First law of thermodynamic for various processes

- **Isothermal process:- ΔT= 0**

System depends on the temperature there is no change in the **internal energy U** of the system. Hence **ΔU = 0.**

$$\Delta U = q + W$$

$$0 \quad = q + W$$

$$+q(\text{expansion}) = -W \text{ or}$$

$$W = -q(\text{consumed}).$$

First law of thermodynamic for various processes

- **Isobaric process:- ΔP = 0**

System performs the work of **expansion** due to volume change . **W = -P_{ex} x ΔV**

q_P heat absorb by the system at constant pressure.

$$\Delta U = q_P + W$$

$$\Delta U = q_P - P_{ex} \Delta V$$

Or $q_P = \Delta U + P_{ex}\Delta V$

q_P heat absorbed used to increase the internal energy of the system.

Isochoric process

ΔV = 0

Hence system doesn't perform mechanical work..

- W = - PΔV = 0.
- ΔU = q + W
- ΔU = q_v
- q_v = heat absorbed at constant volume.
- ΔU and q is state funtion.

Adiabatic process

- **q= 0.**
- **ΔU = q + W**
- **ΔU = W$_{ad}$**
- **System Expansion** - ΔU decrease internal energy and temperature of system decrease.
- **System Compression** - ΔU increase internal energy and temperature of system increase.

Modern form of the first law of thermodynamic

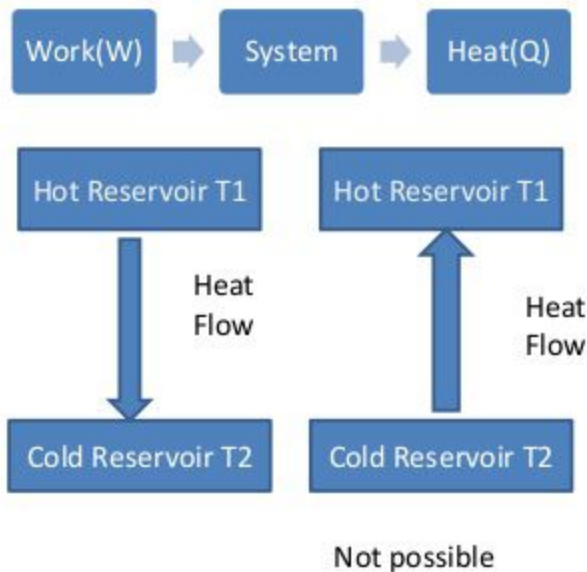- According to Einstein's theory, mass can be converted in to energy.
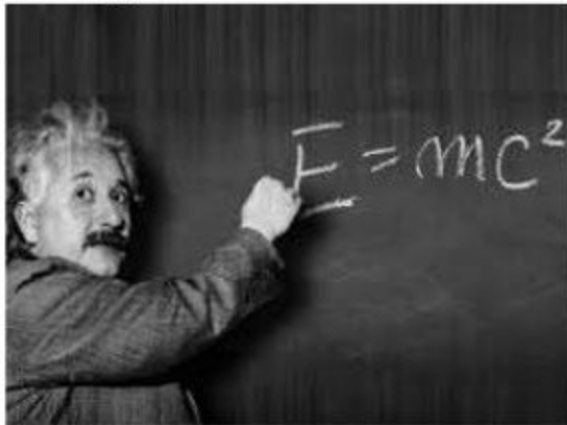
- Hence mass is also form of energy.
- The sum of mass and energy of an isolated system remain constant.

Limitation of "FIRST LAW"

- The first law of thermodynamic states that a certain energy flow takes place when a system undergoes a process or change of state is possible or not.
  - According to first law in 'cyclic process'
    - Work is completely converted into heat or heat is completely converted into work.
    - "HEAT" & "WORK" are mutually converted into each other.
- But from experience this is NOT TRUE!

Limitation of "FIRST LAW"

- First law does not help to predict whether the certain process is possible or not.
- The first law does not give info about Direction.
- It does not provide and specify sufficient condition to process take place.

| Work(W) | → | System | → | Heat(Q) |

| Hot Reservoir T1 | Hot Reservoir T1 |

Heat Flow

Heat Flow

| Cold Reservoir T2 | Cold Reservoir T2 |

Not possible

The "SECOND LAW" of thermodynamic:

- The second low of thermodynamic gives more information about thermodynamic processes.

- Second law may be defined as
  - "*Heat can not flow itself from colder body to a hotter body*".

- The Second law is also used to determine the theoretical limits for the performance of mostly used engineering systems like heat engines and heat pump….

"Kelvin-Plank" statement:

- The Kelvin-Plank statement of the second law of thermodynamic is states that
  - *"It is impossible to for any devise as heat engine that operates on a cycle to receive heat from a single reservoir and produce net amount of work".*
- This statement means that only part of total heat absorbed by heat engine from a high temperature is converted to work, the remaining heat must be rejected at a low temperature.

"Clausius" statement

- Clausius statement of second law of thermodynamic is as below
  - "***It is impossible to construct a device as heat pump that operates in a cycle and produces no effect other than the transfer of heat from lower temperature to higher temperature body***".

- This statement means that heat cannot flow from cold body to hot body without any work input.

COMPARISON

Kelvin-Plank Statement

- It is applied to 'Heat Engine'.

- It is negative statement.

- It is based on experimental observations and no mathematical proof.

