times g_2c_{n_2} \times \ldots\ldots\ldots\ldots.\times g_kc_{n_k}$$

$$w = \frac{g_1!}{n_1!\,(g_1 - n_1)!} \times \frac{g_2!}{n_1!\,(g_1 - n_1)!} \times \ldots.\frac{g_n!}{n_k!\,(g_k - n_k)!}$$

$$w = \prod_{i=1}^{k} \frac{g_i!}{n_i!\,(g_i - n_i)!}$$

where *Π* denotes multiplication of terms for various values of 'i'.

Taking log on both sides,

$$logw = \sum_{i=1}^{k} [\log g_i! \; - \log n! - log(g_i - n_i)!]$$

$$[log\left(\frac{a}{bc}\right) = loga - logb - logc]$$

Using Stirling formula,

$$logn! \; = nlogn - n \rightarrow 2$$

Using (2) in (1) we get,

$$logw = \sum_{i=1}^{k} (g_i \log g_i - g_i) - (n_i \log n_i - n_i) - [(g_i - n_i)!\, log(g_i - n_i)]$$

$$log\, w = \sum_{i=1}^{k} g_i\, log\, g_i - g_i - n_i\, log\, n_i + n_i - (g_i - n_i)\, log(g_i - n_i) + g_i$$
$$- n_i$$

$$log\, w = \sum_{i=1}^{k} g_i\, log\, g_i - n_i\, log\, n_i - (g_i - n_i)\, log(g_i - n_i)$$

differentiating both sides we get,

$$d[log\, w] = \sum_{i=1}^{k} [0 - \left(n_i \times \frac{1}{n_i} dn_i + \log n_i\, dn_i\right) - (g_i - n_i) \times \frac{1}{(g_i - n_i)} \cdot$$
$$\times - dx_i(g_i - n_i) + \log(g_i - n_i)\,(0 - dx)]$$

$$d[log\, w] = \sum_{i=0}^{k} [- dx_i - dx_i logn_i + dx_i + dx_i \log(g_i - n_i)]$$

$$d[log\, w] = \sum_{i=0}^{k} [\log(g_i - n_i) - logn_i]\, dx_i \rightarrow 3$$

Most probable state or equilibrium state is that for which thermodynamical probability W is maximum d[w]=0

$$\mathrm{d}[\log w] = 0 \rightarrow 4$$

Using 4 in 3 we get,

$$0 = \sum_{i=0}^{k} \log(\frac{g_i - n_i}{n_i})\, dn_i \rightarrow 5$$

As $n = \sum_{i=0}^{k} n_i = constant$

So,

$$\sum_{i=0}^{k} dx_i = 0$$

multiplying both sides by α we get

$$\sum_{i=0}^{k} \alpha \ dx_i = 0 \rightarrow 6$$

$$0 = \sum_{i=0}^{k} u_i \, dx_i \rightarrow 7$$

Multiplying 7 both sides byβ

$$0 = \sum_{i=0}^{k} \beta u_i \, dx_i \rightarrow 8$$

Subtracting 6&8 from 5 we get,

$$0 = \sum_{i=0}^{k} \log(\frac{g_i - n_i}{n_i}) \, dn_i - \sum_{i=0}^{k} \alpha \ dx_i - \sum_{i=0}^{k} \beta u_i \, dx_i$$

$$0 = \sum_{i=0}^{k} [\log(\frac{g_i - n_i}{n_i}) \, dn_i - \alpha \ dx_i - \beta u_i] \, dx_i$$

$$\log\left(\frac{g_i - n_i}{n_i}\right) - \ \alpha - \beta u_i = 0$$

$$\log\left(\frac{g_i - n_i}{n_i}\right) = \alpha + \beta u_i$$

$$\frac{g_i}{n_i} - 1 = e^{\alpha + \beta u_i}$$

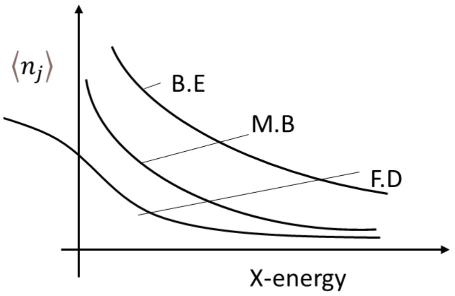
$$\frac{g_i}{n_i} = \frac{1 + e^{\alpha+\beta u_i}}{1}$$

$$n_i = \frac{g_i}{1 + e^{\alpha+\beta u_i}}$$

This is known as Fermi-dirac distribution law.

Comparison of three statistics

Fermi Dirac statistics	**Bose Einstein Statistics**	**Maxwell-Boltzmann Statistics**
1. Fermions have half integral spin. 2. They are indistinguishable. 3. Partition function of fermi Dirac-Statistics. 4. Average occupancy of fermi dirac statistics. • $n_i = \frac{g_i}{1+e^{\alpha+\beta u_i}}$	1. Bose has integral spin. 2. They are indistinguishable. 3. Partition function of Bose Einstein statistics. 4. Average occupancy of Bose- Einstein statistics. • $\frac{n_i}{g_i} = \frac{1}{e^{\propto+\beta\, u_i-1}}$	1. They are distinguishable. 2. Partition function of Maxwell Boltzmann statistics. 3. Average occupancy of Maxwell Boltzmann statistics. • $\frac{n_i}{g_i} = e^{-\alpha-\beta u_i}$



If x = 0 F.D = ½

If X = 0 B.E =infinity

If X = 0 M.D = 1