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ATOMIC ENERGY CENTRAL SCHOOL-KUDANKULAM

Handout –Module-1/5

Subject-Chemistry **Class-XI**

Lesson No.-Unit-6 (Thermodynamics)

Name of the topic-Basic terms involved in thermodynamics

INTRODUCTION

- Thermodynamics is all about energy transformation
- Various types of energies are inter related .Under certain conditions these energies may be transformed from one form to another. Energy stored in the molecules can be released as heat during chemical reactions, when a fuel like methane, cooking gas or coal burns in air.
- The chemical energy may also be used to do mechanical work when a fuel burns in an engine or to provide electrical energy through a galvanic cell like dry cell.
- The study of these energy transformations forms the subject matter of thermodynamics.
- The laws of thermodynamics deal with energy changes of macroscopic systems involving a large number of molecules rather than microscopic systems containing a few molecules.

Thermodynamics is not concerned about how and at what rate these energy transformations are carried out, but is based on initial and final states of a system undergoing the change.

SOME BASIC TERMS

SYSTEM- A system in thermodynamics refers to that part of universe in which observations are made. System is part of the universe with real or imaginary bounderies.eg-A room, an engine, Human body etc.

SURROUNDINGS- The surroundings include everything other than the system.

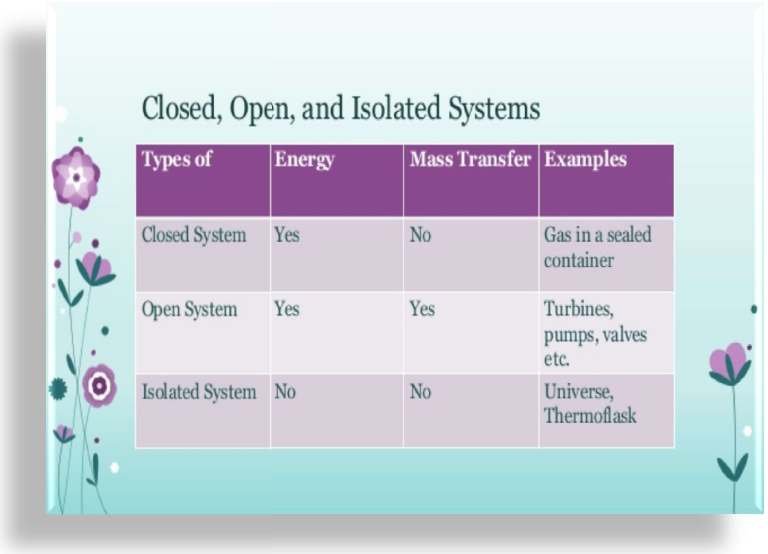
- System and the surroundings together constitute the Universe .Surrounding is adjacent to real or imaginary boundary
- universe = system + surrounding

CLOSED SYSTEM

- In a closed system, there is no exchange of matter, but exchange of energy is possible between system and the surroundings. The presence of reactants in a closed vessel made of conducting material e.g.copper or steel is an example of a closed system.
- Coffee in closed stainless steel is an example of closed system.
- A rubber balloon filled with air and tightly closed.

ISOLATED SYSTEM

- In an isolated system, there is no exchange of energy or matter between the system and the surroundings ,the presence of reactants in a thermos flask or any other closed insulated vessel is an example of an isolated system.Eg –Coffee in Thermos Flask.



PROPERTIES OF A SYSTEM

- State of system is defined by a particular set of measurable quantities called properties by which the system can be described. For example Temperature, pressure, volume defines the thermodynamic state of the system.

Properties can be categorised into intensive and extensive properties on the basis of dependence on the size or mass of the system.

- **Intensive properties**-Property whose value is independent of the size or mass of the system. For example Temperature, Density, Pressure etc.
- Boiling point of water is 100ºC, irrespective of volume of 1 liter or 2 liters at 1 atm. pressure. So boiling point is intensive property.
- **Extensive Properties**—Property whose value depends on the size or mass of the system. For example-mass, volume internal energy, heat capacity, number of moles etc.
- Volume of one mole of gas at STP is 22.4 $dm^{3,}$ but two moles of gas occupies 44.8 $dm^{3\ at}$ STP. So volume is extensive property.
- **Extensive and Intensive properties**
- Extensive properties are additive intensive properties are non additive
- Ratio of two extensive properties gives an intensive property.

