Basic Concepts of Thermodynamics

- B.Sc Chem (H) 3rd Semester
- Physical Chemistry

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Todays learning objectives

- What is Thermodynamics
- Laws related to Thermodynamics
- What is system and surroundings
- Types of system
- Types of process
- Classification of functions
- Statement and mathematical form of Thermodynamics 1st law
- Concepts of Enthalpy

THERMODYNAMICS

- Thermodynamics is a branch of Physical Chemistry in which the motion of heat i.e. the change of heat of any chemical substance during any chemical or physical change is studied.
- Thermodynamics monitors the effects of heat , energy and work of a system
- Thermodynamics is only deals with macroscopic changes and observations.

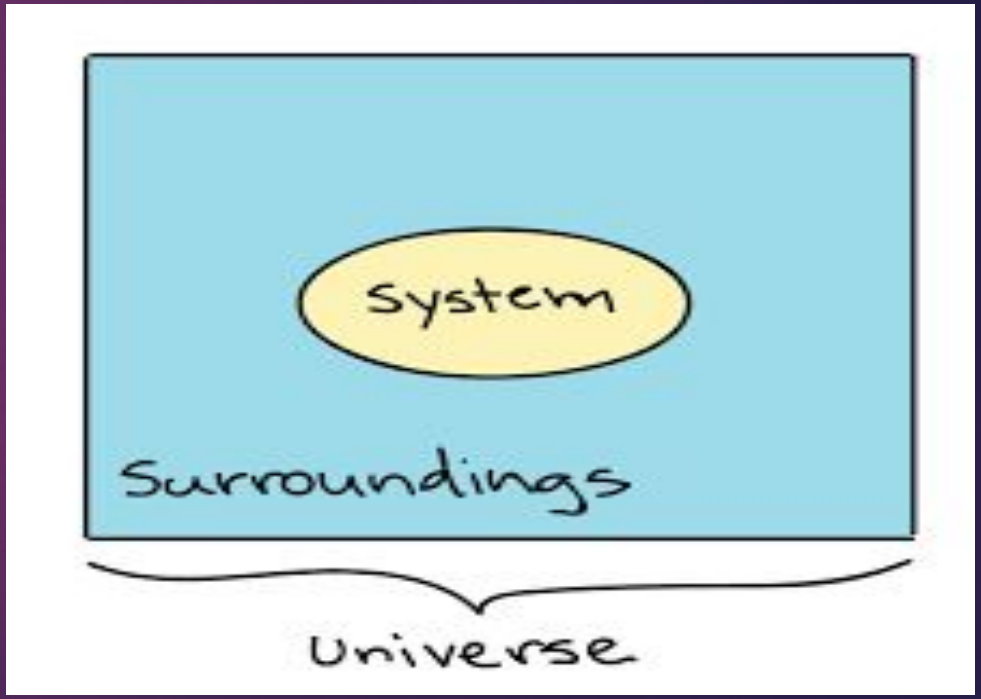
Laws of Thermodynamics

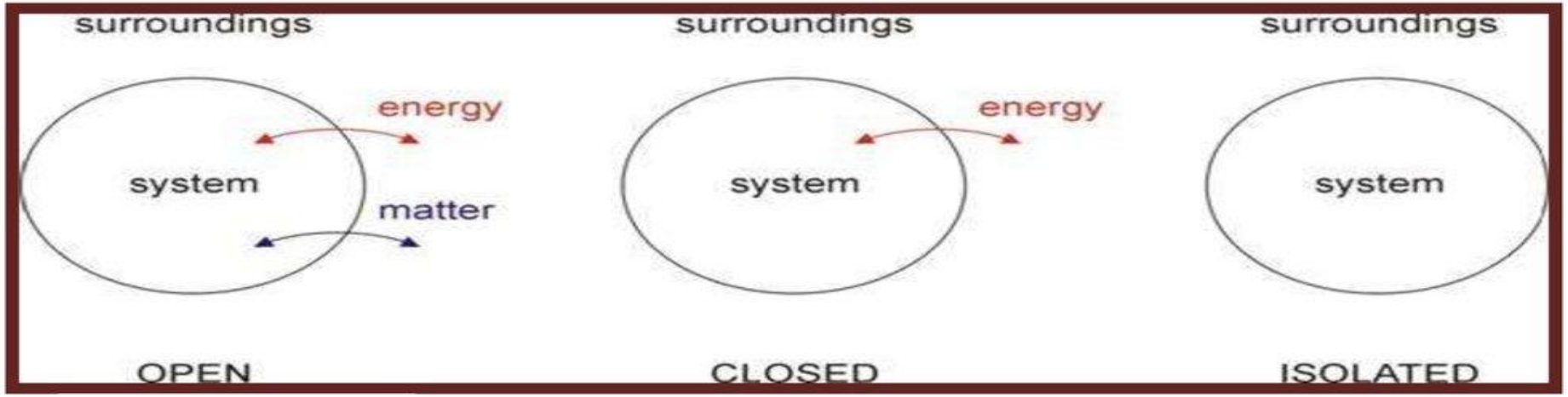
- Zeroth law of Thermodynamics- When two bodies are in thermal equilibrium with a third body, they are also in thermal equilibrium with each other.
- First law of thermodynamics- This law is related to conservation of energy i.e. energy can neither be created nor be destroyed, it can only be transformed from one form to another.
- Second law of thermodynamics- The heat taken from the source is not completely convertible to mechanical work i.e. in other words this is impossible to construct an engine with 100% efficiency.
- Third law of Thermodynamics- For an isolated system e.g. for any perfect crystalline solid at zero kelvin temperature the entropy will be zero.

