VIVEKANANDA COLLEGE THAKURPUKUR

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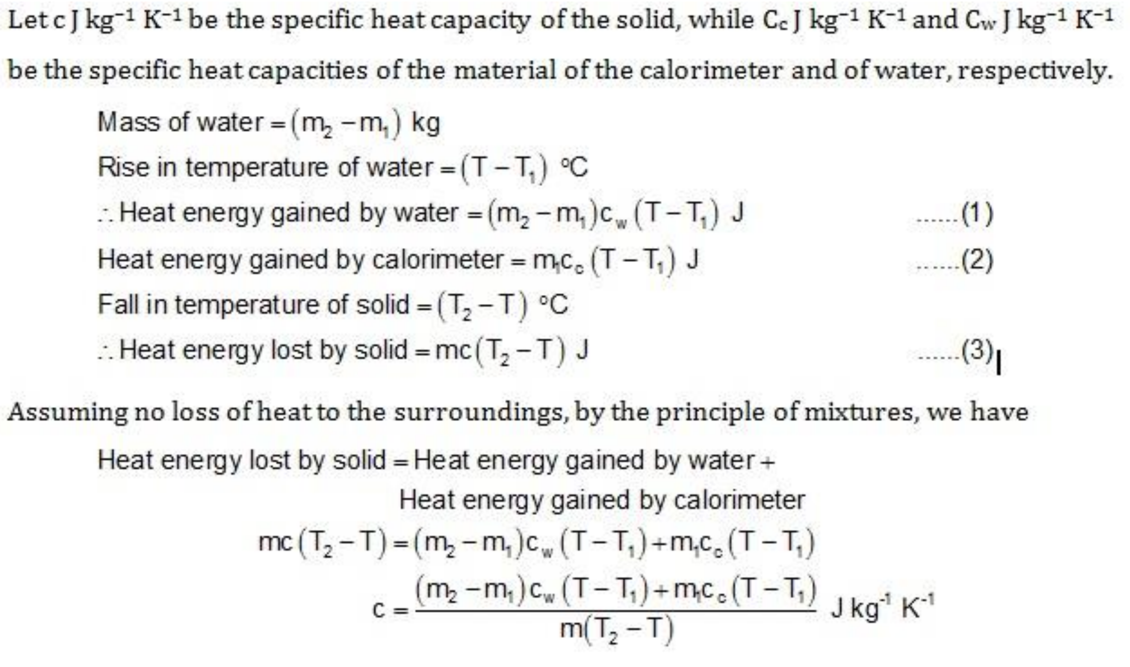
SUBJECT- THERMODYNAMICS

SEMESTER-2 (CC3)

Thermodynamics is the branch of physical science that deals with the relations between heat and other forms of energy (such as mechanical, electrical, or chemical energy), and, by extension, of the relationships between all forms of energy.

SPECIFIC HEAT OF SOLID

Specific heat of a solid or liquid is the amount of heat that raises the temperature of a unit mass of the solid through 1° C. We symbolise it as C. In S.I unit, it is the amount of heat that raises the temperature of 1 kg of solid through 1K .



Let c J kg^{-1} K^{-1} be the specific heat capacity of the solid, while C_c J kg^{-1} K^{-1} and C_w J kg^{-1} K^{-1} be the specific heat capacities of the material of the calorimeter and of water, respectively.

$$\text{Mass of water} = (m_2 - m_1)\ \text{kg}$$
$$\text{Rise in temperature of water} = (T - T_1)\ {}^\circ\text{C}$$
$$\therefore \text{Heat energy gained by water} = (m_2 - m_1)c_w(T - T_1)\ \text{J} \qquad \ldots\ldots(1)$$
$$\text{Heat energy gained by calorimeter} = m_1 c_c (T - T_1)\ \text{J} \qquad \ldots\ldots(2)$$
$$\text{Fall in temperature of solid} = (T_2 - T)\ {}^\circ\text{C}$$
$$\therefore \text{Heat energy lost by solid} = mc(T_2 - T)\ \text{J} \qquad \ldots\ldots(3)$$

Assuming no loss of heat to the surroundings, by the principle of mixtures, we have

$$\text{Heat energy lost by solid} = \text{Heat energy gained by water} + \text{Heat energy gained by calorimeter}$$
$$mc(T_2 - T) = (m_2 - m_1)c_w(T - T_1) + m_1 c_c (T - T_1)$$
$$c = \frac{(m_2 - m_1)c_w(T - T_1) + m_1 c_c (T - T_1)}{m(T_2 - T)}\ \text{J kg}^{-1}\ \text{K}^{-1}$$

PHONON

The study of phonons is an important part of solid state physics, because phonons play an important role in many of the physical properties of solids, such as the thermal conductivity and the electrical conductivity.In insulating solids, phonons are also the primary mechanism by which heat conduction takes place.