  Eg –Density=Mass/Volume

  Molarity=Number of moles of solute/volume of solution
- An extensive property can be converted into intensive property by defining it per gram ,per mole per litre

STATE OF A SYSTEM

- It implies the conditions of existence of a system when its macroscopic properties have definite values
- Macroscopic properties are Pressure (P) volume (V) temperature (T) amount (n).
- **Important features**

- Variation in one or more macroscopic properties brings a change in the state of the system, when other macroscopic properties attain new values .thus these properties are called state variables or state functions.
- Initial state refers to the starting state of system in equilibrium. After interaction with surrounding the system attains another equilibrium state which is referred as final state of the system.
- Thermodynamic state should not be confused with physical state or phase.
- A system is said to be in thermodynamic equilibrium if its macroscopic properties do not change with time

STATE FUNCTION OR STATE VARIABLE

- The system must be described in order to make any useful calculations by specifying quantitatively each of the properties such as its pressure (*p),* volume (V), and temperature (T) as well as the composition of the system. We need to describe the system by specifying it before and after the change. We specify the state of the system by state functions or state variables.
- State function is thermodynamic property whose value depends only on initial and final states of the system. These are independent of manner as to how the change is brought about.
- For example if 'h' is the height of a mountain between top to bottom, then h is independent of the path followed in reaching the top of the mountain. So we can say 'h' is analogous to state function.
- Some common state functions in thermodynamics are Internal Energy(U) ,Enthalpy(H),Entropy(S),Gibb's Free Energy(G),Pressure(P) ,Temperature(T), Volume(V)

PATH FUNCTION

- Function which depends on path i.e. how the process i.e. carried out to reach a state from another state depends on path.
- Example-Work, Heat, Loss of energy to due to friction.

THERMODYNAMIC FUNCTIONS

All state functions and paths functions are referred as thermodynamic functions. If thermodynamic functions doesn't change with time in the system then system is said to achieve a thermodynamic equilibrium.

EQUILIBRIUM TYPES

Thermal equilibrium: - system and surrounding are at same temperature ex: - water in equilibrium with its vapour at constant temperature.

Chemical equilibrium:-When chemical composition of the system does not change. Ex:

$N_2 + 3H_2 = 2NH_3$ (all are gases)

$PCl_5 = PCl_3 + Cl_2$ (all are gases)

Mechanical equilibrium: - there is no macroscopic movement within the system.(equality of pressure between system and surrounding)i.e. there is no movement of matter in the system with respect to its surrounding.

THERMODYNAMIC PROCESS

- It is the operation which brings change in the state of the system.
- Thermodynamic processes are of following types-
- (i) **Isothermal process** in which temperature remains constant, i.e., ($dT = 0, \Delta U = 0$).
- internal energy depends on temperature of system as there is no change in temperature
- $\therefore U_1 = U_2$
- $\therefore \Delta U = 0$
- **(**ii) **Isochoric process** in which volume remains constant, i.e., ($\Delta V = 0$).
- (iii) **Isobaric process** in which pressure remains constant, i.e., ($\Delta p = 0$).
- All the process carried out in natural environment are isobaric as atmospheric pressure remains constant

- (iv) **Adiabatic process** In which heat is not exchanged by system with the surroundings, i.e., ($\Delta q = 0$). It can be achieved by insulating system boundaries for heat transfer
- (v) **Cyclic process** It is a process in which system returns to its original state after undergoing a series of change, i.e., Δ U cyclic = 0;

  Δ H cyclic = 0
- **REVERSIBLE PROCESS**
- Reversible process a process that follows the reversible path, i.e., the process which occurs in infinite number of steps in this Way that the equilibrium conditions are maintained at each step, and the process can be reversed by infinitesimal change in the state of functions.
- **Important features of reversible process**
- Driving force is infinitesimally small
- PV work is done across the pressure difference dp
- A reversible heat transfer takes place across temperature difference dT
- It takes infinite time for completion of process
- It is an imaginary process and cannot be realised in actual practice
- Throughout the process ,the system remains infinitesimally closer to state of equilibrium and exact path of process can be drawn
- It's an ideal process
- **IRREVERSIBLE PROCESS**
- Irreversible process The process which cannot be reversed and amount of energy increases. All natural processes are Irreversible**.**
- **Important features of reversible process**
- Driving force is large and finite
- PV work is done across the pressure difference $\triangle$P
- A reversible heat transfer takes place across temperature difference $\triangle$T

- It takes finite time for completion of process
- It is a natural process and takes place in particular direction under given conditions.
- The system is far away from state of equilibrium and exact path of process cannot be defined as different part of the system is in different conditions.
- It’s a real process.
