# Equilibrium and Non-equilibrium Thermodynamics: Concept of Entropy

## Part-1

- Equilibrium and non-equilibrium thermodynamics
- Non-ideal solutions
- Excess functions
- The third law of thermodynamics
- Entropy-temperature relation and absolute entropy

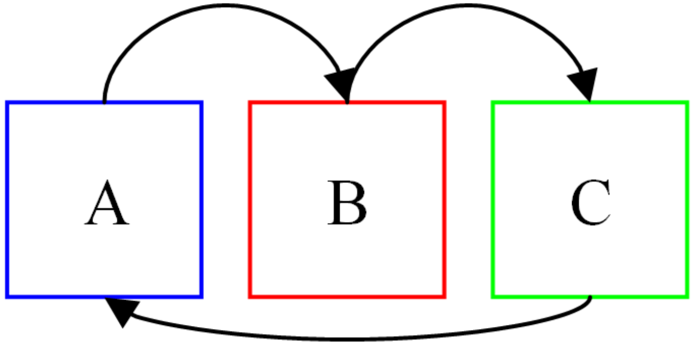
**Dr. Rakesh Kumar Pandey**
**Associate Professor, Department of Chemistry**
**MGCU, Bihar**

**Thermodynamic Equilibrium:** A system is called to be in thermodynamic equilibrium when there is no net flow of matter or of energy, either within a system or between different systems.
Thermodynamic equilibrium is the unique stable stationary state that is approached or eventually reached as the system interacts with its surroundings over a long time.

**Equilibrium Thermodynamics:** The study of a system that is in thermodynamic equilibrium with its surroundings is called equilibrium thermodynamics. A majority of the systems in the nature are not in thermodynamic equilibrium and there is always some inherent flow of matter or energy in and out of the system.

**Non-equilibrium Thermodynamics:** It is the study of systems that are not in thermodynamic equilibrium and thus undergo a constant exchange of matter and energy to and from the system.

**Zeroth Law of thermodynamics:** The Zeroth Law of Thermodynamics states that if two systems are in thermodynamic equilibrium with a third system, the two original systems are in thermal equilibrium with each other. Basically, if system A is in thermal equilibrium with system C and system B is also in thermal equilibrium with system C, system A and system B are in thermal equilibrium with each other.



***Example of* Zeroth Law :** *When you turn on AC to keep the room at 23$^{o}$C, the book kept in the bookshelf also acquires 23$^{o}$C.*

*Note: Students should also go through 1st and 2nd law of thermodynamics*

## Properties of a non-ideal solution:

A non-ideal solution is a solution that does not abide to the rules of an ideal solution where the interactions between the molecules are identical (or very close) to the interactions between molecules of different components. That is, there is no forces acting between the components: no Van-der-Waals nor any Coulomb forces. Non-ideal solutions cannot be defined by Raoult's law or by Henry's law, which are properties specifically unique to ideal mixtures:

Non-ideal solutions can occur two ways:

(1) When intermolecular forces between solute and solvent molecules are ***less*** strong than between molecules of the same type.
(2) When intermolecular forces between dissimilar molecules are ***greater*** than those between similar molecules.

**Example:**
**Mixtures of carbon disulfide and acetone.** Carbon disulfide is *non-polar* and acetone is *polar*. Since carbon disulfide is non-polar, the intermolecular attractions are London dispersion forces, which are known to be weaker compared to other types of intermolecular forces. However, since acetone is polar, it has dipole-dipole forces, which are known to be very strong. Therefore in this situation, the $CS_2$ and acetone molecules will experience difference intermolecular force than that in their pure forms.

**Excess functions:**

The excess functions signifies the deviation from ideal behavior of a liquid or gas mixture or in other words inform about the type of molecular interactions, i.e., attraction or repulsion, related to the the state of pure compounds before mixing.

As as example, if a liquid mixture present an excess molar volume greater than 0, it can be said that the molecules of these compounds repel each other when mixed. On the other hand, an excess molar volume in negative suggests the opposite.

