Entropy, S

Entropy, S, is a measure of the disorder or randomness of the system. The more disordered or random the system, the larger the value of S (increase the degree of **FREEDOM**).

Entropy is not a form of energy and has a unit of Joules/K.

A process is more likely to occur if it is accompanied by an increase of entropy that is ΔS > 0.

Entropy is a state function. It is independent of the path.

For a system:

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

If $\Delta S > 0$, the randomness increases
If $\Delta S < 0$, the randomness decreases.

Unit of ΔS is J/mole K

The entropy of a perfect pure crystal at 0 K (absolute zero) is zero.

Standard molar entropies of elements are not zero.

$$S^o \text{ gas} > S^o \text{ liquid or } S^o \text{ solid}$$

Factors that affect entropy

The higher the disorder, the higher the entropy. Gas particles are more disordered than liquids or solids.

In general entropy will increase when:

liquids or solutions are formed from solids

gases are formed from solids or liquids

the number of gas molecules increases

the reaction produces more gas particles

the pressure of a gas is reduced

dispersion or diffusion increases

the solution is more dilute

the total number of moles of products are greater than the total number of moles of reactant

the crystalline sodium chloride (ordered) dissolved in water

the number of atoms in the formula of the substance increases
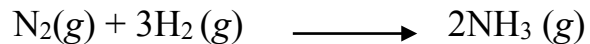
the molar mass increases.

Entropy decreases when sodium chloride forms from 2 moles of sodium and 1 mole of aqueous chloride.

Hess's Law applied to entropy.

For a chemical reaction which produces n products from m reactants.

$$\Delta S^o{}_{rxn} = \Sigma n\, S^o\, (\text{products}) - \Sigma m\, S^o\, (\text{reactants})$$

Example:

$$N_2(g) + 3H_2\,(g) \longrightarrow 2NH_3\,(g)$$

$$\Delta S^o{}_{rxn} = \Sigma n\, S^o\,(\text{products}) - \Sigma m\, S^o\,(\text{reactants}).$$

$$\Delta S^o{}_{rxn} = 2\, S^o\,(NH_3) - [S^o\,(N_2) + 3\, S^o\,(H_2)]$$

Gibbs Free Energy (spontaneity, Thermodynamically favored)

Gibbs free energy: is the energy of a system that is available for work. Free energy is a state function, For a process occurring at constant temperature, the free energy change is:

$$\Delta G = \Delta H + T\,\Delta S$$

The sign is is important in predicting the spontaneity (thermodynamically favorable) of the reaction.

If **$\Delta G < 0$** then the forward reaction is spontaneous (thermodynamically favorable).

If $\Delta G = 0$ then the reaction is at equilibrium and not net reaction will occur.

If $\Delta G > 0$ then the forward reaction is not spontaneous (thermodynamically favorable). However, the reverse reaction is spontaneous (thermodynamically favorable).

Melting (fusion) and boiling point (vaporization)

For a system at the melting point (T fusion or T mp) , the solid and liquid are in equilibrium.

$$\Delta G = \Delta H_{fusion} - T_{fusion}\ \Delta S_{fusion} = 0,$$

$$T_{fusion,\ mp} = \Delta H_{fusion} / \Delta S_{fusion}$$

For a system at the boiling point (T bp or T vaporization)

$$\Delta G = \Delta H_{vaporization} - T_{vaporization}\ \Delta S_{vaporization} = 0,$$

$$T_{vaporization,\ bp} = \Delta H_{vaporization} / \Delta S_{vaporization}$$

Standard Free-Energy Changes

Standard states are: pure solid, pure liquid, 1 atm (gas), 1M concentration (solution), 25°C or 298 K as the temperature.

$$\Delta G^o = 0 \text{ for elements.}$$

he standard free energy change for a precess is given by

$$\Delta G^o = \Sigma n\, \Delta G^o\, \textbf{(products)} - \Sigma m\, \Delta G^o\, \textbf{(reactants).}$$

The quantity of ΔG^o for a reaction tells us whether a mixture of substance will spontaneously react to produce more reactants ($\Delta G^o > 0$) or more products ($\Delta G^o < 0$)