ENTROPY AND GIBB'S FREE ENERGY

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'Entropy is a measure of randomness or disorder of the system'. The greater the randomness, the higher is the entropy. The crystalline solid state has the lowest entropy. The gaseous state has the highest entropy. The liquid state has the entropy in-between the two. It is represented by 'S'. It is a state function. The change in its value during a process i.e the entropy change (ΔS) from initial state to final state, is given by

$$\Delta S = S_{\text{final state}} - S_{\text{initial state}} .$$

For chemical reactions: - $\Delta S = \Sigma S \text{ (products)} - \Sigma S \text{ (reactants)}$

For a reversible process at equilibrium, the change in entropy may be expressed as:

$$\Delta S = \frac{q\ rev,iso}{T}$$

" So we can express ΔS as the entropy change during a process and is defined as the amount of heat (q) absorbed isothermally and reversibly divided by the absolute temperature (T) at which the heat is absorbed."

The quantity $\frac{q}{T}$ is a measure of disorder. It is justified on the basis of the following two reasons,

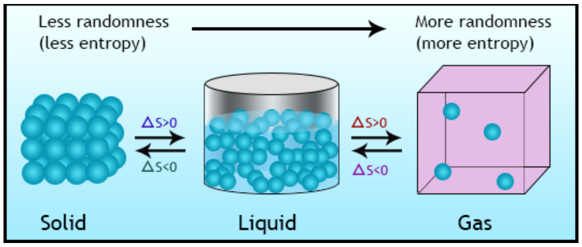
(i) When a system absorbs heat, the molecules start moving faster because kinetic energy increases. Hence, the disorder increases. More the heat absorbed, greater is the disorder.

(ii) For the same amount of heat absorbed at low temperature, the disorder is more than at higher temperature. This shows that entropy change is inversely proportional to temperature. Thus, there is large increase in entropy when a lot of energy is transferred to a system at a low temperature.

Units of entropy change:- As $\Delta S = \frac{q}{T}$, it is an extensive property. In C.G.S. system the unit of entropy are calories/K/mol and in S.I units are Joules/K/mol.

The physical significance of the entropy:- The physical meaning of entropy is the measure of degree of disorder or randomness of a system. This concept may be further understood with the help of the following examples:

(i) Melting of ice



(ii) In a school, when all classes are being held, all students are sitting in their respective class rooms and the disorder is minimum. As soon as the bell goes, the students of different classes come out to go to other rooms and thus get mixed up. In other words, the disorder or the randomness increases.

(iii)In the game of hockey or football, to start with all the players take up some definite positions and are thus said to be in order. As soon as the game starts, the players start running and thus they are said to have an increased randomness which increases further as the game catches more and more momentum.

Entropy as a state function:- Consider a system consisting of a cylinder containing a gas and fitted with frictionless and weightless piston and placed in contact with a large heat reservoir. Suppose the system absorbs heat 'q' isothermally and reversibly at temperature T and expands from volume V_1 to V_2, then the change in entropy of the system is given by $\Delta S_{sys} = \frac{q\ rev}{T}$

As equivalent amount of heat is lost by the reservoir, change in entropy of the reservoir, $\Delta S_{res} = -\frac{q\ rev}{T}$ $\therefore$ Total change in entropy $\Delta S_1 = \Delta S_{sys} + \Delta S_{res} = \frac{q\ rev}{T} + [-\frac{q\ rev}{T}] = 0$

Now, if we compress the gas isothermally from volume V_2 to V_1, heat q_{rev} will be given out by the system and absorbed by the reservoir so that $\Delta S_{sys} = -\frac{q\ rev}{T}$ and $\Delta S_{res} = \frac{q\ rev}{T}$ $\therefore$ Total entropy, $\Delta S_2 = -\frac{q\ rev}{T} + \frac{q\ rev}{T} = 0$. Total change in entropy for the complete cycle = $\Delta S_1 + \Delta S_2 = 0$. Thus, at the end of the cyclic process, the entropy of the system remains the same as it originally had. This proves that entropy is a state function.

Spontaneity in terms of entropy change:- Consider the following spontaneous process in an isolated system: (i) Mixing of the two gases on opening the stopcock (ii) spreading of a drop of ink in a beaker filled with water. These processes do not involve any exchange of matter and energy with the surroundings. Hence, these are isolated systems. Further, these processes are accompanied by increase of randomness and hence increase of entropy, i.e., for these processes, entropy change (ΔS) is positive. Hence , it may be concluded that for spontaneous processes in the isolated systems, the entropy change is positive ($\Delta S > 0$).

