

CHMMAJ202-4 (Physical Chemistry - 1)

Unit 1: Chemical Thermodynamics I

Some Basic Terms Used in Thermodynamics

System : A system may be defined as any specified portion of matter under study which is separated from the rest of the universe with a bounding surface. A system may consist of one or more substances.

Surroundings : The rest of the universe which can ~~exchange~~ exchange energy and matter with the system is called the surroundings.

Example - a water bath in which a system under examination is immersed.

Different Types of System :

- (i) Isolated system : The system in which neither energy nor matter can be exchanged with the surroundings.
- (ii) Closed system : The system in which only energy can be exchanged with the surroundings.
- (iii) Isolated system : The system in which neither energy nor matter can be exchanged with the surroundings.

State of system : When microscopic properties have definite value, the conditions of existence of the system is known as the state of system.

State functions : When values of a system are independent of path followed and depend only on initial and final state, it is known as state function, e.g. ΔU , ΔH , ΔG etc.

Path functions : These depend upon the path followed e.g. Work, heat, etc.

Thermodynamic properties

Intensive properties: Properties of the system which depend only on nature of matter but not on the quantity of matter are called intensive properties, eg. pressure, temperature, specific heat, etc.

Extensive properties: Properties of the system which are dependent on the quantity of matter are called extensive properties

eg. internal energy, volume, enthalpy, etc.

Thermodynamic Process

- (i) Isothermal process: In which temperature remains constant
i.e. $(dT=0, \Delta U=0)$
- (ii) Isochoric process: In which volume remains constant
i.e. $(\Delta V=0)$
- (iii) Isobaric process: In which pressure remains constant,
i.e. $(dp=0)$
- (iv) Adiabatic process: In which heat is not exchanged by system with the surroundings, i.e. $(dq=0)$
- (v) Cyclic process: It is a process in which system returns to its original state after undergoing a series of change, i.e. $\Delta U_{\text{cyclic}}=0$; $\Delta H_{\text{cyclic}}=0$
- (vi) Reversible process: A process that follows the reversible path, i.e. the process which occurs in infinite number of steps in a way that the equilibrium conditions are maintained at each step, and the process can be reversed by infinitesimal change in the state function.
- (vii) Irreversible process: The process which cannot be reversed and amount of energy increases. All natural processes are irreversible.

Internal Energy (U)

It is the total energy within the substance. It is the sum of many types of energies like vibrational energy, translational energy, etc. It is an extensive property and state function.

Its absolute value cannot be determined but experimentally change in internal energy (ΔU) can be determined by $\Delta U = U_2 - U_1$

For exothermic process, $\Delta U = -ve$

Whereas for endothermic process, $\Delta U = +ve$

U depends on temperature, pressure, volume and quantity of matter and is independent of the method by which state has been attained.

Zeroth law of Thermodynamics or Law of Thermal Equilibrium

The law states that if the two systems are in thermal equilibrium with a third system then they are also in thermal equilibrium with each other.

First law of Thermodynamics: Energy can neither be created nor

destroyed although it can be converted from one form to the other.

Mathematically, $\Delta U = q + w$

where, $\Delta U =$ internal energy change

$q =$ heat added to system

$w =$ work added to system.

Sign convention:

- (i) q is $+ve$ = heat is supplied to the system
- (ii) q is $-ve$ = heat is lost by the system
- (iii) w is $+ve$ = work done on the system
- (iv) w is $-ve$ = work done by the system