**Entropy**

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**Entropy**

**Introduction**

Entropy is one of the important concepts that students need to understand clearly while studying Chemistry and Physics. More significantly, entropy can be defined in several ways and thus can be applied in various stages or instances such as in a thermodynamic stage, cosmology, and even in economics.

The concept of entropy basically talks about the spontaneous changes that occur in the everyday phenomenon or the tendency of the universe towards disorder.

## What is Entropy?

Generally, entropy is defined as a **measure of randomness or disorder of a system**. This concept was introduced by a German physicist named Rudolf Clausius in the year 1850.

Apart from the general definition, there are several definitions that one can find for this concept. From a thermodynamics viewpoint of entropy, we do not consider the microscopic details of a system. Instead, entropy is used to describe the behaviour of a system in terms of thermodynamic properties such as temperature, pressure, entropy, and heat capacity. This thermodynamic description took into consideration the state of equilibrium of the systems.

Meanwhile, the statistical definition which was developed at a later stage focused on the thermodynamic properties which were defined in terms of the statistics of the molecular motions of a system. Entropy is a measure of the molecular disorder.

### Properties of Entropy

* It is a thermodynamic function.
* It is a state function. It depends on the state of the system and not the path that is followed.
* It is represented by S but in the standard state, it is represented by S°.
* It’s SI unit is J/Kmol., Molar Entropy is written in JK-1mol-1
* It’s CGS unit is cal/Kmol.
* Entropy is an extensive property which means that it scales with the size or extent of a system.

**Note:** The greater disorder will be seen in an isolated system, hence entropy also increases. When chemical reactions take place if reactants break into more number of products, entropy also gets increased. A system at higher temperatures has greater randomness than a system at a lower temperature. From these examples, it is clear that entropy increases with a decrease in regularity. Thus, the greater the disorderliness in an isolated system, the higher is the entropy.

**Entropy order: gas > liquid > solids**

The decrease in enthalpy may contribute to the spontaneity of a process but it cannot explain spontaneity in all the cases. Since we acknowledge many spontaneous endothermic reactions around us. For example: an isothermal reversible expansion of an ideal gas, where change in enthalpy, Δ*H* = 0. Hence, we define a new state function to explain the spontaneity of a process. This state function is named as entropy. Entropy is generally defined as the degree of randomness of a macroscopic system.

**What is Entropy Change?**

Since entropy is a state function, the entropy change of a system depends only on initial and final state irrespective of the path taken. Hence, change in entropy does not differ with the nature of the processes.

In a chemical reaction, the change in entropy can also be attributed to rearrangement of atoms or ions from one pattern to another. In the products, if the molecules are very much disordered in comparison to the reactants, there will be a resultant increase in entropy during the reaction. Thus, the change in entropy accompanying a chemical reaction can be estimated qualitatively by considering the disorderliness of the structures of the species involved in the reaction. For example, the crystalline solid state generally exhibits lower entropy in comparison to other solids.

### ****Expression for entropy change:****

A large element of chance is inherited in the natural processes. For example, the spacing between trees is a random natural process. Likewise, falling of tree leaves on the ground with the random arrangement is also a random process. Entropy is the measure of disorders or randomness of the particular system. Since it depends on the initial and final state of the system, the absolute value of entropy cannot be determined. You need to consider the difference between the initial and final state to determine the change in entropy.

The change in Entropy Formula is expressed as



The thermodynamic definition of entropy concentrates on the change in entropy, d*S*, that occur as a result of a physical or chemical change (in general, as a result of a ‘process’). The def­inition is motivated by the idea that a change in the extent to which energy is dispersed in a disorderly way depends on how much energy is transferred as heat, not as work. As it is considered that heat stimulates random motion of atoms whereas work stimulates their uniform motion and so does not change the extent of their disorder. According to the thermodynamic definition entropy is expressed as



where *q*rev is the energy transferred as heat reversibly to the system at the absolute temperature *T*.

For a measurable change between two states initial i and final f,

∆S = Sf –Si = ʃ dqrev / T

∆S = qrev, iso / T

That is, to calculate the difference in entropy between any two states of a system, find a *reversible* path between them, and in­tegrate the energy supplied as heat isothermally and reversibly at each stage of the path divided by the temperature at which that heat is transferred.