Common terms using in thermodynamics

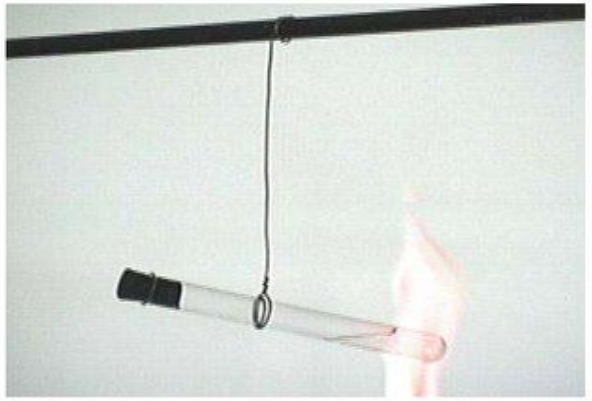
System- The part of the system which is under thermodynamic observation

Surroundings-
The remaining part other than system is called surroundings

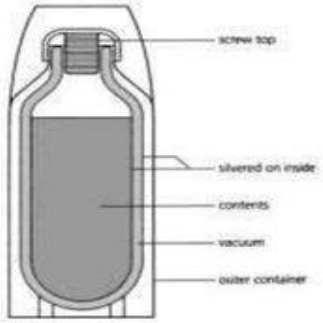




water in an open beaker is an open system as it can exchange both energy and matter with the surrounding