PHONON HEAT CAPACITY

Heat Capacity or thermal capacity is a physical property of matter, defined as the amount of heat to be supplied to a given mass of a material to produce a unit change in its temperature. The SI unit of heat capacity is joule per kelvin (J/K). Heat capacity is an extensive property.

Debye T^3 law :

In thermodynamics and solid state physics, the Debye model is a method). It treats the vibrations of the atomic lattice (heat) as phonons in a box, in contrast to the Einstein model, which treats the solid as many individual, non-interacting quantum harmonic oscillators. The Debye model correctly predicts the low temperature dependence of the heat capacity, which is proportional to – the Debye T^3 law.

THERMAL ELECTRICITY :

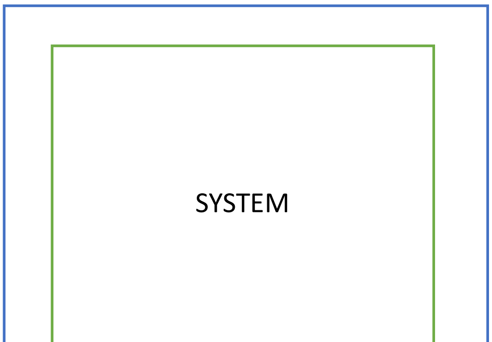
Thermal electricity means electricity generated due to heat. Power station in which heat energy is used to convert water to steam and spins the steam turbine which drives an electrical generator. Heat source can be of any type like coal, petrolium, solar thermal electric etc.

Surroundings and the boundary :

By surroundings of the system is meant everything near but outside it that may influence its behaviour. The boundary of a system is the envelope that encloses the system and thereby separates its from its surroundings . This is illustrated in Fig 1 , The importance of the boundary of a system lies in visualising distinctly and it may be real or imaginary.

The boundary that doesnot allow any exchange of matter and energy between the system and its surroundings is called an isolating boundary. A system bounded by an isolating boundary is an isolated system and is not important thermodynamically.

A system with a boundary that permits exchange of matter and energy between the system and its surroundings is called an open system . The system however is said to be a closed system if its boundary allows exchange of energy , but prevents exchange of matter between the system and the surroundings. A closed system , however , is not an isolated system.



The exchange of energy between the system and the surroundings may take place either thermally or by doing work on the system. A system is said to be dynamically insulated if any exchange of energy in the form of work between the system and the surroundings is impossible. The surface or boundary that prevents thermal iteraction with surroundings is called adiabatic, and the system is thermally isolated. However heat exchange can occur through the boundary , it is said to be diathermic . A system with a diathermic boundary is in thermal contact with the suroundings.

Chemical Potential:

The chemical potential μ is the amount of energy required to add a single particle to a thermodynamic system in equilibrium. The process of addition of the particle is such that the equilibrium is retainedeven on addition. It appears that the energy should be zero which however is not true, since for equilibrium after the addition requires that the energy of the added particle is comparable to the average energy of a particle already in the system.

So if dN be the change in the number of particles of the system, then the work done is given by

$$\partial W = \mu dN$$

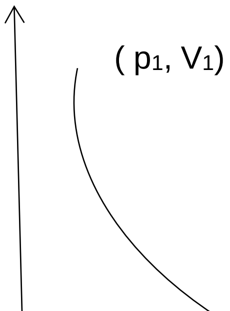
If the system is heterogeneous having many species,

