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Spontaneous Processes and Spontaneity of the Processes

"The processes which have strong tendency to take place by itself are called spontaneous processes and this inherent tendency of the spontaneous processes is called spontaneity of the processes."

The spontaneous processes are of following two types-

(1) Spontaneous Processes which need No Initiation-

(i) Dissolution of salts or sugar in water

(ii) Mixing of different gases with one another

(iii) Evaporation of water from water reservoirs such as ponds, lakes, rivers etc.

$$H_2O\ (l) \rightarrow H_2O\ (g)$$

(iv) Transfer of heat from hot body to cold body

(v) Combination of Nitric oxide and oxygen to form Nitrogen dioxide

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$$

(vi) Combination of H_2 and I_2 to form HI

$$H_2\ (g) + I_2\ (g) \rightarrow 2HI\ (g)$$

(2) Spontaneous Processes which need Initiation-

(i) Burning of fuel (coal)

(ii) Combination of Hydrogen and oxygen to form water

$$2H_2\ (g) + O_2\ (g) \xrightarrow{\text{Heat spark}} 2H_2O\ (g)$$

If a mixture of hydrogen and oxygen is taken in a closed vessel, there is no reaction by itself. However, if the reaction is once started by using an electric spark, it becomes spontaneous until one or both the reactants are consumed up.

(iii) Decomposition of $CaCO_3$-

$$CaCO_3 \xrightarrow{\text{Heat}} CaO\ (s) + CO_2(g)$$

All the naturally occurring processes are spontaneous and unidirection in nature.

Entropy (S)-

"The degree of disorder or randomness present in a system is called Entropy of the system".

The entropy of the system is represented by S.

The greater the degree of disorder or randomness present in a system, more is the entropy of the system.

For example, the order of entropy of all the three states of matter is as under-

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$$S_{Solid} < S_{Liquid} < S_{Gas}$$

Here, in solid state, the matter is the most ordered and therefore, it has the least entropy. On the other hand, in gaseous state, the matter is the least ordered and therefore, it has the highest entropy. The entropy of liquid state is in between solid and gaseous state.

Entropy is a state function and therefore, its value depends only upon the state of the system and is independent of the path or agency by which the state has been attained. The absolute value of entropy cannot be determined experimentally. However, the change in entropy (ΔS) during a process can be determined easily and is given by following expression-

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

For a chemical reaction, the change in entropy,

$$\Delta S = S_{products} - S_{reactants}$$

Here, the value of ΔS also depends only upon initial and final states of the system and is independent of the path followed during the process or manner by which the process has been carried out (i.e. whether the process has been carried out reversibly or irreversibly).

Unit of Entropy- $JK^{-1}mol^{-1}$

Mathematical definition of ΔS-

"The change in entropy during a process is equal to the integral of all the terms of heat exchange (q) divided by absolute temperature during each infinitesimally small change of the process carried out isothermally and reversibly".

Mathematically,

$$\int dS = \frac{1}{T}\int \delta q_{rev}$$

or

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

Here, if heat is absorbed during the process then ΔS is positive (Entropy increases), but if heat is evolved during the process then ΔS is negative (Entropy decreases).

Entropy change in Reversible Processes-

Let, a system absorbs q amount of heat isothermally and reversibly from its surroundings at temperature T. Then, increase in entropy of the system,

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$$\Delta S_{system} = + \frac{q_{rev}}{T}$$

Here, the surroundings loses the same amount of heat at same temperature so that, its entropy decreases. Thus, decrease in entropy of the surroundings,

$$\Delta S_{surr} = - \frac{q_{rev}}{T}$$

Thus, the total change in entropy during the process,

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$$
$$= + \frac{q_{rev}}{T} + [- \frac{q_{rev}}{T}]$$
$$= 0$$

Thus, during isothermal reversible processes, the total entropy change is zero.

If the reversible processes is adiabatic, then there will be no exchange of heat between system and surroundings.

Thus, for an adiabatic and reversible process,

$$q_{rev} = 0$$

$$\therefore \quad \Delta S_{system} = \Delta S_{surr} = 0$$

Thus,

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr}$$
$$= 0$$

Physical Significance of Entropy-

The entropy is the measure degree of disorder or randomness present in a system. The greater the degree of disorder or randomness present in a system, more is the Entropy of the system.

For example, the order of entropy of all the three states of matter is as under-

$$S_{Solid} < S_{Liquid} < S_{Gas}$$

Here, in solid state, the matter is the most ordered and therefore, it has the least entropy. On the other hand, in gaseous state, the matter is the least ordered and therefore, it has the highest entropy. The entropy of liquid state is in between solid and gaseous state.