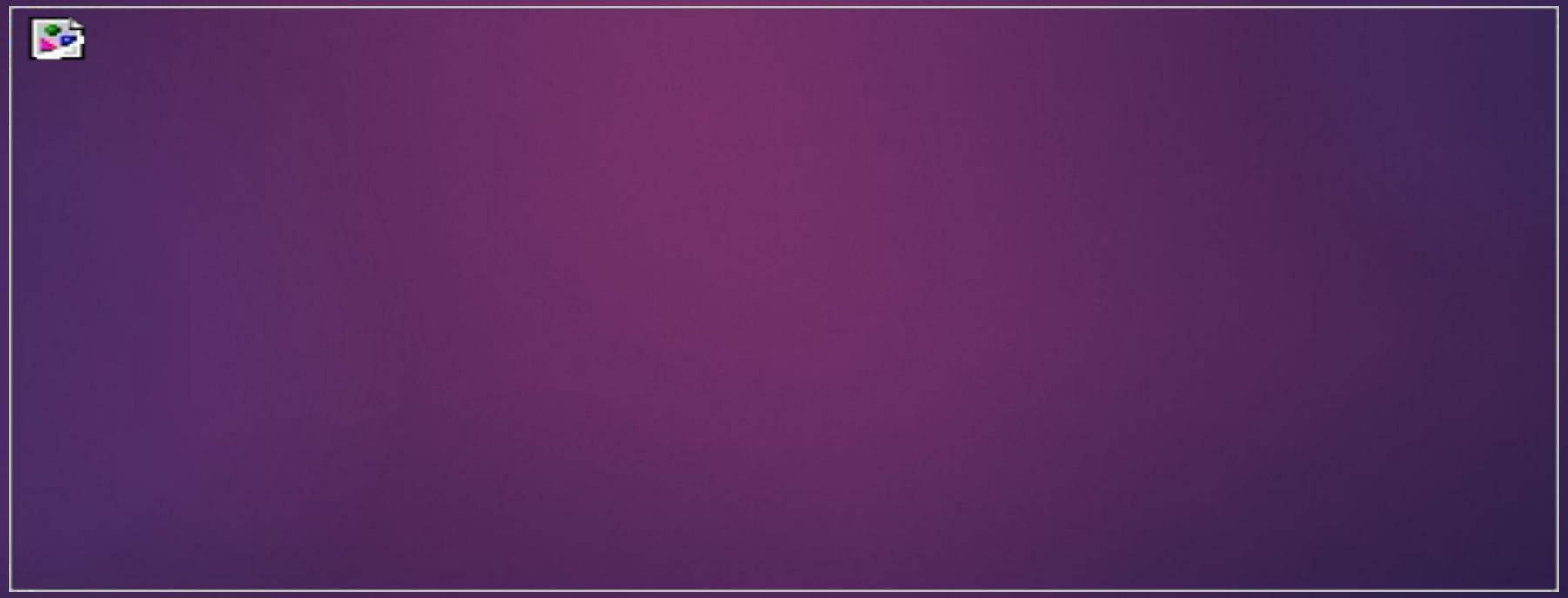


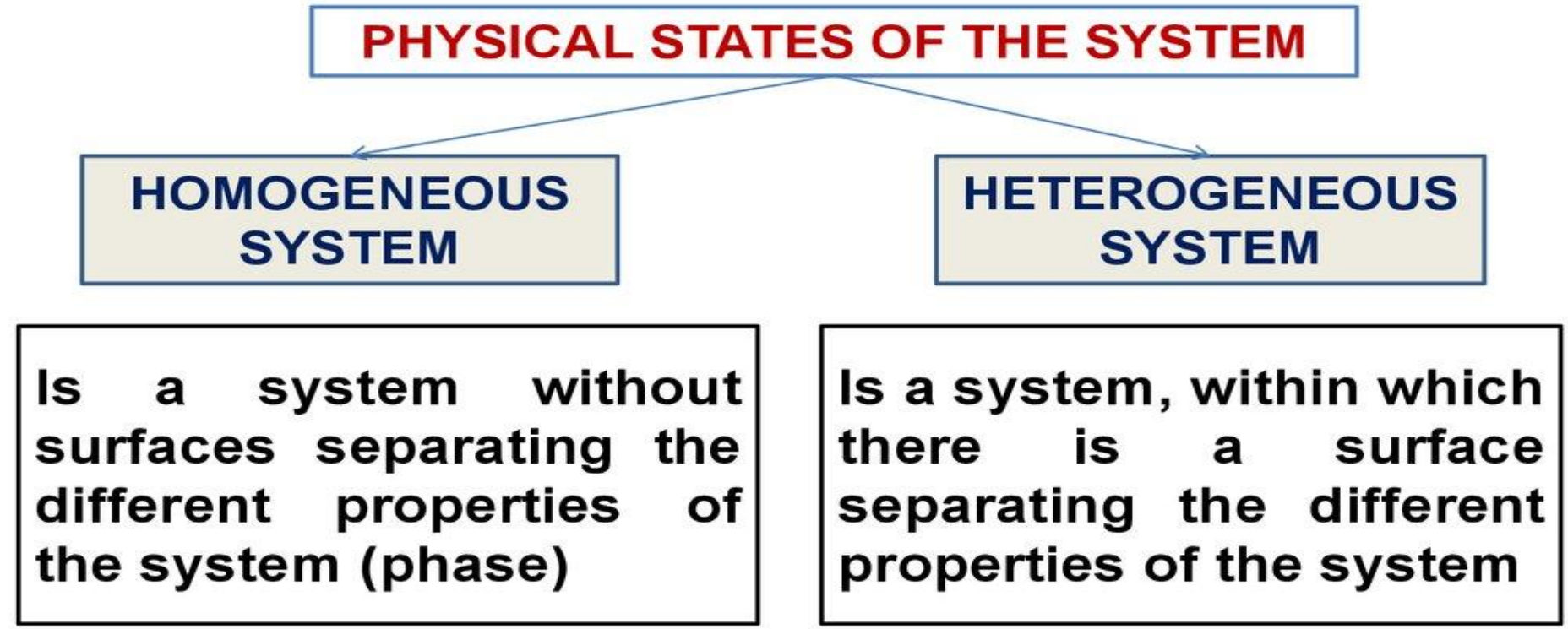
Hot water in contact with its vapour in a closed container



Water in contact with its vapour in a closed insulated vessel is an isolated system

Thermodynamic systems





PHASE *is a set of homogeneous parts of a heterogeneous system, with identical physical and chemical properties, and separated from other parts through visible surfaces*

Properties of a system

Properties of a system is a measurable characteristic of a system that is in equilibrium.

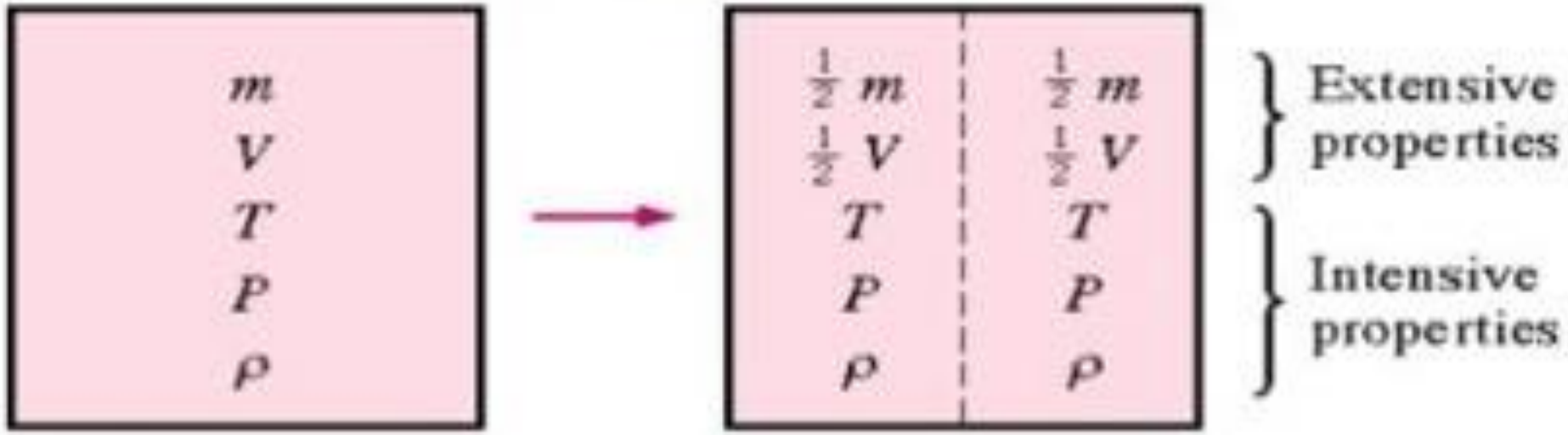
Properties may be intensive or extensive.