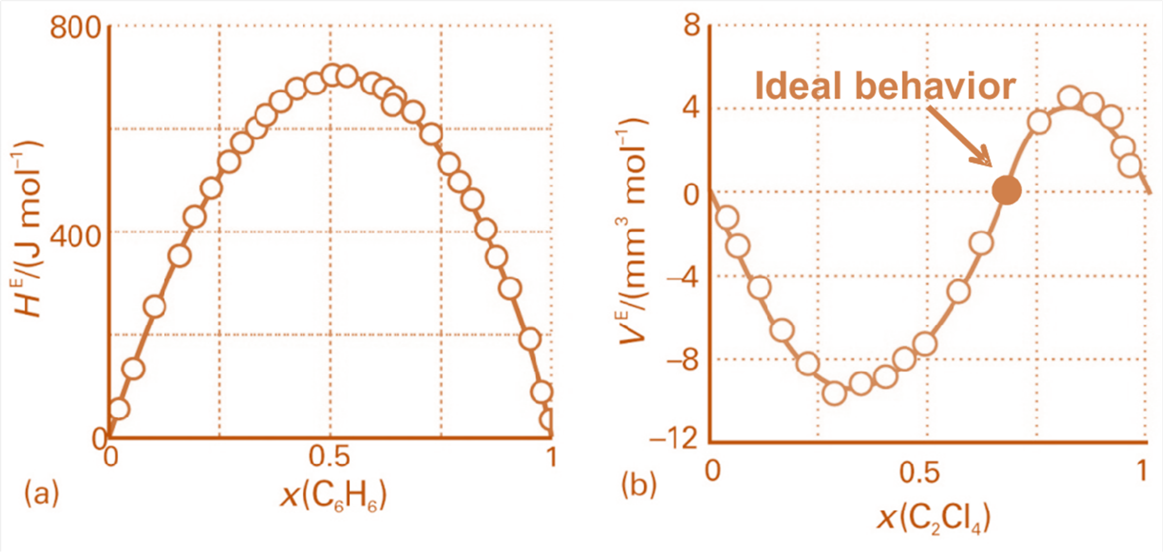


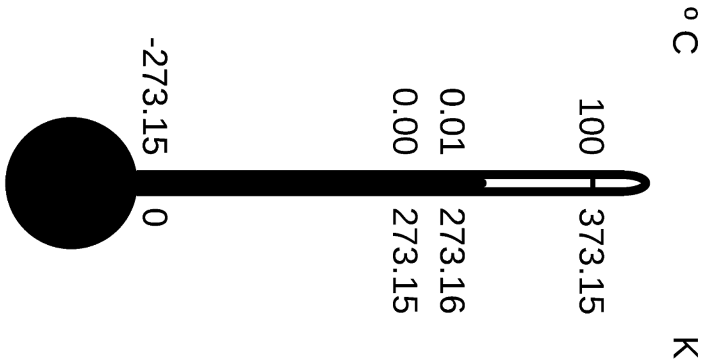
**Figure:** Examples of excess functions. a) Excess enthalpy for mixing of benzene ($C_6H_6$) and cyclohexane (i.e. endothermic reaction); b) excess volume for mixing of tetrachloroethene and cyclopentane (i.e. contraction for small mole fraction and expansion for high mole fraction of tetrachloroethene).

## The third law of thermodynamics and concept of absolute zero:

The third law of thermodynamics predicts the properties of a system and the behavior of entropy in a unique environment known as absolute temperature. At absolute zero the entropy of the system becomes constant.

**Absolute Zero:** The lowest possible temperature where no heat energy remains in the substance is called the absolute zero.
It is considered to be 0 K or -273.15 C.

**At absolute zero:**
(1) nearly all molecular motions cease
(2) change in entropy becomes zero
(3) Perfect crystals never occur



**Why absolute zero is impossible to reach:** In order to decrease the temperature of any system we need to take the heat out of the system. The difficulty here is that the amount of work necessary to remove heat from a substance increases substantially the colder you try to go. To reach 0 K, we require an infinite amount of work. And even if we reach there, the quantum mechanics will make the atoms and molecules to acquire some irreducible motion. The coldest temperature recorded in the laboratory is few hundred nanoKelvin.

**Nernst heat theorem:** The Nernst heat theorem says that as absolute zero (0 K or -273 C) is approached, the entropy change ΔS for a chemical or physical transformation approaches zero. This can be expressed mathematically as follows:

$$\lim_{T \to 0} \Delta S = 0$$

## Entropy and temperature

While entropy is a measurement of the amount of disorder contained in a body, temperature describes how strong the atomic agitation, that means the intensity of random particle motion is. Temperature is something like a level of agitation that is low when the atoms and molecules are gently oscillating and rotating. Temperature is high when atomic motion becomes hectic and turbulent (rapid oscillations of molecules).

When we heat a cup of tea we increase the entropy that in turn results in heating the tea: Unfortunately, the name “heat” was given to another quantity which robbed S of its natural meaning, making S an abstract concept that is more difficult to understand than heat.

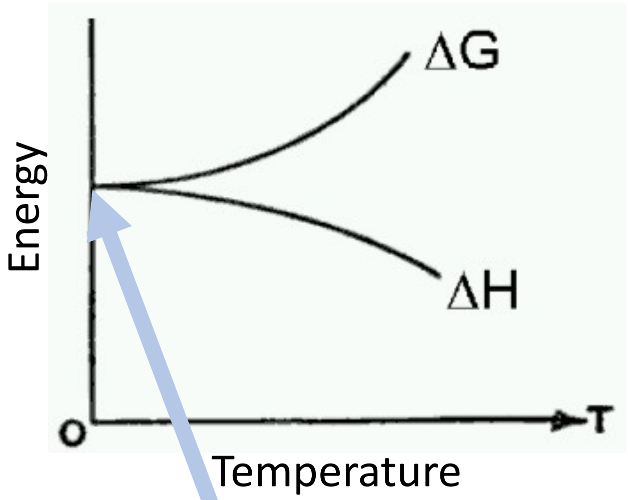
$\Delta G = \Delta H - T\Delta S$

$\Delta S = (\Delta H - \Delta G)/T$

at T= 0, $\Delta G = \Delta H$

Therefore

$\Delta S = 0$



$$\lim_{T \to 0} \Delta S = 0$$

A cup of green tea with high entropy

**Absolute Entropy:** The ***absolute entropy*** of a pure substance at a given temperature is the sum of all the entropy it would acquire on warming from absolute zero (where S=0) to the particular temperature.