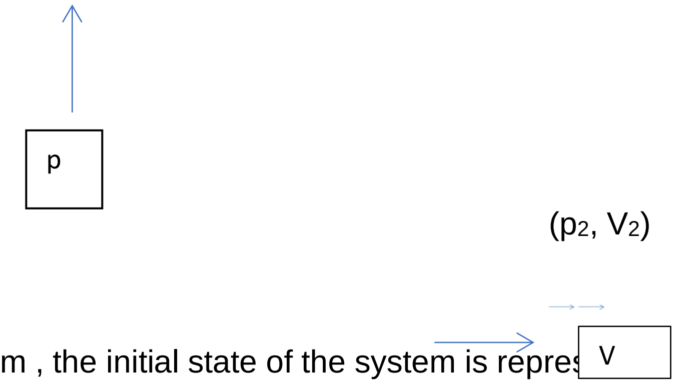
$$\partial W = \mu_1 dN_1 + \mu_2 dN_2 + \mu_3 dN_3 + \ldots\ldots\ldots\ldots\ldots + \ldots\ldots\ldots$$

Where dN_i is a change in the particle number of ith species of the system with a chemical potential μ_i .

Thermodynamic Process : Concept of reversibility :

In thermodynamics, a reversible process is a process whose direction can be returned to its original position by inducing infinitesimal changes to some property of the system via its surroundings. Having been reversed, it leaves no change in either the system or the surroundings.

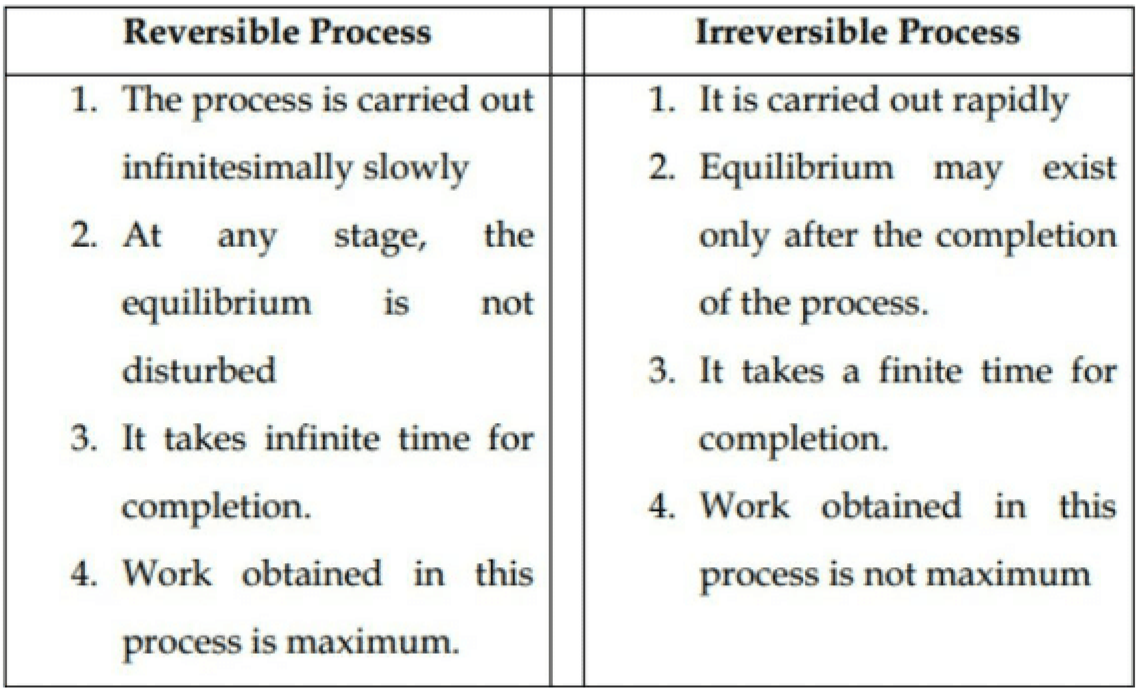




In this adjacent diagram , the initial state of the system is repres by the point (p_1,V_1) , the system undergoes an expansion , and the final state of the system is defined by the point (p_2,V_2) . This diagram is called the **Indicator Diagram**.