- **Intensive – Are independent of the amount of mass:**

e.g: Temperature, Pressure, and Density,

- **Extensive – varies directly with the mass**

e.g: mass, volume, energy, enthalpy



INTENSIVE PROPERTIES

- Chemical potential
- Concentration
- Density (or specific gravity)
- Ductility
- Elasticity
- Hardness
- Melting point and boiling point
- Pressure
- Specific energy
- Specific heat capacity
- Specific volume
- Spectral absorption maxima (in solution)
- Temperature
- Viscosity

EXTENSIVE PROPERTY

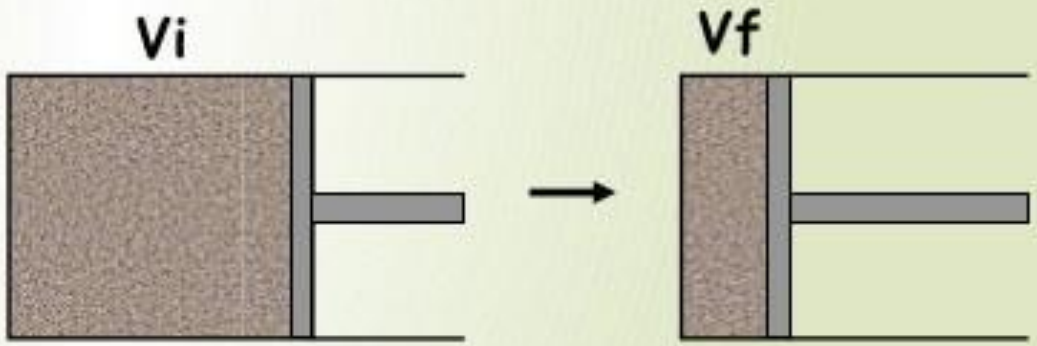
- Energy
- Entropy
- Gibbs energy
- Length
- Mass
- particle number
- number of moles
- Volume
- electrical charge
- Weight

A Thermodynamic "State Function"

State Functions only depend on the current (thermodynamic) state of the system.

<u>How</u> the system attained that state does not matter!

Example: Compression of a gas inside a piston.



Path function

A path function does depend on the path followed in getting from the starting to the final step. They are inexact differentials.

Path function

Work (W) and heat (q) are path functions.