It has been found that, isolated systems have tendency to move in the direction where entropy increases. Thus, it can be concluded that, for isolated systems, the most entropic state is the most stable state of the system.

Entropy is also considered to be measure of unavailable energy of the system.

$$\text{Entropy} = \frac{Unavailable\ Energy}{Temperature\ (K)}$$

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Second Law of Thermodynamics in terms of Entropy

According to this law, "During all the naturally occurring spontaneous processes the total entropy of the system and the surrounding always increases and the total change in entropy of the system and the surrounding is always positive."

Mathematically,

$$\mathbf{\Delta S_{System} + \Delta S_{Surr} > 0 \ (+ve)}$$

For an isolated system,

$$\mathbf{\Delta S_{Surr} = 0}$$

$$\mathbf{\therefore \quad \Delta S_{System} > 0 \ (+ve)}$$

Thus, "During all the spontaneous processes occurring in an isolated system, the total entropy of the system always increases and the total change in entropy of the system is always positive."

Since, universe is an isolated system. The second law of thermodynamics can also be defined as under-

"During all the naturally occurring spontaneous processes, the total entropy of the universe always increases and the total change in entropy of the universe is always positive."

Mathematically,

$$\mathbf{\Delta S_{Universe} > 0 \ (+ve)}$$

Entropy of Phase Transformation-

The change of a substance from one state to another is called phase transformation. Phase transformation occurs at a definite temperature and is accompanied by change in entropy. Here, if heat is absorbed, the entropy increases but it heat is evolved then entropy decreases.

Mathematically, the entropy of phase transformation,

$$\Delta S_{trans.} = \frac{q_{rev}}{T}$$

Where, q_{rev} = heat absorbed or evolved

T = Temperature of phase transition

(i) Entropy of Fusion (ΔS_{fusion})-

"The change in entropy when one mole of a solid substance changes into liquid at its fusion temperature (melting point) is called the entropy of fusion of the substance." .

Mathematically, the entropy of fusion,

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f}$$

Where, ΔH_{fusion} = Molar enthalpy of fusion (Latent heat of fusion)

T_f = Fusion temperature or Melting point (K)

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(ii) Entropy of Vaporisation (ΔS_{vapour})-

"The change in entropy when one mole of a liquid substance changes into vapours at its boiling point is called the entropy of vaporisation of the substance."

Mathematically, the entropy of vaporisation,

$$\Delta S_{vapour} = \frac{\Delta H_{vapour}}{T_b}$$

Where, ΔH_{vapour} = Molar enthalpy or Latent heat of vaporisation

T_b = Boiling point of liquid (K)

Free Energy (G)-

If a system is not in equilibrium with its surrounding, then there is some energy difference between the system and the surrounding. This energy difference can be converted into the useful work and is called the free energy of the system. It is represented by G. By definition,

"The maximum available energy to a system during a process which can be converted into the useful work is called the free energy of the system".

Mathematically, the free energy of the system,

$$G = H - TS$$

Where, H = Enthalpy of the system

S = Entropy of the system

T = Absolute temperature

Free energy is a state function and therefore, its value depends only upon the state of the system and is independent of the path or agency by which the state has been attained. The absolute value of free energy cannot be determined experimentally. However, the change in free energy (ΔG) during a process can be determined easily and is given by following expression-

$$\Delta G = G_{final} - G_{initial}$$

For a chemical reaction, the change in entropy,

$$\Delta G = G_{products} - G_{reactants}$$

Here, the value of ΔG also depends only upon initial and final states of the system and is independent of the path followed during the process.

Gibbs-Helmholtz Equation-

Mathematically, the free energy of the system,

$$G = H - TS$$

Where, H = Enthalpy of the system

S = Entropy of the system

T = Absolute temperature

$\because$ $H = E + PV$

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$$\therefore \quad G = E + PV - TS$$
$$\therefore \quad \Delta G = \Delta E + \Delta(PV) - \Delta(TS)$$
$$\text{or} \quad \Delta G = \Delta E + P\Delta V + V\Delta P - T\Delta S - S\Delta T$$

For the processes occurring at constant temperature and pressure,

$$V\Delta P = 0 \quad \text{and} \quad S\Delta T = 0$$
$$\therefore \quad \Delta G = \Delta E + P\Delta V - T\Delta S$$
$$\text{Here,} \quad (\Delta E + P\Delta V) = \Delta H$$
$$\therefore \quad \Delta G = \Delta H - T\Delta S$$

This expression is called Gibbs-Helmholtz equation. It is helpful in determining spontaneity of the processes at a given temperature.

