Thermodynamic Properties of system

- Variable on which property of the system depend. For eg. P, T, V, D, E etc
- The property of the system classified as

1. Extensive Property
2. Intensive Property

Extensive Property

- Whose **magnitude** depend on the **amount** of the matter present in the system.
- When the amount of matter **change** its magnitude also **change**.
- Additive.

Example- enthalpy, mass, volume, energy, weight.

Intensive property

- Magnitude **independent** of the amount of matter.
- The ration of **extensive** property represent an **intensive** property. Eg. Density= M/V.

Example- B.P- take either 1ml or 1L B.P of water is 100°C.

M.P, F.P, Surface tension, specific heat, molar heat capacity, T, P, D, viscosity.

State and state function

State variable-

- Measurable property of a system like P, T, V etc.
- State describe value of these variable.
- When one or more variable change system change to new state.
- Macroscopic properties of a system depend on these state variable.

State function

- Which depend on initial and final state but independent of the path followed by the system during the process.
- Eg. Mass (initial to final product), P, T, V etc.
- It depend on state.
- Diagram shown by board.
- It shows changes are independent of all three path but depend on initial and final state.

Thermodynamic Equilibrium

- **No change** in any thermodynamic **function** or state function like energy, pressure etc with time.
- **Type-**

1. Thermal equilibrium
2. Chemical equilibrium
3. Mechanical equilibrium

Thermal equilibrium

- System and surrounding at same temperature and no exchange of heat.
- Total energy remain const. eg. Water with its vapour at constant temperature.

Chemical equilibrium

- Chemical composition doesnot change with time.
- Eg.

$N + 3H_2 \rightarrow 2NH_3$

Composition of Reactant and product does not change with time.

Mechanical equilibrium

- **No moment of matter in system with respect to its surrounding.**
- **Mechanical property remain constant.**

Thermodynamic process

- An operation or transition by which a state of a system changes from initial state to final state.

Type of process-

1. Isothermal process($\Delta T=0$)
2. Isobaric process($\Delta P=0$)
3. Isochoric process($\Delta V=0$)
4. Adiabatic process($q=0$)
5. Reversible process
6. Irreversible process

Isothermal process

Temperature of the system constant. $\Delta T = 0$

1. **In this process temperature at initial state and final state is constant.**
2. **In this process system exchange heat energy with its surrounding to maintain constant temperature.**
3. **Occur in close system.**
4. **Internal energy of the system remains constant, hence $\Delta U = 0$.**
5. **In this process, gaseous system P, V of a change.**

Reversible process

- **A process carried out in such a manner that every stage, the driving force is only infinitesimally greater then the opposing force and it can be reversed by an infinitesimal increase in opposing force and the system exists in equilibrium with its surrounding throughout, is called a reversible process.**
- **Slow, infinite number of step.**

Irreversible process

- Unidirectional process which proceeds in a definite direction and cannot be reversed at any stage and in which driving force and opposing force differ in a large magnitude.
- Also called spontaneous process.
- They are real process not hypothetical.
- Eg. Flow of heat from high T to lower T.

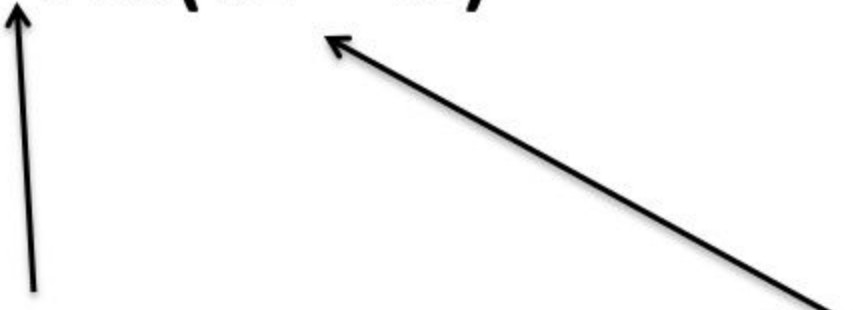
Work

- **W = F.s**
- **Work is one of the ways by which a system can exchange energy with its surrounding by changing the state of the system.**

Example- Object move by applying force(object energy)