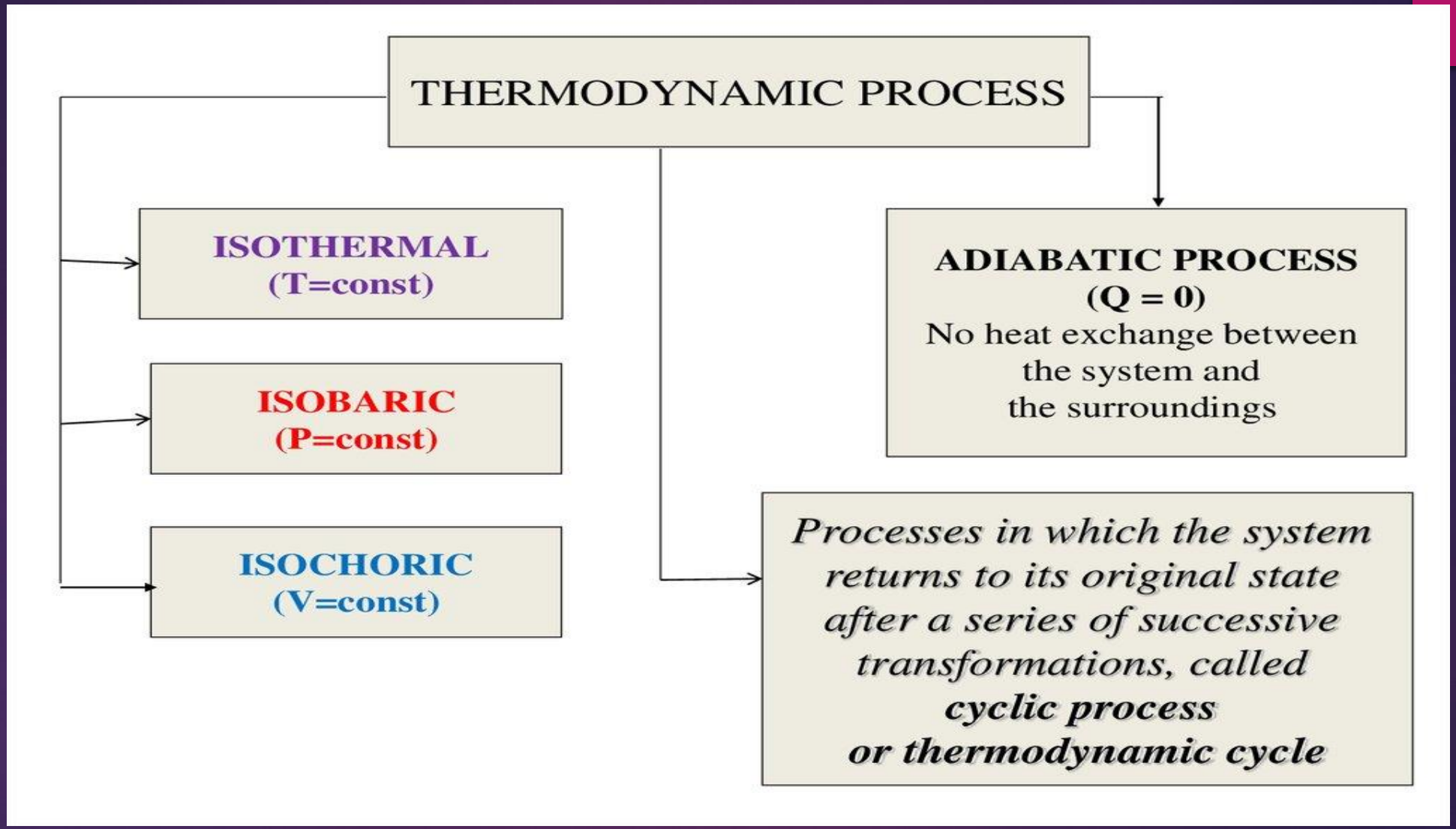
Two mountain climbers of equal mass scale the same cliff. One climbs straight up while the other backslides numerous times on the way up…

Who did more work?

Any change of parameter in the system called the thermodynamic process.

Major Types of Thermodynamic Processes:

- **Adiabatic process** - a process with no heat transfer into or out of the system.
- **Isochoric process** - a process with no change in volume, in which case the system does no work.
- **Isobaric process** - a process with no change in pressure.
- **Isothermal process** - a process with no change in temperature.


THERMODYNAMIC PROCESS
ISOTHERMAL
(T=const)
ISOBARIC
(P=const)
ISOCHORIC
(V=const)
ADIABATIC PROCESS
(Q = 0)
No heat exchange between
the system and
the surroundings
Processes in which the system
returns to its original state
after a series of successive
transformations, called
cyclic process
or thermodynamic cycle

Define Reversible and Irreversible Process

There are two main types of thermodynamic processes: *reversible process and the irreversible process.*

- Processes in which both the system and its surroundings can be simultaneously returned to their initial states after the process has been completed are called a **reversible process**.

- Processes in which the system and its surroundings cannot be simultaneously returned to their initial states after the process has been completed are called a **irreversible**.

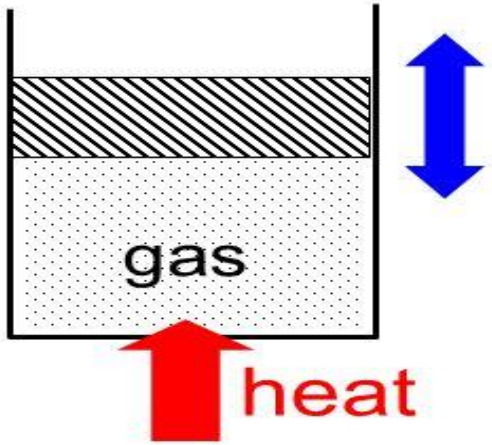
DIFFERENCE BETWEEN REVERSIBLE AND IRREVERSIBLE PROCESSES

Reversible Process	Irreversible Process
1. The process is carried out infinitesimally slowly	1. It is carried out rapidly
2. At any stage, the equilibrium is not disturbed	2. Equilibrium may exist only after the completion of the process.
3. It takes infinite time for completion.	3. It takes a finite time for completion.
4. Work obtained in this process is maximum.	4. Work obtained in this process is not maximum

First Law of Thermodynamics

Heat, work, and internal energy

- The gas has internal energy, as measured by its temperature
- if heat is added its internal energy increases
- if the gas expands and does work on the atmosphere, its internal energy decreases
- Heat and work are forms of energy which can change the internal energy
- the 1st law of thermodynamics keeps track of the balance between the heat, work and internal energy of the gas