Here, if for a process,

(1) ΔG = -ve, then the process is spontaneous in given direction.

(2) ΔG = +ve, then the process is not spontaneous in given direction but it is spontaneous in opposite direction.

(3) ΔG = 0, then the process is in equilibrium

Determination of Spontaneity of Reactions using Gibbs-Helmholtz Equation-

Spontaneous processes occur in the direction in which free energy of the system decreases i.e. change in free energy (ΔG) of the system is negative. Thus, for spontaneous processes-

$$\Delta G = -ve$$

Gibbs-Helmholtz equation is helpful in deciding the conditions in which ΔG is negative and therefore, it is helpful in deciding the spontaneity of the processes. Here, if for a process-

(1) ΔH = -ve (favourable)
and ΔS = +ve (favourable)
Then, $\Delta G = -\Delta H - T(+\Delta S)$
$= -\Delta H - T\Delta S$
= -ve (always)

Thus, the process will be spontaneous at all the temperatures.

(2) ΔH = -ve (favourable)
and ΔS = -ve (unfavourable)
Then, $\Delta G = -\Delta H - T(-\Delta S)$
$= -\Delta H + T\Delta S$

Here, following two cases may arise-

(a) At low temperature, $T\Delta S < \Delta H$
$\therefore \quad \Delta G$ = -ve

Thus, the process will be spontaneous in given direction at low temperatures.

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(b) At high temperature, $T\Delta S > \Delta H$

$\therefore \quad \Delta G = +ve$

Thus, the process will not be spontaneous in given direction at high temperatures, but it will be spontaneous in opposite direction.

(3) $\Delta H = +ve$ (unfavourable)

and $\Delta S = +ve$ (favourable)

Then, $\Delta G = +\Delta H - T(+\Delta S)$

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

Here, also following two cases may arise-

(a) At low temperature, $T\Delta S < \Delta H$

$\therefore \quad \Delta G = +ve$

Thus, the process will not be spontaneous in given direction at low temperatures, but it will be spontaneous in opposite direction.

(b) At high temperature, $T\Delta S > \Delta H$

$\therefore \quad \Delta G = -ve$

Thus, the process will be spontaneous in given direction at high temperatures.

(4) $\Delta H = +ve$ (unfavourable)

and $\Delta S = -ve$ (unfavourable)

Then, $\Delta G = +\Delta H - T(-\Delta S)$

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

$= +ve$ (always)

Thus, the process will not be spontaneous in given direction at any temperatures.

Physical Significance of ΔG

From first law of thermodynamics, change in internal energy during a process (ΔU) is given by following expression-

$$\Delta U = q - w \qquad \text{------(1)}$$

Where, q = heat absorbed by the system

w = work done by the system

Here, work done includes two types of works i.e. expansion work (w_{exp}) and non-expansion work ($w_{non\text{-}exp}$) or useful work ($w_{non\text{-}exp}$). Thus,

$$\Delta U = q - w_{exp} - w_{non\text{-}exp}$$

$\because \quad w_{exp} = P\Delta V$

$\therefore \quad \Delta U = q - P\Delta V - w_{non\text{-}exp}$

or $\quad q = \Delta U + P\Delta V + w_{non\text{-}exp}$

$\because \quad \Delta U + P\Delta V = \Delta H$

$\therefore \quad q = \Delta H + w_{non\text{-}exp} \qquad \text{------(2)}$

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From second law of thermodynamics, change in entropy during an isothermal reversible process is given by the expression-

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

$$\therefore \quad q_{rev} = T\Delta S$$

Putting this value of q in eq. (2), we get-

$$T\Delta S = \Delta H + w_{non\text{-}exp}$$

$$\text{or} \quad -w_{non\text{-}exp} = \Delta H - T\Delta S \qquad \text{------(3)}$$

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

$$\therefore \quad -w_{non\text{-}exp} = \Delta G$$

$$\text{or} \quad w_{non\text{-}exp} = -\Delta G$$

$$\text{or} \quad w_{useful} = -\Delta G \qquad \text{-------(4)}$$

Thus, the non-expansion (non-mechanical) or useful work done during a process is equal to the decrease in free energy during the process. The greater the value of decrease in free energy during a process, more is the useful work that can be obtained during the process. This is the physical significance of ΔG. This correlation is used in assessment of electrical work that can be obtained by the electrochemical cells and fuel cells.

