Thermodynamics

TOPICS COVERED

- ➢ Concept of Entropy

- ➢ Calculation of Entropy for different processes

  - ➢ Adiabatic Process

  - ➢ Phase Change

  - ➢ Heating and Cooling in case of Solid/Liquid and Gas

- ➢ Reversible and Irreversible calculations of entropy

- ➢ Limitation of "FIRST LAW" of Thermodynamics

- ➢ Zeroth Law of Thermodynamics

Entropy

- **Entropy** is a thermodynamic state quantity that is a **measure of the randomness** or **disorder of the molecules of the system**.

- The symbol of entropy is *S, while the change in disorder accompanying a process from start to* completion is represented by ΔS.

- *The entropy of a system is a state function and depends only on the* initial and final states of the system. The change in entropy, ΔS, *for any process is given by the* equation,

- $\Delta S = S_{final} - S_{initial}$
  When $S_{final} > S_{initial}$, *ΔS is positive.*

Unit of Entropy

- *calories per degree per mole i.e., cal mol⁻¹ K⁻¹.*
- In the SI system, the units are joules per mole per degree *i.e., J mol⁻¹ K⁻¹.*
- *1eu = 4.184*

Calculation of change in entropy for different processes

- **Adiabatic Process – means q_{rev} =0**

$$\Delta S = \frac{q_{rev}}{T} = 0$$

$$\Delta S_{initial} = \Delta S_{final}$$

- **Phase Change –** When we change into phase of any system then temperature is constant.
  - q = m× l , where m is the mass and l is latent heat

- **Cooling / Heating:** **If** temperature change then q is also exchange. So, there is no constant variable like temperature and heat.

  - **For Solid/Liquid:** For this case calculate heat (q)

    q = m × S_0 × ΔT, where m is the mass, S_0 is specific heat and ΔT is change in temp.

    We know that
    $\Delta S = \dfrac{q_{rev}}{T}$,
    put the value of q in this above equation

$$\Delta S = \frac{m \times S_0 \times \Delta T}{T} \ ,$$

$$dS = m \times S_0 \ \frac{\Delta T}{T} \ ,$$

For complete change we apply integration

$$\int_{S_1}^{S_2} dS = \ m \times S_0 \int_{T_1}^{T_2} DT/T$$

$$S_2 - S_1 = m \times S_0 \ (\ln T_2 \ - \ln T_1)$$

$$\Delta S = m \times S_0 \ \ln \left(\frac{T_2}{T_1}\right)$$

$$\Delta S = 2.303 \ m \times S_0 \ \log_{10}\left(\frac{T_2}{T_1}\right)$$

Here, two cases are possible i.e.

1. By heating
$T_2 > T_1$, ΔS (+ve)

2. By Cooling
$T_2 < T_1$, ΔS (- ve)

- **For Gases:**

1. At constant Pressure

$q_p = nc_p \Delta T$,

$$\Delta S = \frac{q_{rev}}{T} = \frac{nc_p \Delta T}{T}$$

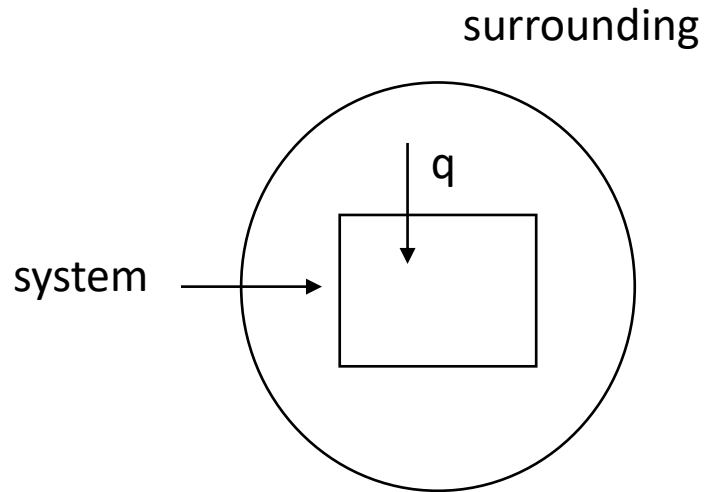$$\Delta S = 2.303 \, nc_p \log_{10} \frac{T_2}{T_1}$$

2. At constant Volume

$q_p = nc_v \Delta T$,

$$\Delta S = \frac{q_{rev}}{T} = \frac{nc_v \Delta T}{T}$$

$$\Delta S = 2.303 \, nc_v \log_{10} \frac{T_2}{T_1}$$

Reversible process of change in entropy

surrounding

q

system

Suppose that system absorb q heat from the surroundings so heat of system increase and heat of surroundings decreases, but temp
In both cases (reversible and irreversible) are constant

$\Delta S_{system} = \dfrac{+q}{T}$ using q is positive because system absorb heat