First Law of Thermodynamics

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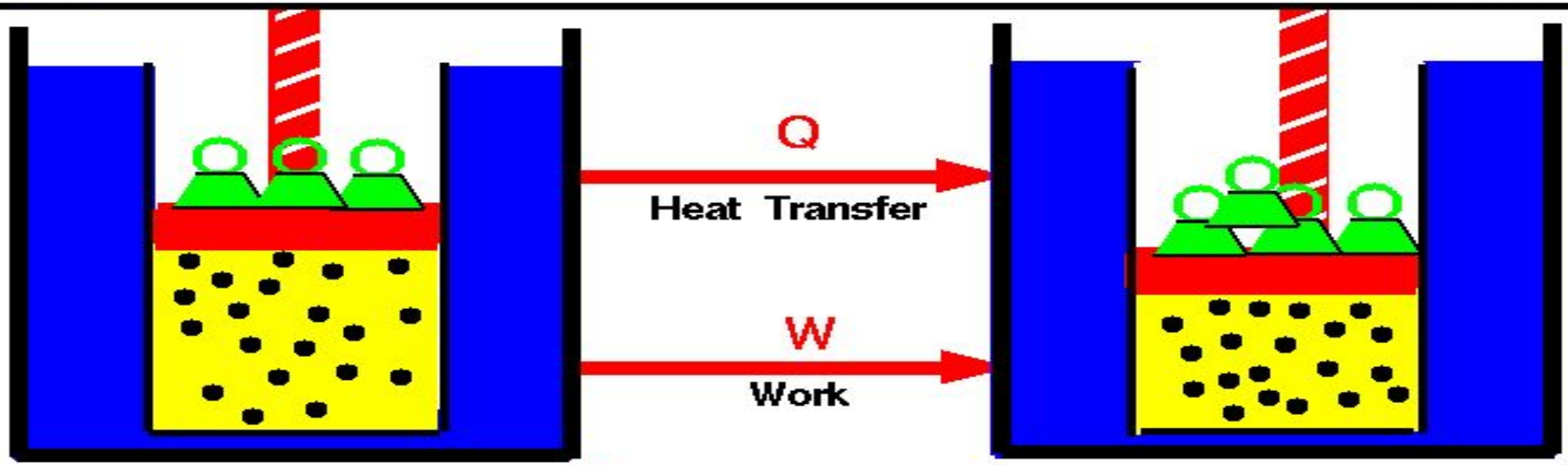
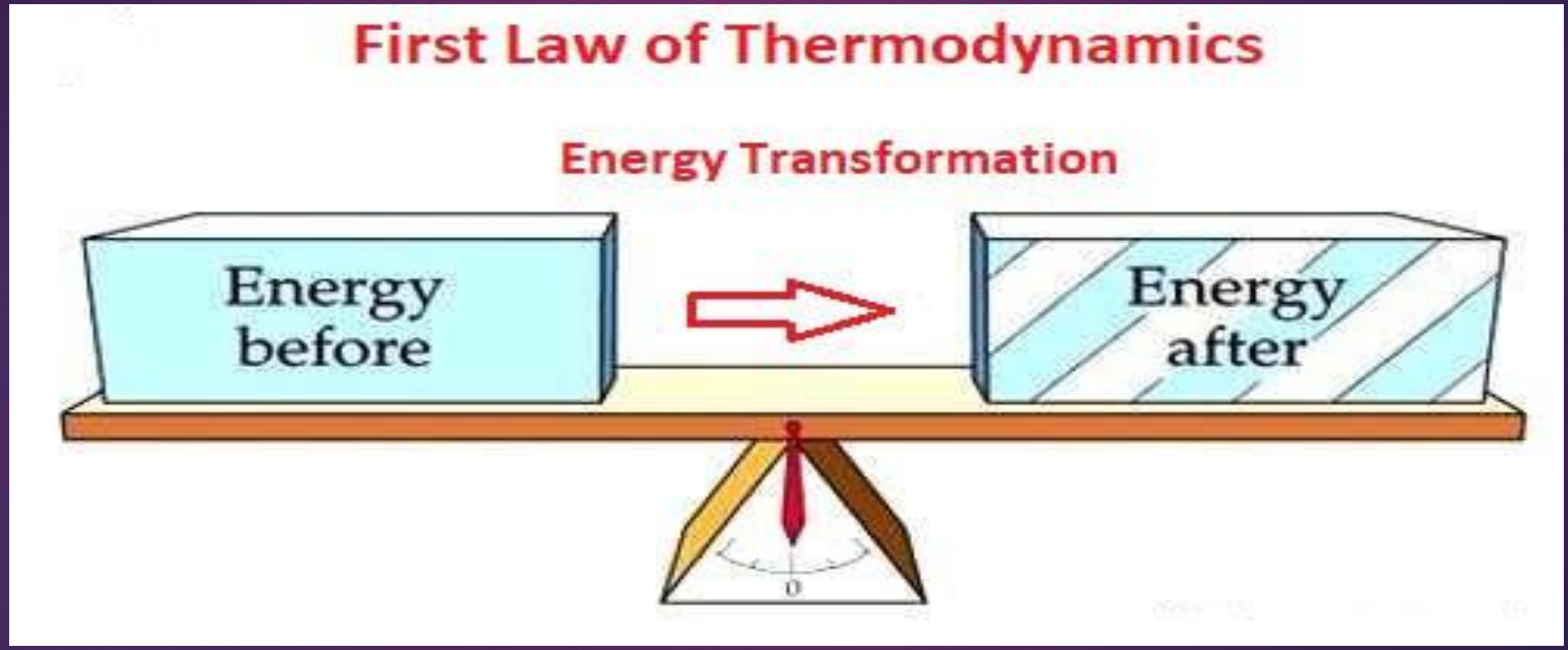