Irreversible Process:

An irreversible process is a thermodynamic process that departs from equilibrium. In terms of pressure and volume, it occurs when the pressure (or the volume) of a system changes dramatically and instantaneously that the volume (or the pressure) do not have the time to reach equilibrium



Reversible Process	Irreversible Process
1. The process is carried out infinitesimally slowly 2. At any stage, the equilibrium is not disturbed 3. It takes infinite time for completion. 4. Work obtained in this process is maximum.	1. It is carried out rapidly 2. Equilibrium may exist only after the completion of the process. 3. It takes a finite time for completion. 4. Work obtained in this process is not maximum

Quasistatic Process :

In thermodynamicss, a **Quasi-static process** is a thermodynamic processs that happens slowly enough for the system to remain in internal equilibrium. An example of this is quasi-static compression, where the volume of a system changes at a slow rate enough to allow the pressure to remain uniform and constant throughout the system.

Quasi means 'as if'. This process is a succession of equilibrium states and infinite slowness is its characteristic feature.

Only in quasistatic process can we define intensive
quantities (like Pressure, Temperature, Specific volume, Specific entropy) of the system at every instant during the whole process; Otherwise, since no internal. equilibrium is established, different parts of the system would have different values of these quantities.

1st law of thermodynamics : The thermodynamic equilibrium states that if a system whose temperature is different from the surroundings and on which work may be performed , undergoes a transformation , thee energy transferred by means other than performance of work (non – mechanical) is equal to the difference between the adiabatic work (Uf-Ui) and non-adiabatic work (-W) and is called heat.

Q= (Uf-Ui) - (-W) = Uf – Ui + W …… (1)

may be stated as the mathematical formulation of the 1st law of thermodynamics.

Mathematical Formulation Of 1st Law :

The equation 1 may be written as

dQ = dU + dW

For a *hydrostatic or chemical* system

dQ = dU + pdV

Entropy:

Ithe measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. Because work is obtained from ordered molecular motion, the amount of **entropy** is also a measure of the molecular disorder, or randomness, of a system. The entropy of inhomogeneous systems is the sum of the entropies of the various subsystems. The laws of thermodynamics hold rigorously for inhomogeneous systems even though they may be far from internal equilibrium. The only condition is that the thermodynamic parameters of the composing subsystems are (reasonably) well-defined.

Free Energy :

In physics and physical chemistry, **free energy** refers to the amount of internal **energy** of a thermodynamic system that is available to perform work. ... Helmholtz **free energy** is **energy** that may be converted into work at constant temperature and volume.

Helmholtz Free Energy

Helmholtz free energy in thermodynamics is a thermodynamic potential which is used to measure the work of a closed system with constant temperature and volume. It can be defined in the form of the following equation:

$$F = U - TS$$

Where,

- F is the Helmholtz free energy in Joules
- U is the internal energy of the system in Joules
- T is the absolute temperature of the surroundings in Kelvin
- S is the entropy of the system in joules per Kelvin

Gibbs Free Energy (G) - The energy associated with a chemical reaction that can be used to do work. The free energy of a system is the sum of its enthalpy (H) plus the product of the temperature (Kelvin) and the entropy (S) of the system: **Gibbs free energy** (*G*) of the system, which reflects the balance between these forces.

The Gibbs free energy of a system at any moment in time is defined as the enthalpy of the system minus the product of the temperature times the entropy of the system.

$$G = H - TS$$

The Gibbs free energy of the system is a state function because it is defined in terms of thermodynamic properties that are state functions. The change in the Gibbs free energy of the system that occurs during a reaction is therefore equal to the change in the enthalpy of the system minus the change in the product of the temperature times the entropy of the system.

$$\Delta G = \Delta H - \Delta(TS)$$

Relation between chemical potential and Fermi energy

The **Fermi energy** is as you describe: it is the highest occupied **level** at absolute zero. The **Fermi level** is the **chemical potential**. It is the **energy level** with 50% chance of being occupied at finite temperature T.
The **Fermi energy** does not depend on temperature; the **Fermi level** does depend on temperature. The Fermi level is the total chemical potential for electrons (or electrochemical potential for electrons) and is usually denoted by µ .The Fermi level of a body is a thermodynamic quantity, and its significance is the thermodynamic work required to add one electron to the body (not counting the work required to remove the electron from wherever it came from). A precise understanding of the Fermi level—how it relates to electronic band structure in determining electronic properties, how it relates to the voltage and flow of charge in an electronic circuit—is essential to an understanding of solid-state physics."