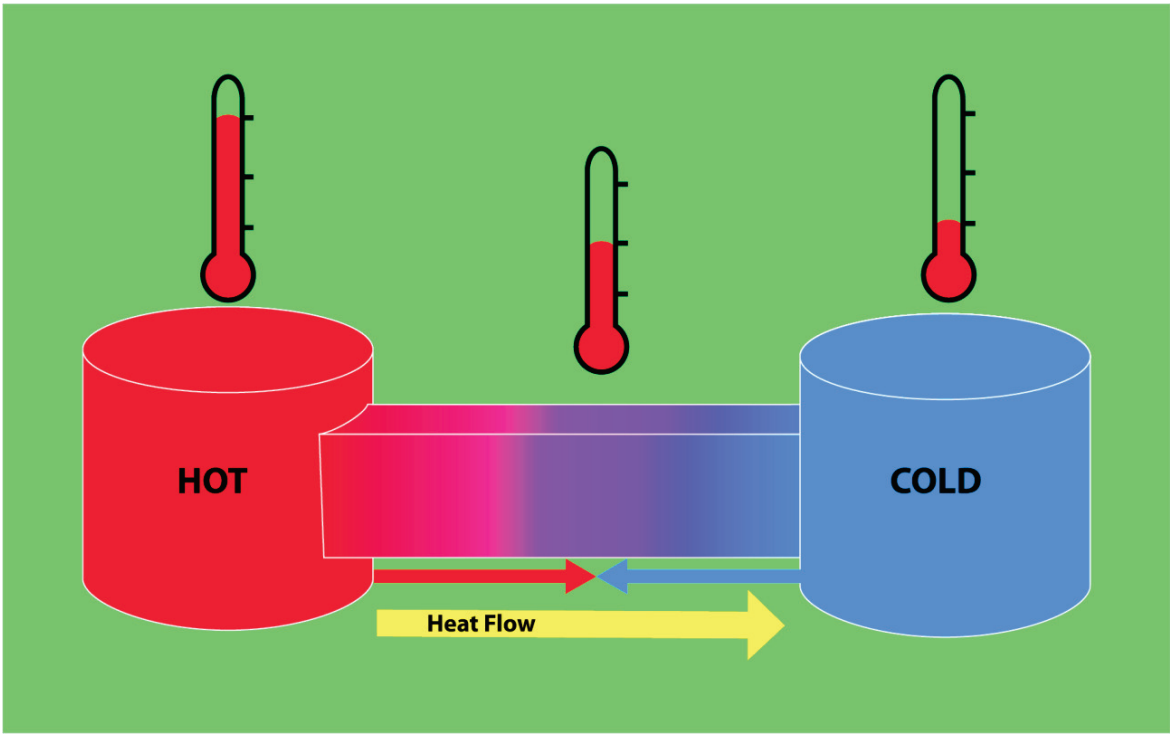
THERMODYNAMICS



THERMODYNAMICS

Introduction

Chemical thermodynamics deals with the relationship between various form of energy in a process. Thermodynamics deals with macroscopic properties. This chapter introduces a major subsidiary thermodynamic property, the Gibbs free energy which lets us express the spontaneity of a process in terms of the properties of the system. This chapter helps to explain why gases expand or diffuse.

System and Surrounding

1. **System:** A specific portion of universe under study which is seperated from rest of the universe with a boundary is called system.

2. **Surroundings:** Rest of the universe which might be in a position to exchange energy and matter with the system is known as surrounding.

Types of System:

1. **Open system:** System can be open if it can exchange both energy and matter with surroundings.

2. **Closed system:** System can be closed if it can exchange energy but not matter with surroundings.

3. **Isolated system:** System can be isolated if it can neither exchange energy nor matter with surroundings.

Extensive Properties

The properties which depend upon mass of the substance is known as extensive properties i.e., mass, volume, internal energy, enthalpy etc.

Intensive Properties

The properties which are independent of mass of the substance is known as intensive properties i.e., temperature, pressure, density, refractive index.

Thermodynamic State of a System

A state is the condition of a system as specified by its physical properties. We can describe the state of a gas by quoting its pressure (p), volume (V), temperature (T), amount (n) etc. Variables like p, V, T are called state variables or state functions because their values depend only on the state of the system and not on how it is reached.

State Functions

The thermodynamic parameters which depends only on initial and final states of system is known as state function. i.e., internal energy(E), Enthalpy (H), entropy (S), Gibb's free energy (G).