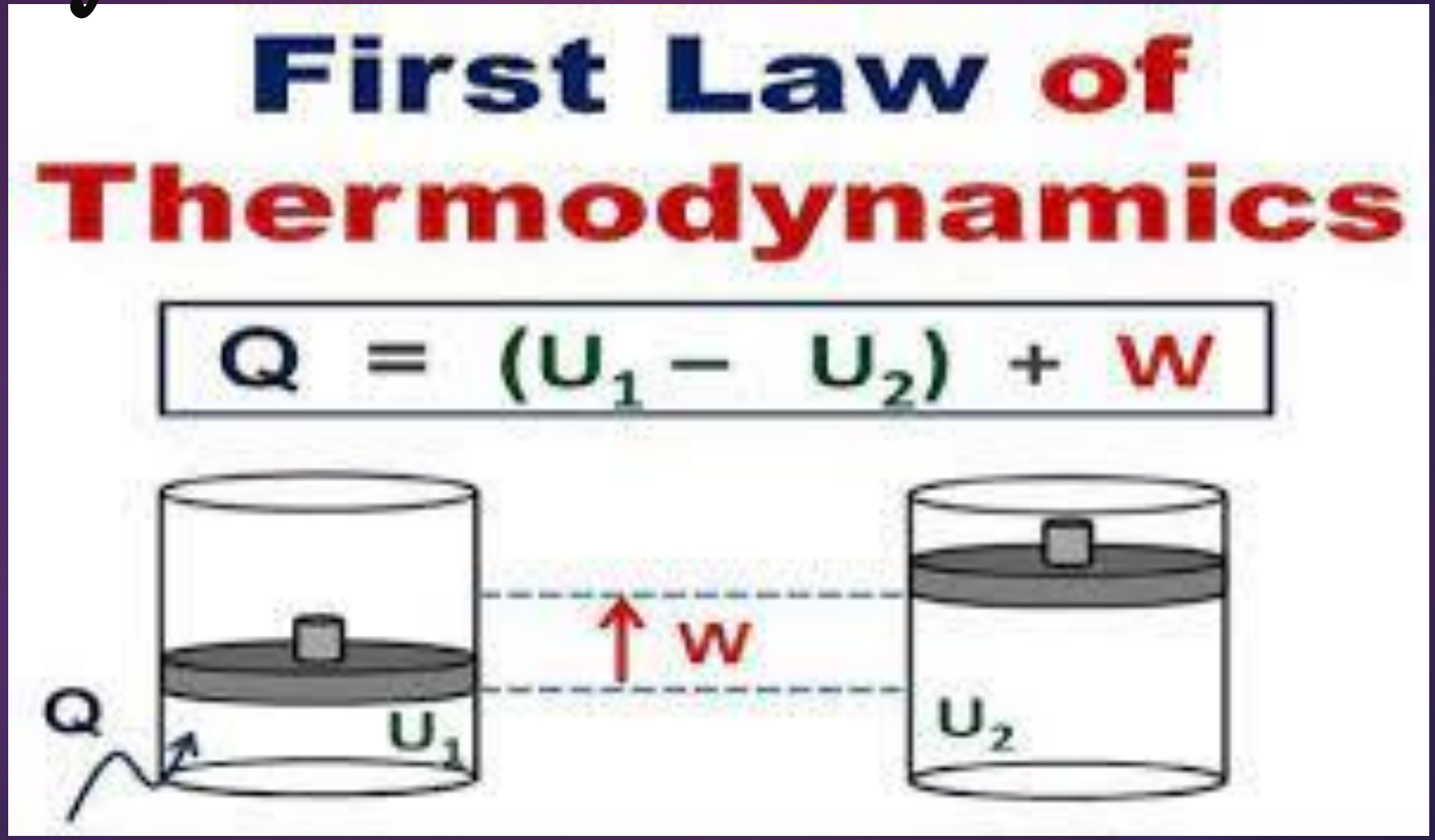
E = Internal Energy

$E_2 - E_1 = Q - W$

Any thermodynamic system in an equilibrium state possesses a state variable called the internal energy (E). Between any two equilibrium states, the change in internal energy is equal to the difference of the heat transfer into the system and work done by the system.