Addition of heat to a system increases the randomness in the system due to an increase in molecular motions. Generally, **a system at a higher temperature** has greater randomness than at lower temperature. Thus, temperature too helps in the measurement of the randomness of particles in a system. **Heat added to a system at lower temperature** causes greater randomness than in comparison to when heat is added to it at a higher temperature. Hence, it suggests that entropy change is inversely proportional to the temperature of the system.

## Entropy Change and Calculations

Total entropy change, ∆Stotal  = ∆Ssurroundings + ∆Ssystem

Total entropy change is equal to the sum of entropy change of system and surroundings.

If the system loses an amount of heat q at a temperature T1, which is received by surroundings at a temperature T2 then ∆Stotal can be calculated

∆Ssystem= -q/T1

∆Ssurrounding = q/T2

∆Stotal = -q/T1 + q/T2

For a spontaneous process, entropy change for the system and the surrounding must be greater than zero that is Δ*Stotal*  > 0. The general expression can be given as:

Δ*Stotal* = Δ*Ssys* + Δ*Ssurr* > 0

● If ∆Stotal is positive, the process is spontaneous.

● If ∆Stotal is negative, the process is non-spontaneous.

● If ∆Stotal is zero, the process is at equilibrium.

**Points To Remember**

* A spontaneous process is thermodynamically irreversible.
* The irreversible process will attain equilibrium after some time.

**Entropy change during the different processes**

To make progress, and to turn the Second Law into a quanti­tatively useful expression, the entropy change accompanying various processes needs to be defined and calculated.

1. **Entropy change during the isothermal reversible expansion of an ideal gas**

∆S = qrev,iso/T

According to the first law of thermodynamics,

∆U=q+w

For the isothermal expansion of an ideal gas, ∆U = 0

qrev = -wrev = nRTln(V2/V1)

Therefore,

∆S = nRln(V2/V1)

### Entropy Change during Reversible Adiabatic Expansion

For an adiabatic process heat exchange will be zero (q=0), therefore reversible adiabatic expansion is taking place at a constant entropy (isentropic),

q = 0

 Therefore, ∆S = 0

**Even though the reversible adiabatic expansion is isentropic, irreversible adiabatic expansion is not isentropic.**

**∆S not equal to Zero.**

## Entropy Changes During Phase Transition

### i) Entropy of Fusion

It is the increase in entropy when a solid melt into liquid. The entropy increases due to freedom of movement of molecules get increased with phase change.

The entropy of fusion is equal to the enthalpy of fusion divided by melting point(fusion temperature)

∆fusS = ∆fusH / Tf

A natural process such as a phase transition (eg.fusion) will occur when the associated change in the Gibbs free energy is negative.

Most of the time ∆fusS is positive

Exception : Helium-3 has a negative entropy of fusion at temperatures below 0.3 K. Helium-4 also has a very slightly negative entropy of fusion below 0.8 K.

### ii) Entropy of Vaporization

The entropy of vaporization is a state when there is an increase in entropy as liquid changes into vapours. This is due to an increase in molecular movement which creates a randomness of motion.

The entropy of vaporization is equal to the enthalpy of vaporization divided by boiling point. It can be represented as;

∆vapS=∆vapH / Tb

## Standard Entropy of Formation of a Compound

It is the entropy change that takes place when one mole of a compound in the standard state is formed from the elements in the standard state.

## Spontaneity

Exothermic reactions are spontaneous because ∆Ssurr is positive which make ∆Stotal positive.

Endothermic reactions are spontaneous because ∆Ssystem is positive and ∆Ssurroundings is negative but overall ∆Stotal is positive.

**Note**: Free energy change criteria for predicting spontaneity is better than entropy change criteria because the former requires only free energy change of system whereas the latter needs entropy change of both system and surroundings.

## Negentropy

It is a reverse of entropy. It means things becoming more in order. By ‘order’ it means in organisation, structure and function. It is opposite of randomness or chaos. One example of negentropy is a star system such as a solar system.

**The entropy as a state function**

Entropy is a state function. To prove this assertion, it is nec­essary to show that the integral of d*S* between any two states is independent of the path between them. To do so, it is suf­ficient to prove that the integral of above equation around an arbi­trary cycle is zero, for that guarantees that the entropy is the same at the initial and, it is necessary to show that final states of the system regardless of the path taken between them. That is

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where the symbol denotes integration around a closed path.