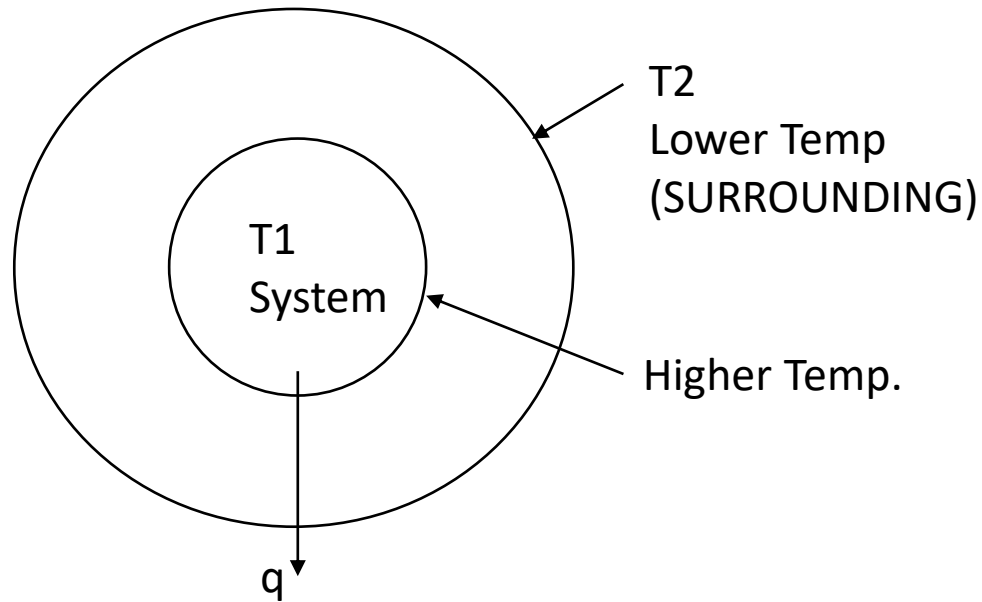$\Delta S_{surr} = \dfrac{-q}{T}$ using q is positive because system absorb heat

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$

$$= \dfrac{+q}{T} - \dfrac{q}{T} = 0$$

For reversible isothermal ΔS_{change} is zero

Irreversible process of change in entropy

T2
Lower Temp
(SURROUNDING)

T1
System

Higher Temp.

q

System have higher temperature i.e. T_1 & surrounding have lower temperature is T_2 so if we observe the temperature difference means heat transfer from higher to low temperature system give heat to the surroundings.

$$\Delta S_{system} = \frac{-q}{T1}$$

$$\Delta S_{surr} = \frac{+q}{T2}$$

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$$

$$= \frac{-q}{T1} + \frac{q}{T} = 0$$

$$\Delta S_{total} = q\left(\frac{T1 - T2}{T1\ T2}\right)$$
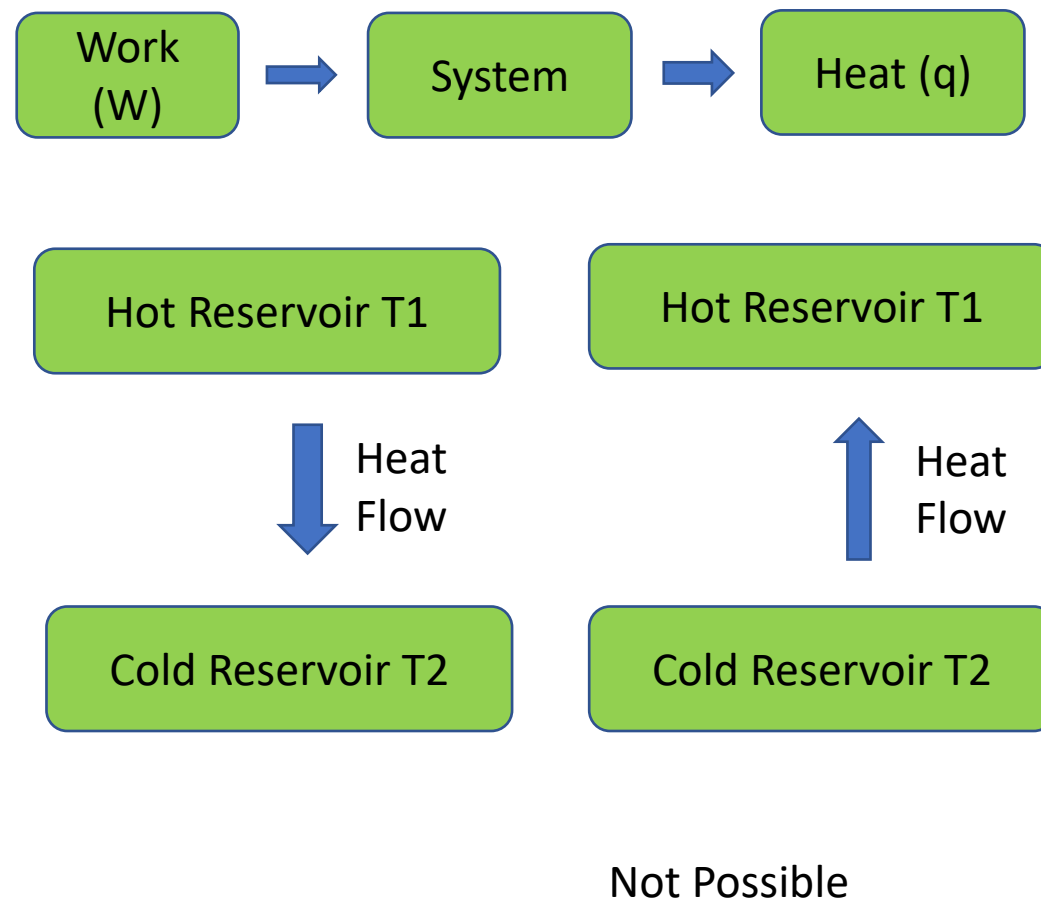
$$T_1 > T_2 \,,\, T_1 - T_2 \,=\, +ve$$

