THERMODYNAMICS

SPONTANEITY

Spontaneous Process is the time-evolution of a system in which it releases free energy and moves to a lower, more thermodynamically stable energy state.

A Non-Spontaneous Reaction is a chemical reaction in which the standard change in free energy is positive and energy is absorbed.

Example of Natural Processes

(i) Water flowing down hill

(ii) Heat flowing from hot body towards cold body on it's own

(iii) mixing of two gases.

(iv) Rusting of iron

(v) Evaporation of water at room temperature.

(vi) Formation of $NH_3(g)$ from $N_2(g)$ and $H_2(g)$ gas in a closed container.

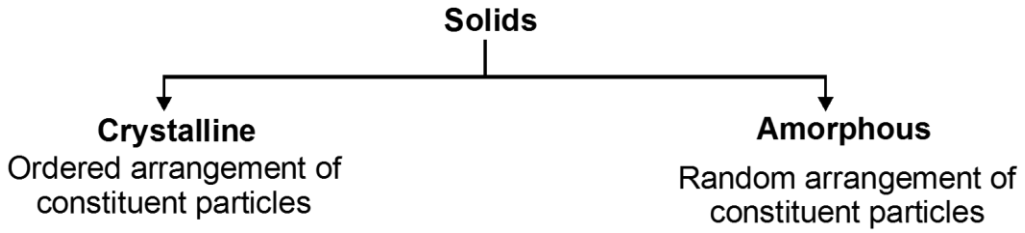
(vii) Expansion of ideal gas in vacuum

(viii) Burning of coal in O_2

Every natural process leads to production of disorder. (During irreversible process system moves from ordered state to disordered state).

ENTROPY (*S*)

It is the measure of degree of randomness of a system. More random is the system, higher will be its entropy.



For same amount of substance,

$$S_{Solid} < S_{liquid} < S_{gas}$$

$$S_{crystalline} < S_{amorphous}$$

As number of atoms in a molecule increases, it becomes more complex and hence entropy increases.

Ex. $NO < NO_2 < N_2O_3 < N_2O_5$

Ex. Raw Egg $\xrightarrow{boil}$ boiled egg

Weather the entropy of the system will increase or decrease?

Sol. As raw egg contains proteins, entropy will increase due to breaking of H – bond. Proteins molecules which were associated by H – bonding will be free and thus their will be more free protein molecules in boiled eggs as compared to raw eggs.

Thus, entropy will increase. Entropy is an extensive property and is a state function. Therefore, we can only calculate change in entropy.

Change in Entropy (ΔS) = $S_{final} - S_{initial}$

Entropy and Criteria of Spontaneity of Chemical Process

The entropy changes of chemical reaction together with entropy change of surrounding determine spontaneity of a chemical process under given set of condition.

$\Delta S_T > 0$ the reaction will be Spontaneous.

$\Delta S_T < 0$ the reaction will be non-Spontaneous.

$\Delta S_T = 0$ Equilibrium

Ex. $C_2H_2(g) + \longrightarrow 2CO_2(g) + H_2O(\lambda)$