Path Functions

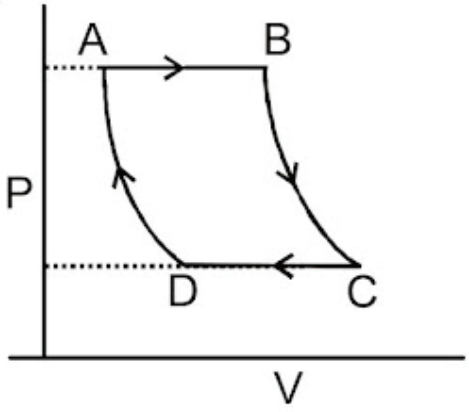
The thermodynamic parameters where value does not depend merely on initial and final state but depends upon the path followed is known as path function. i.e., heat (q), work done (W).

Thermodynamic Process

The sequence followed to change one thermodynamic state of a system into another is called thermodynamic process. The types of thermodynamic processes are:

1. **Isothermal process:** It is the process in which temperature is kept constant means temperature of initial and final state of system along with entire path of process is same.
2. **Isobaric process:** It is the process in which pressure is kept constant for entire process.
3. **Isochoric process:** It is the process in which volume is kept constant.
4. **Adiabatic process:** The process in which heat transaction across boundary is not allowed.
5. **Reversible process and Irreversible process:** In thermodynamics, a process is said to be reversible when energy change in each step of the process can be reversed by changing the variables such as pressure, volume or temperature acting on them. In such a process, the driving and opposing forces differ infinitesimally and the process can be reversed completely by increasing the opposing force by an infinitesimally small amount.

   Any process which does not take place in the above mentioned manner is said to be an irreversible process. In an irreversible process the driving and opposing force differ by a large amount.
6. **Cyclic process:** It is the process which run in close loop means process in which initial and final states are identical.

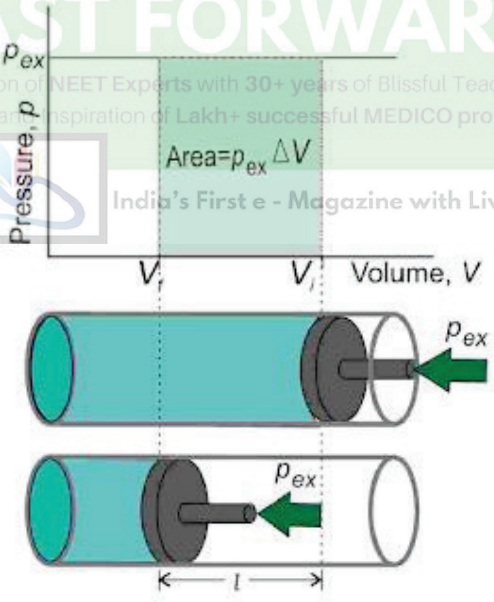


Internal Energy

Every substance is associated with definite amount of energy that is called internal energy. It is an extensive property and a state function. Internal energy of ideal gases is a function of temperature only.

Pressure-Volume Work

It is the work done when the gas expands or contracts against the external pressure. Consider a cylinder containing one mole of an ideal gas fitted with a frictionless and weightless piston having an area of cross-section A. The total volume of the gas is Vi and the initial pressure of the gas inside P.



Let the external pressure acting on the piston is Pex. If the external pressure Pex is slightly greater than P piston moves downward till the pressure inside the cylinder becomes equal to Pex. Let this change be achieved in a single step and the final volume be Vf. During this compression, suppose the piston moves a very small distance Δl. Thus, the work done on the gas is given by,

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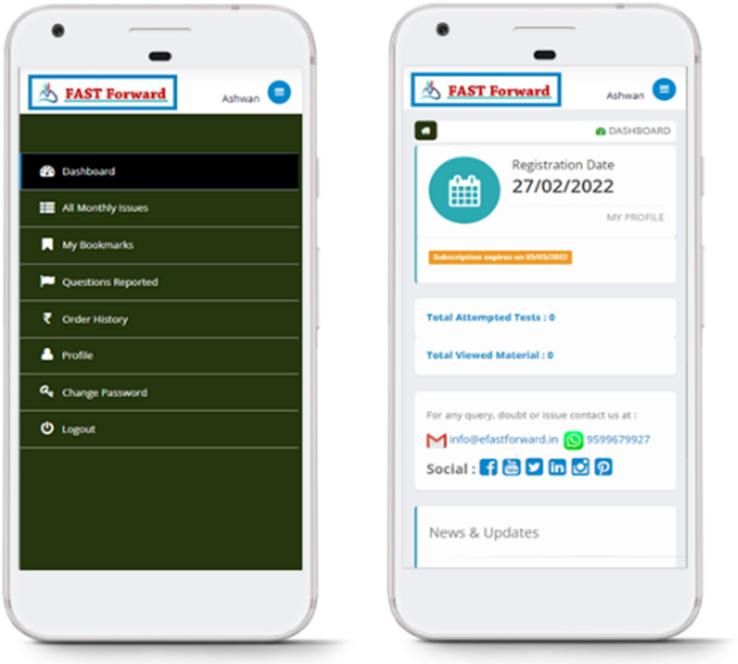

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