B: Physical Chemistry

Paper IV - Physical and organic Chemistry

B.Sc. Part II

By
Sonu Ram Shankar
Assistant Professor
Department of Chemistry

Marwari College, Darbhanga

A constituent Unit of
Lalit Narayan Mithila University, Kameshwar Nagar, Darbhanga

Thermodynamics

In thermodynamic study, universe is divided in two parts, viz system and surrounding.

System: Region of universe under observation
Surrounding: Part of universe other than system

Boundary: Surface that separate system and surrounding. It can be real or imaginary

Based on movement two type of boundary
Rigid: If the boundary inhibits the system from changing its volume or shape
Non-rigid; If the boundary allows the system to change its volume or shape

Based on flow of heat
Adiabatic: If the boundary prevents thermal interactions
Diathermal: Walls that allow thermal interactions between the system

Thermodynamics

Types of system based on exchange of matter and energy with surrounding

System	Exchange	
	Matter	Energy
Open	Yes	Yes
Closed	No	Yes
Isolated	No	No

Types of properties of system
Macroscopic: average property of all the particles. (Classical thermodynamic)
Microscopic: Property of individual particles (Statistical thermodynamics)

Thermodynamics

Macroscopic properties

Based on dependence on amount there are two types of microscopic properties: intrinsic and extrinsic

Intrinsic properties: these are not dependent on the amount of particle. Example: temperature, pressure, density, concentration, viscosity, surface tension, refractive index etc.

Extrinsic properties: these are dependent on amount of particle included. Example: mass, volume and energy.

Thermodynamics

Thermodynamic equilibrium of state of system

Equilibrium state
state in which all the bulk physical properties of a system are uniform throughout the system and do not change with time.

- *Thermal equilibrium*: Two systems have the same temperature.
- *Chemical equilibrium*: When no chemical reaction occurs
- *Mechanical equilibrium*: The system experiences no unbalanced forces.

Thermodynamic equilibrium: thermal, mechanical and chemical equilibria

Thermodynamics

State variables (or thermodynamic variables or thermodynamic coordinates):
measurable variables to specify the equilibrium state of a simple system.

Example: for a gas, specifying the equilibrium values of a pair of independent variables *P* and *V*, and mass, fixes all the macroscopic (bulk) properties of the gas.

Equation of state

Equation which defines a state as function of state variables

Example: For and ideal gas,

a functional relationship between *P,V*, and *T.*

The state of a gas may be specified by stating (*P,V*), (*P,T*) or (*V,T*).

The equation of state takes the form

$$\Theta(P, V) = T$$
$$PV = nRT$$

An equilibrium state corresponds to specific values of the system parameters.

Thermodynamics

Reversible and irreversible processes

A **process**
The mechanism of bringing about changes in the different state functions when the system moves from an equilibrium state to another.

Process may be reversible or irreversible

Reversible process
if, its direction can be reversed by an infinitesimal change in the conditions.
Two conditions:
quasi-static: the process is very slow that the equilibrium state is always maintained
no dissipation of energy: If dissipation of energy occurs, the system does not retrace its previous path if the process is reversed.

Irreversible
fast and energy dissipating process.

Ideal reversible process is not possible.
All natural processes are irreversible

Thermodynamics

There are four types of processes: isothermal, isochoric, isobaric and adiabatic

Isothermal process

When temperature is maintained constant. $\Delta T = 0$

Adiabatic process

When there is no change in heat content. $\Delta Q = 0$

Isochoric process

When there is no change in volume. $\Delta V = 0$

Isobaric process

When there is no change in pressure. $\Delta P = 0$

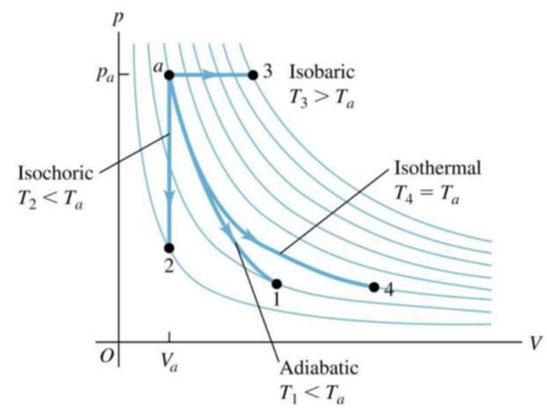

Figure 1: Different thermodynamic processes.

Thermodynamics

Perfect differentials

There are two types of function state and path function

State functions:
Quantities whose values are independent of path,
their differentials are exact and called perfect differential.
example: dP, dV, dG, dT.

Path functions:
Quantities that depend on the path followed between states
work (w) and heat (q),
their differentials are inexact

Understanding the perfect differential helps in calculation of the function through other function when it cannot be directly measured.

Thermodynamics

Mathematically
Perfect differential mean

if there is ordinary differential equation of form

$$P(x,y)dx + Q(x,y)dy$$

Is exact if

$$\frac{\partial P}{\partial y} = \frac{\partial Q}{\partial x}$$

This means

There exists a function u(x,y)

$$du = \frac{\partial u}{\partial x}dx + \frac{\partial u}{\partial y}dy$$

$$du = Pdx + Qdy$$

$$du = 0$$

$$du = C, constant$$