- The expansion and non-expansion works done during a process can be explained by taking the example of electrolysis of water to produce $H_2(g)$ and $O_2(g)$ with increase in volume of the system. Here, decomposition of water involves non-expansion or useful work while, the expansion in volume of the system involves expansion work (mechanical work).

Free Energy Change and Electrical work done

Free energy change (ΔG) is related with EMF of the cell as per the following relation-

$$\Delta G = -nFE$$

Where, n = No. of electrons involved in balanced electrochemical reaction

F = Faraday's constant = 96500 C

E = emf of the electrochemical cell

If the reactants and products involved in electrochemical reaction are in their standard state, then standard free energy change,

$$\Delta G^0 = -nFE^0$$

Where, E^0 = standard emf of the electrochemical cell

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Free energy of formation ($\Delta_f G$)

"The free energy change when one mole of a compound is formed by combination of its elements is called free energy of formation of the compound ($\Delta_f G$)".

If the free energy of formation of the compounds is measured in standard state (298 K temperature, 1atm pressure), then it is termed as the standard free energy of formation of the compounds ($\Delta_f G^0$).

For example, when one mole of CO_2 is formed by combination of carbon and oxygen in standard state (298 K temperature, 1atm pressure), standard free energy change is -394.4 kjmol^{-1}. Hence, standard free energy of formation of CO_2 will be -394.4 kjmol^{-1}.

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g); \qquad \Delta_f G^0 = -394.4 \text{ kjmol}^{-1}$$

Similarly, standard free energy of formation of water is -228.6 kjmol^{-1}.

$$H_2(g) + \tfrac{1}{2} O_2\,(g) \rightarrow H_2O\,(l); \qquad \Delta_f G^0 = -228.6 \text{ kjmol}^{-1}$$

Since, the process of formation of a compound may either be exothermic or endothermic, the standard free energy of formation of the compounds may be positive or negative.

By convention, the standard free energy of formation of the elements are taken to be zero.

Free energy of the reaction ($\Delta_r G$)

"The free energy change when total number of moles of reactants represented in balanced chemical equation, react completely to form products is called free energy of the reaction ($\Delta_r G$)".

If free energy of reaction is measured in standard state (298 K temperature, 1 atm pressure), then it is called standard free energy of reaction ($\Delta_r G^0$).

For example, when one mole of CO_2 is formed by combination of carbon and oxygen in standard state (298 K temperature, 1atm pressure), standard free energy change is -394.4 kj. Hence, standard free energy of the reaction involved will be -394.4 kj.

$$C\,(s) + O_2\,(g) \rightarrow CO_2\,(g); \qquad \Delta_r G^0 = -394.4 \text{ kj}$$

Similarly, standard free energy of reaction for the combustion of methane is -817.4 kj.

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l); \quad \Delta_r G^0 = -817.4 \text{ kj}$$

Since, the reactions may either be exothermic or endothermic, the standard free energy of the reaction may be positive or negative.

The standard free energy of the reactions is found to be equal to the difference of the summation of standard free energy of the formation of products

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and the summation of the standard free energy of the formation of the reactants. Thus, the standard free energy of the reaction,

$$\Delta_r G^0 = \sum \Delta_f G^0 \text{ (products)} - \sum \Delta_f G^0 \text{ (reactants)}$$

For example, for following reaction-

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(l)$$

The standard enthalpy of the reaction,

$$\Delta_r G^0 = [\Delta_f G^0\{CO_2(g)\} + 2\times\Delta_f G^0\{H_2O(l)\}] - [\Delta_f G^0\{CH_4(g)\} + 2\times\Delta_f G^0\{O_2(g)\}]$$

Relation Between Standard Free Energy Change and Equilibrium Constant-

Let us consider following reversible reaction-

$$A + B \rightleftharpoons C + D$$

Free energy change for this reaction is given by following expression-

$$\Delta G = \Delta G^0 + RT\ln Q \qquad \text{-------(1)}$$

Where, ΔG^0 = Standard free energy change

R = Universal gas constant

T = Absolute temperature

Q = Reaction quotient

At the equilibrium of the reaction-

$$\Delta G = 0$$

and $Q = K_c$

$\therefore \quad 0 = \Delta G^0 + RT\ln K_c$

or $\Delta G^0 = -RT\ln K_c \qquad \text{--------(2)}$

Changing the base of logarithm from e to 10, we get-

or $\Delta G^0 = -2.303RT\log K_c \qquad \text{--------(3)}$

Here, Eq. (2) and (3) give the relation between standard free energy change and equilibrium constant of the reversible reactions.

