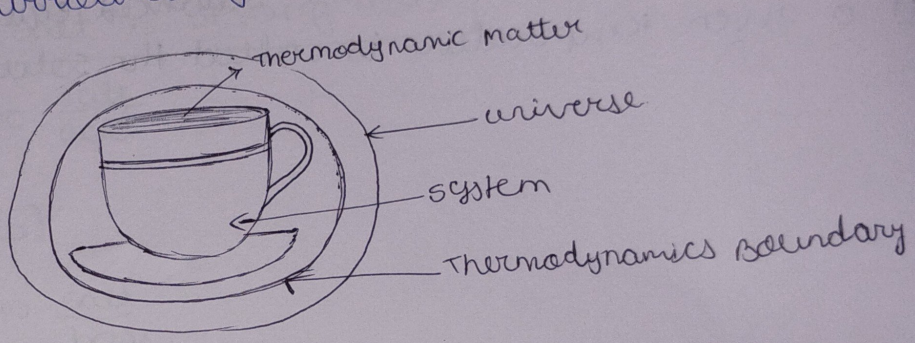
4. Chemical Thermodynamics

- Thermodynamics is concerned with the energy changes in physical and chemical transformations.

1.) System : Part of universe under the thermodynamic study is called as system.

2.) Surrounding : Part of universe other than system is called as surrounding.

3.) Boundry : The real or imaginary surface which separates system from surrounding.



* Types of systems.

1.) Open system : the system which exchanges both energy and matter with surroundings is called as open system.

2.) Closed system : the system exchanges only energy with the surroundings, is called as the closed system.

3.) Isolated system : A system that does not exchange energy as well as matter is called as isolated system.

* Properties of system.

Extensive property :

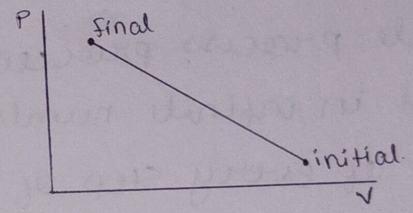
- A property which depends on the amount of matter present in a system is called an extensive property.

Ex. mass, volume, no's of moles, internal energy.

Intensive property:
- A property which does not depend upon the quantity of matter, present in a system, is called as intensive property.
Ex. Temp, Pressure.

* Path function:
- The property which depend on the path are called as Path function.
Ex. Work (W) and Heat (Q).

* State function.
- The property which depends only upon the initial and final state of the system and not on the path followed by the system is called as state function.
Ex. Entropy, internal energy.



* Thermodynamic equilibrium.
- A system is said to be in thermodynamic equilibrium when its state functions do not vary with time.
Thermodynamics considered here is limited to equilibrium states.

1.) Isothermal process:
- The process in which temperature of system remains constant during the transformation is called Isothermal process.
T = constant $\Delta T = 0$ $\Delta U = 0$. (T = temperature)

2.) Isobaric process:
- The process in which the pressure of system remains constant during the transformation is called as Isobaric process. P = constant $\Delta P = 0$ (P = pressure)

3.) Isochoric process :

- The process in which the volume of system remains constant during the transformation is called as Isochoric process. V = constant $\Delta V = 0$ (V = volume)

4.) Reversible process :

- The process in which the driving force is slightly greater than the opposing force by infinitesimal amount and be reversed, is called as reversible process.

* Features of reversible process.

i.) The driving and opposing forces differ by an infinitesimal amount.

ii.) The process can be reversed by an infinitesimal change in conditions.

iii) A reversible process proceeds infinitely slowly and takes place in infinite number of steps.

iv.) At the end of every step of the process, the system attains mechanical equilibrium with the surroundings

* Expression for pressure-volume (PV) work :

Derive the equation : $w = -P_{ext} \Delta V$

$F = -P_{ext} \times A$

$w = F \times d$

$w = -P_{ext} \times A \times d$

$w = -P_{ext} \cdot \Delta V$

$w = -P_{ext} (V_2 - V_1)$

remains as

Expression for the maximum work : [March 10; Oct 15; Feb 2
(isothermal and reversible process)

$dw = -P_{ext} \cdot dv$

$P - P_{ext} = dP$

$\boxed{P - dp = P_{ext}}$

$dw = -(P - dP) \cdot dv$

$dw = -P \cdot dv + dP \cdot dv$

$dP \cdot dv$ = very small

$dw = -P \cdot dv$

$$\int_{initial}^{final} dw = -\int_{V1}^{V2} P \, dv$$

$$w_{max} = -\int_{V1}^{V2} P \cdot dv$$

$\boxed{PV = nRT}$

$$P = \frac{nRT}{V}$$

$$w_{max} = -\int_{V1}^{V2} \frac{nRT}{V} \cdot dv$$

$$w_{max} = -nRT \int_{V1}^{V2} \frac{dv}{V}$$

$$w_{max} = -nRT \ln (V)_{V1}^{V2}$$

$$w_{max} = -nRT \ln (V2 - V1)$$

$$w_{max} = -nRT \ln \frac{V2}{V1}$$

$$w_{max} = -2.303 \, nRT \log_{10} \frac{V2}{V1}$$

$$\frac{V2}{V1} = \frac{P1}{P2}$$

$$\boxed{w_{max} = -2.303 nRT \log_{10} \frac{P1}{P2}}$$

* Internal Energy

- The definite amount of energy stored in a substance is called as internal energy. Change in Internal energy = ΔU (it is a state function.)

$$\boxed{\Delta U = U_2 - U_1}$$

* First Law of Thermodynamics.

1) Energy can be neither be created nor be destroyed, but can be converted from one form to another.
2) Energy of the universe remains constant.
3) The total internal energy of an isolated system is constant

Q. Deduce first law of thermodynamics for isothermal process.

⇒ First law of thermodynamics = $\Delta U = Q + W$.

For isothermal process, $\Delta U = 0$.

$\therefore 0 = Q + W$.

$\therefore \boxed{Q = -W}$.

Q. Deduce first law of thermodynamics for isochoric process

⇒ First law of thermodynamics = $\Delta U = Q + W$.

For isochoric process, $\Delta V = 0$.

$\therefore \Delta U = Q + W$

$\therefore \Delta U = Q + (-P_{ext} \cdot \Delta V)$ ..... $(W = -P_{ext} \Delta V)$

$\therefore \Delta U = Q + 0$

$\therefore \Delta U = Q_V$.

Write the mathematical equation for the first law of thermodynamics for adiabatic process.

In adiabatic process, there is no exchange of heat between system and its surroundings that is,

$$Q = 0$$

$$\therefore \Delta U = 0 + W.$$

$$\therefore \Delta U = W.$$

Q. Isothermal Process

i) The temperature of the system remains constant ($\Delta T = 0$).

ii) Heat is exchanged with surroundings ($Q \neq 0$)

iii) Internal energy of the system remains constant ($\Delta U = 0$)

iv) System is either open or close.

v) System is not thermally insulated.

Adiabatic Process.

i) The temperature of the system does not remain constant ($\Delta T \neq 0$).

ii) Heat is not exchanged with surroundings ($Q = 0$)

iii) Internal energy of the system does not remain constant. ($\Delta U \neq 0$)

iv) System is always isolated.

v) System is thermally insulated.