Kind of work in chemical thermodynamics

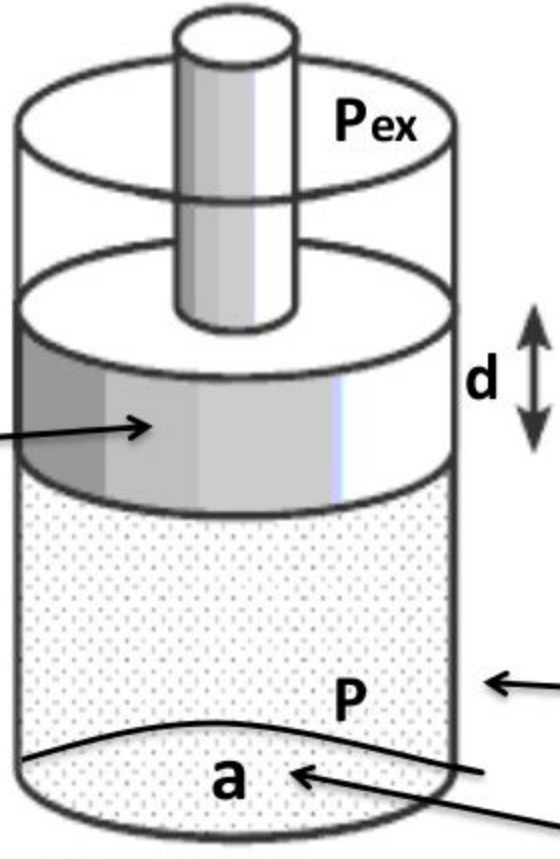
- The type of work is mechanical work i.e. pressure volume work.
- $W = - P_{ex} (V_2 - V_1)$



external pressure apply change in volume

- Work is also obtain due to chemical process or reaction.

Expression for pressure- volume work



$W = - F \times d$

Massless, frictionless Piston.

As the gas Expand it pushes Piston upward through Distance d against external force.

Ideal gas

Area of cross section

Figure 18.1 Gas in a cylinder with a moveable piston.

Expression for pressure- volume work

- If ‘a’ is the cross section area of the cylinder or piston, then

$$W = \frac{-F}{a} \times d \times a$$

Now the pressure is $P_{ex} = F/a$ and $\Delta V = d \times a$.

$$W = - P_{ex} \times \Delta V$$

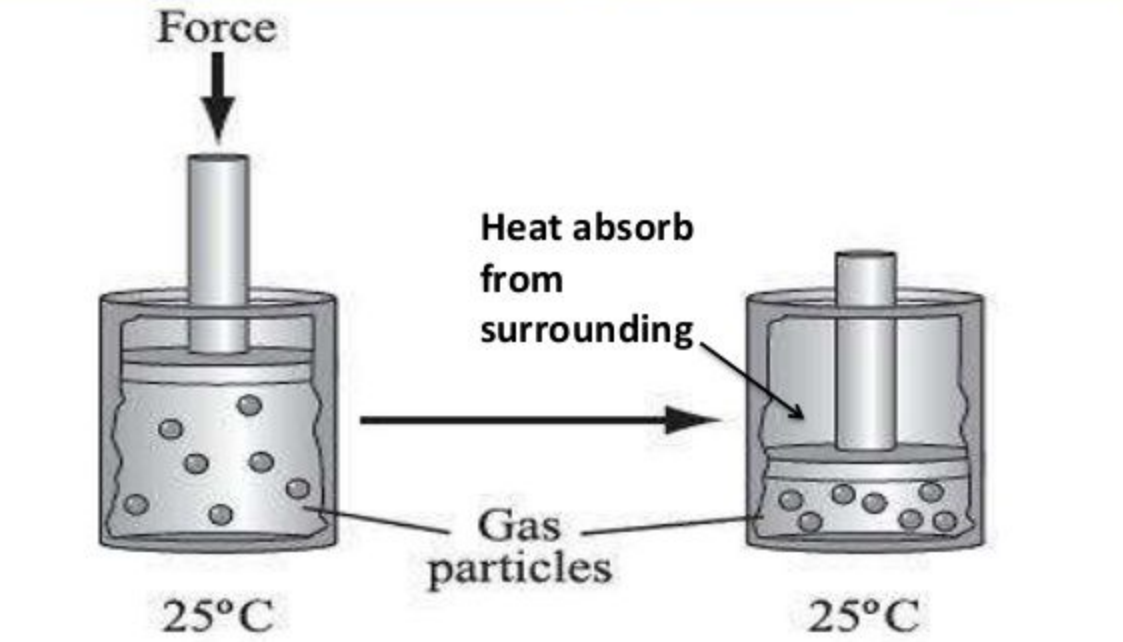
First law of thermodynamics

- **Law of conservation of energy.**
- **1 kind of energy consumed another kind of energy disappears.**
- **It is impossible to construct a perpetual motion machine.**

$$U = q + W$$

Total amount of work is converted into heat energy.

Mathematical equation of 1st Law of thermodynamic



(V_2, U_2)Final state

Initial state(V_1, U_1)

Mathematical equation of 1st Law of thermodynamic

- Due to **volume change**, the **system** perform the **work** W, hence **total energy U_2** of the system in the **final state** is,
- **$U2 = U1 + q + W$**
- **$U2 - U1 = q + W$**
- **$\Delta U = q + W$**
- For **infinitesimally small** change the mathematical expression is,
- **$dU = dq + dW$**