Third Law of Thermodynamics

This law was for the first time proposed by Nernst. It governs the entropy of perfectly crystalline substances. According to this law,

"At absolute zero temperature, the entropy of perfectly crystalline substances is zero."

Mathematically,

$$\lim_{T \to 0} S \rightarrow 0$$

In fact, entropy of substances decreases with decrease of temperature and at absolute zero temperature it approaches zero. Thus, at absolute zero temperature, the perfectly crystalline substances are in state of perfect order.

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Applications of Third law of Thermodynamics

Third law of thermodynamics is useful in calculation of absolute entropies of solids, liquids and gases at different temperatures. It is also useful in calculation change in entropy during a physical or chemical process.

$$\because \quad dS = \frac{dq}{T}$$

$$\therefore \quad dS = Cp\frac{dT}{T}$$

$$\text{or} \quad S_T - S_0 = Cp\frac{dT}{T}$$

from third law of thermodynamics-

$$S_0 = 0$$

$$\therefore \quad S_T = Cp\frac{dT}{T}$$

On integrating this equation between the temperature 0 and T, we get-

$$S_T = \int_0^T Cp\,\frac{dT}{T}$$

$$= Cp \ln T$$

$$= 2.303\ Cp \log T$$

Here, if $\frac{C_P}{T}$ is plotted against T, then the area under curve from 0 to T K corresponds to the value of integral i.e. the absolute entropy of substance at temperature T.

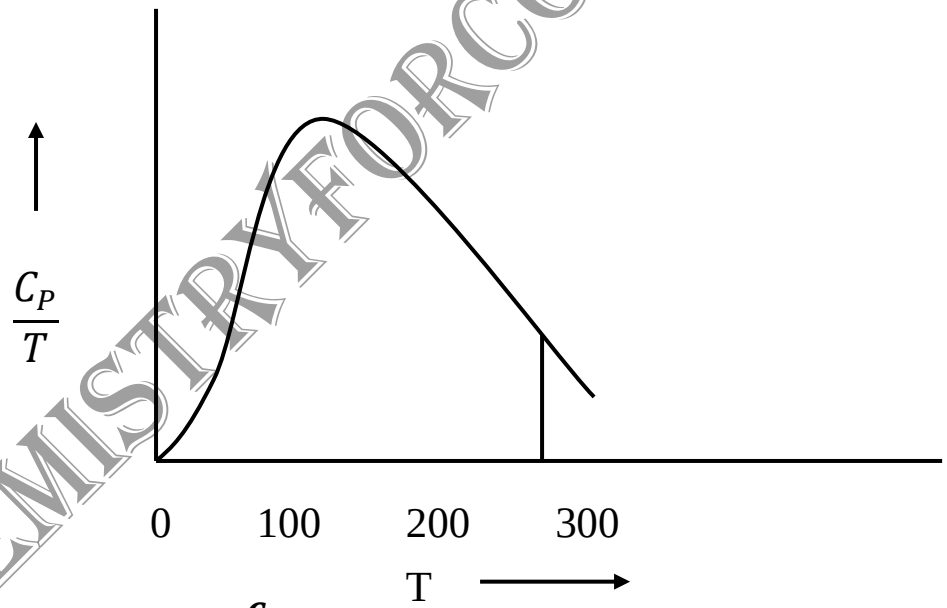


Fig.- Plot of $\frac{C_P}{T}$ against absolute temperature T

Standard Entropy of the Substance-

"The entropy of a substance in standard state (298K, 1atm) is called standard entropy of the substance." It is denoted by S^0.

The standard entropy change for a chemical reaction (ΔS^0) is given by following expression-

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$$\Delta S^0 = \sum S^0 \text{ (products)} - \sum S^0 \text{ (reactants)}$$

$$= \left[\begin{array}{c}\text{Sum of standard} \\ \text{entropies of products}\end{array}\right] - \left[\begin{array}{c}\text{Sum of standard} \\ \text{entropies of reactants}\end{array}\right]$$

For example, for following reaction-

$$C_2H_6\,(g) \rightarrow C_2H_4\,(g) + H_2\,(g)$$

The standard enthalpy of the reaction,

$$\Delta S^0 = [S^0\{C_2H_4\,(g)\} + S^0\{H_2(g)\}] - [S^0\{C_2H_6(g)\}]$$

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