Clausius Statement

- It is applied to 'Heat Pump' and 'Refrigeration'.

- It is also negative statement.

- It is based on experimental observations and no mathematical proof.

Heat Capacity

☀ Heat capacity is defined as the amount of energy needed to raise the temperature of a substance by 1°C or 1K.

Calculating Heat Capacity

$$C = \frac{E}{\Delta T}$$

Total Energy

Heat capacity

Difference/Change in temperature

Unit for heat capacity: **J/K or J/ᵒC**

Specific Heat Capacity

☀ Specific heat capacity is defined as the amount of energy needed to raise the temperature of 1kg of the substance by 1°C or 1K.

Calculating Specific Heat Capacity

$$c = \frac{E}{m\Delta T}$$

Total energy

Specific heat capacity

mass

Change/ difference in temperature
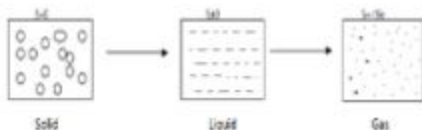
Unit for Specific Heat Capacity: **JK⁻¹kg⁻¹**

ENTROPY

- Measure of degree of Disorder or randomness in a molecular system is called ENTROPY

- EXAMPLES:

  When solid change to liquid (entropy increases).

  When liquid change to solid (entropy decreases).

  When gas change to liquid (entropy decreases).

Solid   Liquid   Gas

Mathematical Expression Of Entropy

Mathematical expression is

$$\Delta S = q_{rev}/T$$

ΔS ⟶ Change in entropy

q_{rev} ⟶ Heat change

T ⟶ Temperature

Ratio of the heat change (q) to the Temperature of the reversible cyclic Process units is Cal/Deg or $Jk^{-1} mol^{-1}$ or cal k⁻

Entropy & Randomness:

- It is increase in entropy there is change from order state to disorder state

Entropy & Probability:

- A irreversible spontaneous process tends to proceed from less process to more probable state and so in spontaneous process entropy increase

Entropy changes in isothermal expansion of ideal gas

According to 1st law of thermodynamic

$$dE = q - PdV$$

or $\quad dE = q - W \longrightarrow$ (i)

In reversible isothermal process change in

Internal energy($dE = 0$)

Equation (i) becomes

$$q_{rev} - W = 0 \longrightarrow$$

$$q_{rev} = W \qquad \text{(ii)}$$

The work done is expansion of moles of Gas from volume V_1 to V_2 at constant Temperature 'T' is

$W = nRT \ln V_2/V_1$ $\longrightarrow$ (iii)

Sub(iii) in (ii)

$q_{rev} = nRT \ln V_2/V_1$

We know tha $\Delta S = q_{rev}/T$

So, $q_{rev} = \Delta S * T$

$T\Delta S = nRT \ln V_2/V_1$

$\Delta S = 1/T \, nRT \ln V_2/V_1$

$$\Delta S = nRT\ln V_2/V_1$$

$$\Delta S = 2.303nR\log V_2/V_1 \longrightarrow \quad \text{(iv)}$$

$$P_1V_1 = RT \quad \text{(or)} \quad V_1 = RT/P_1$$

$$P_2V_2 = RT \quad \text{(or)} \quad V_2 = RT/P_2$$

$$\Delta S = 2.303nR\log P_1/P_2$$

Entropy change in reversible process (Non-spontaneous) :

- Consider isothermal expansion of ideal gas

- If system absorbs 'q' amount of heat from surroundings at Temperature "T" then Entropy increase of system

$$\Delta S_{system} = +q/T$$

Entropy decrease of surrounding

$$\Delta S_{surroundings} = -q/T$$

Net change in entropy

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surrounding}$$

$$= q/T + (-q/T)$$

$$\Delta S_{Total} = 0$$

Therefore in reversible isothermal
  process
No change in Entropy

Entropy change in irreversible (spontaneous) Process:

- Consider system at higher temperature 'T_1' ,surrounding at lower temperature T_2
- 'q' amount of heat passes irreversibly from system to surrounding
- Decrease in ϵ $\Delta S_{system} = -q/T_1$ stem

- Increase in entropy of surrounding
$$\Delta S_{surrrounding} = q/T_2$$

Net change $\Delta S_{Total} = \Delta S_{system} + \Delta S_{surrounding}$

$$= -q/T1 + q/T_2$$

$$= q[1/T2 - 1/T1]$$

$$= q[T1 - T2/T1T2]$$

As $T_1 > T_2$

$T1 - T2 = +ve$

$\Delta S_{Total} = +ve$ $\Delta S_{total} > 0$

Entropy change in Physical transformations :

- Entropy change takes place when system under goes physical transformation like vapourise fusion etc$_{\Delta H}$

- Let   be quantity of heat absorbed in calories at constant temperature and pressure.

- Entropy change

$$\Delta S = \Delta H / T \longrightarrow$$

(i)

- But enthalpy change $\Delta H = L * M$ $\longrightarrow$
  (ii) $\longrightarrow$
    L $\longrightarrow$ Latent heat in calories
    M $\longrightarrow$ Molecular weight in Grams
    T   Temperature in Kelvin

Sub (ii) in (i) $\Delta S = L * M / T$

Latent heat of Vapourisation of H_2O: 540cal /gm at 100°C

Latent heat of fusion of ice: 80cal/gm at 0°C