First Law of Thermodynamics
Energy Transformation
Energy before
Energy after
0

Mathematical expression of first law of thermodynamics



Concepts of Enthalpy

Enthalpy

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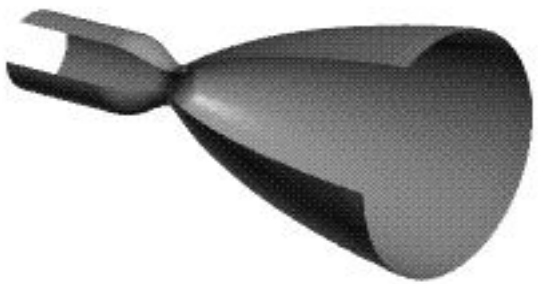


E = Internal Energy
T = Temperature
p = Pressure
V = Volume

Q = Heat Transfer
W = Work
C_p = Heat Capacity (constant pressure)

Define a new state variable that is a combination of other state variables.

$$\text{Enthalpy} = H = E + pV$$

$$\text{Specific Enthalpy} = \frac{\text{Enthalpy}}{\text{mass}} = h = e + pv$$

1st Law of Thermodynamics: $E_2 - E_1 = Q - W$

For a constant pressure process, the work is given: $W = p(V_2 - V_1)$

Substitute: $E_2 - E_1 = Q - p(V_2 - V_1)$

Re-group: $(E_2 + pV_2) - (E_1 + pV_1) = Q$

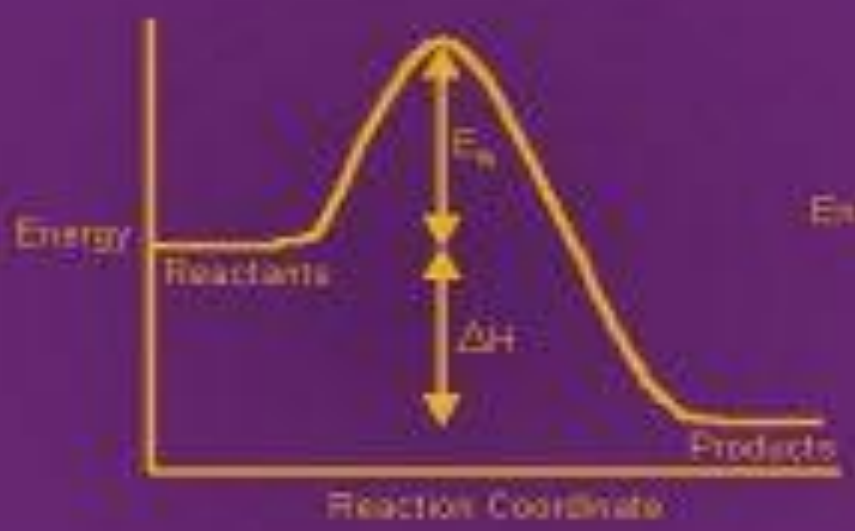
Heat Transfer at constant pressure: $Q = C_p(T_2 - T_1)$

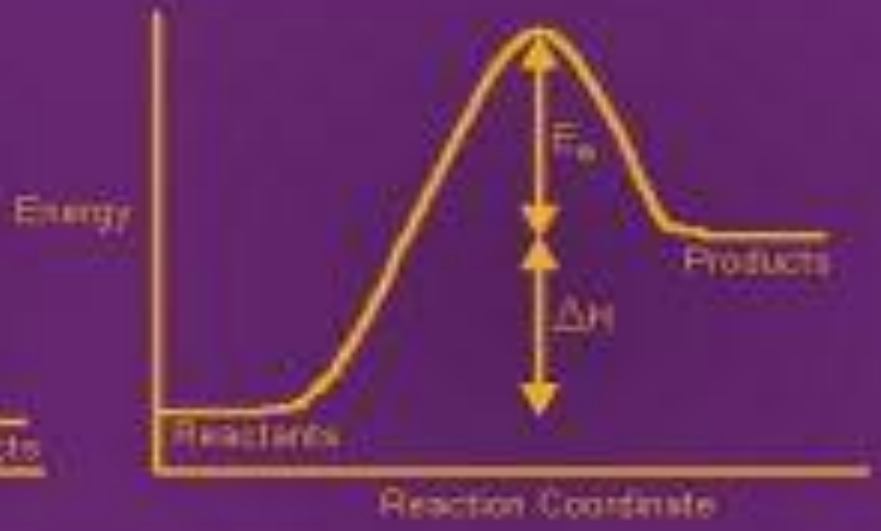
Definition of Enthalpy: $(H_2 - H_1) = C_p(T_2 - T_1)$

(specific enthalpy) $\boxed{(h_2 - h_1) = c_p(T_2 - T_1)}$

WHAT IS ENTHALPY ?

- ΔH, Heat energy
- ENDOthermic: heat is taken in by the reactants
- EXOthermic: heat is released as a product





Next class's objectives

1. Heat Capacity
2. Joule's Experiment
3. Joule Thomson Experiment


THANK YOU