$$\Delta S_{process} > 0$$

Limitation of "FIRST LAW" of Thermodynamics

❑ 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.

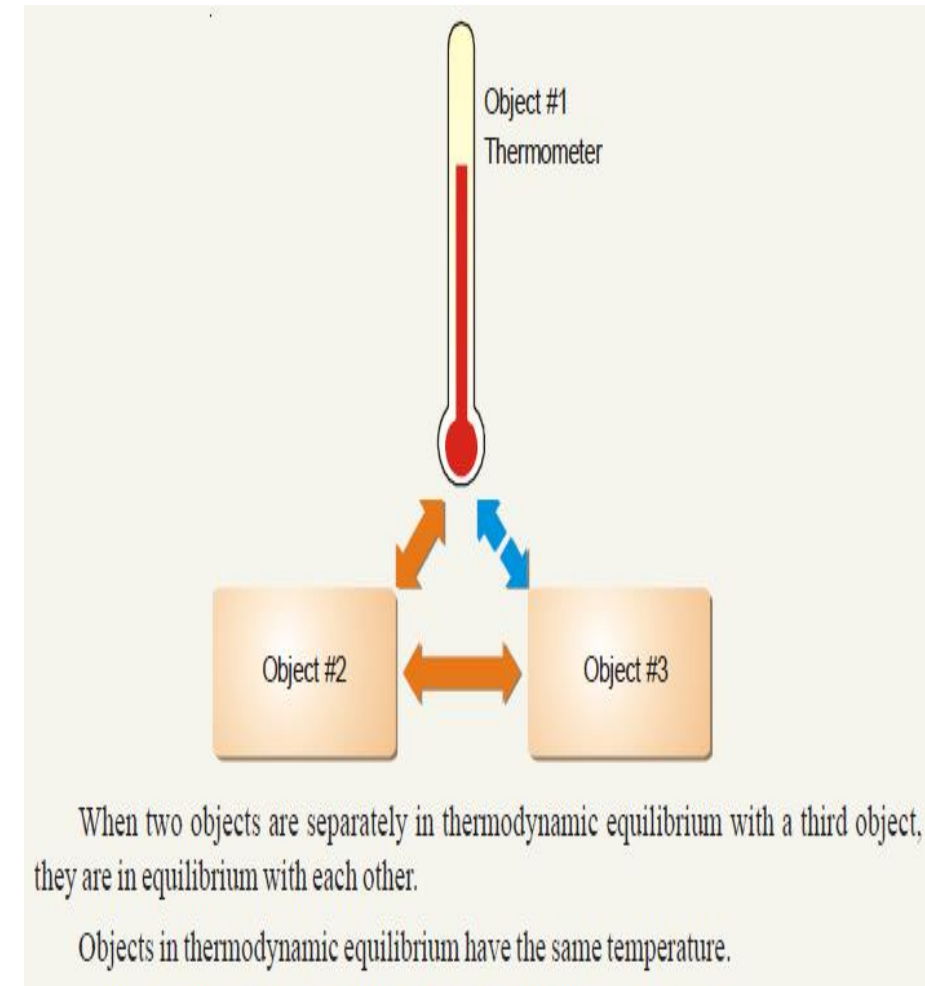• But from experience this is NOT TRUE!

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

Zeroth Law of Thermodynamics

Zeroth Law of Thermodynamics is a generalized statement about bodies in contact at thermal equilibrium and is the basis of for the concept of temperature the most common definition of Zeroth Law of Thermodynamics is '**If two thermodynamic system are in thermal equilibrium with a third, they are also in thermal equilibrium with each other.**

The term zeroth law was coined by Ralph H. Fowler. I many ways, the law is more fundamental than any of the others

Object #1
Thermometer

Object #2   Object #3

When two objects are separately in thermodynamic equilibrium with a third object, they are in equilibrium with each other.

Objects in thermodynamic equilibrium have the same temperature.

References

Text Books

1. Atkins, P. W. & Paula, J. de *Atkin's Physical Chemistry* 10th Ed., Oxford University Press (2014).

Reference Books

1. Castellan, G. W. *Physical Chemistry* 4th Ed. Narosa (2004).
2. Engel, T. & Reid, P. *Physical Chemistry* 3rd Ed. Pearson (2013).
3. Levine, I .N. *Physical Chemistry* 6th Ed., Tata Mc Graw Hill (2010)
4. Puri Sharma Pathania Physical Chemistry Book.