Absolute entropy increases as we increase the temperature until the melting point is reached, where it jumps suddenly as the substance undergoes a phase change from a highly ordered solid to a disordered liquid ($\Delta S_{fus}$). The entropy again increases steadily with increasing temperature until the boiling point is reached, where it jumps suddenly as the liquid undergoes a phase change to a highly disordered gas ($\Delta S_{vap}$).

The standard entropy change ($\Delta So$ΔSo) for any process may be computed from the standard entropies of its reactant and product species like the following:

$$\Delta s^o = \sum \nu S^o 298(\text{products}) - \sum \nu S^o 298(\text{reactants})$$

Here, $\nu$ represents stoichiometric coefficients in the balanced equation representing the process. For example, $\Delta S^o$ for the following reaction at room temperature

$$mA+nB \longrightarrow xC+yD$$

is computed as the following:

$$\Delta S^o = [xS^o_{298}(\text{C}) + yS^o_{298}(\text{D})] - [mS^o_{298}(\text{A}) + nS^o_{298}(\text{B})]$$

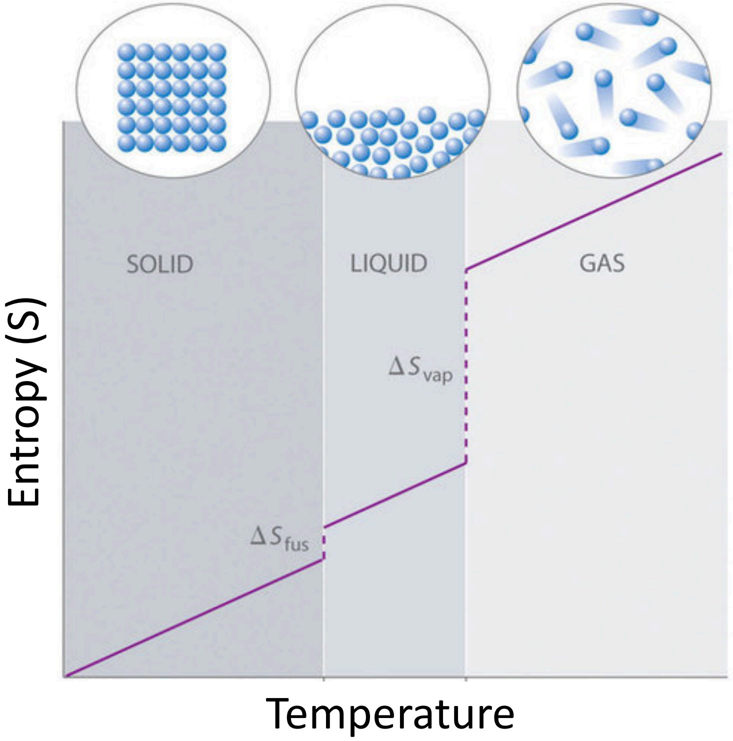


Figure: Absolute entropy increases steadily with increasing temperature

## Calculating $\Delta S$ from Thermodynamic Cycles

We can also calculate a change in entropy using a thermodynamic cycle.

The molar heat capacity ($C_p$) is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant pressure.

Similarly, $C_v$ is the amount of heat needed to raise the temperature of 1 mol of a substance by 1°C at constant volume. The increase in entropy with increasing temperature is approximately proportional to the heat capacity of the substance.

As we know that the entropy change ($\Delta S$) is related to heat flow ($q_{rev}$) by $\Delta S = q_{rev}/T$.

$q_{rev} = nC_p\Delta T$ at constant pressure

or $nC_v\Delta T$ at constant volume, where n is the number of moles of substance present, the change in entropy for a substance whose temperature changes from $T_1$ to $T_2$ is as follows:

$$\Delta S = q_{rev}T = nC_p\Delta T/T \text{ (constant } P\text{)}$$

Or $\Delta S = nC_p \ln T2/T1$ (constant $P$)

Similarly,

$\Delta S = nC_v \ln T2/T1$ (constant $V$)

## Numerical questions for students:

(1) Calculate the entropy change (J/K) when 4.35 g of liquid bromine are heated from 30.0°C to 50.0°C if the molar heat capacity ($C_p$) of liquid bromine is 75.1 kJ/(mol·K).

(2) Calculate the molar heat capacity ($C_p$) of titanium tetrachloride if the change in entropy when a 6.00 g sample of $TiCl_4(l)$ is heated from 25.0°C to 40.0°C is 0.154 J/K.