Now, let us consider the following spontaneous processes in an open vessel: (i) Cooling down of a cup of tea (ii) reaction taking place between a piece of marble ($CaCo_3$) or sodium hydroxide ($NaOH$) and hydrochloric acid in an open vessel. These are not isolated systems because they involve exchange of matter and energy with the surroundings. Hence, for these processes, we have to consider the total entropy change of the system and the surroundings. i.e., $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$. For the process to be spontaneous, ΔS_{total} must be positive. Hence, it can be generalized that "for all spontaneous processes the total entropy change (ΔS_{total}) must be positive" i.e.,

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

Further, in all the above spontaneous processes, there is randomness. Hence, the entropy keeps on increasing till ultimately an equilibrium is reached, e.g., uniform distribution of gases after mixing or uniform distribution of ink in water is a stage of equilibrium. Thus, the entropy of the system at equilibrium is maximum and there is no further change of entropy, i.e., $\Delta S = 0$. Hence, it may be concluded that "for a process in equilibrium, $\Delta S = 0$". Arguing in a similar manner, it can be proved that if ΔS_{total} is negative, the direct process is non-spontaneous whereas the reverse process may be spontaneous.

Combining all the results discussed above, it may be concluded that the criterion for the spontaneity in terms of entropy change is as follows:

(i) If ΔS_{total} is positive, the process is spontaneous.
(ii) If ΔS_{total} is negative, the direct process is non-spontaneous; the reverse process may be spontaneous.
(iii) If ΔS_{total} is zero, the process is in equilibrium.

Apply the entropy criterion: for example, consider conversion of water into ice at 1 atmosphere pressure $H_2O\ (l) \rightarrow H_2O\ (s)$

The total entropy change for three different temperatures:

I. At 272K (-1°C) $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = -21.85 + 21.93 = +0.08\ Jk^{-1}\ mol^{-1}$. So ΔS_{total} is positive at 272K. And hence freezing of water into ice is spontaneous.

II. At 273K (0°C) $\Delta S_{total} = \Delta S_{sym} + \Delta S_{surr} = -21.99 + 21.99 = 0$. Since ΔS_{total} is zero, process is at equilibrium i.e., neither freezing nor melting is spontaneous. At this temperature water and ice are in equilibrium at 273K. No net change is observed.

III. At 274K (+1°C) $\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} = -22.13 + 22.05 = -0.08 Jk^{-1}mol^{-1}$. Since ΔS_{total} is negative. So the process is non-spontaneous at 274K. But for the reverse process ΔS_{total} will be positive. $\Delta S_{total} = +0.08\ Jk^{-1}mol^{-1}$. Melting of ice is spontaneous at 274K.

Thus, we have observed ΔS_{total} is a criterion for spontaneity of a change.

CHRACTERISTICS OF ENTROPY

(i) Entropy is an extensive property (Its value depends upon the amount of the substance present in the system).

(ii) Entropy of a system is a state function, $\Delta S = \Delta S_{final\ state} - \Delta S_{initial\ state}$ (depends upon the state variables T, P, V, n) (Independent of the path).

(iii) The change in entropy for a cyclic process is always zero.

(iv) The total entropy change of an isolated system is equal to the entropy change of system and entropy change of surrounding. $\Delta S_{universe} = \Delta S_{sys} + \Delta S_{surr}$. The sum is called entropy change of universe.

(v) In a reversible process $\Delta S_{universe} = 0$ therefore $\Delta S_{sys} = -\Delta S_{surr}$

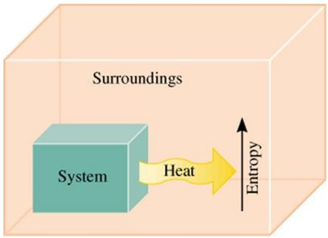
(vi) In a irreversible process, $\Delta S_{universe} > 0$ spontaneous change

In term of entropy the definition of the second law may be given as follows: All spontaneous processes are accompanied by a net increase of entropy, i.e., for all the spontaneous processes, the total entropy change (sum of the entropy changes of the system and the surroundings) is positive.

Entropy changes in system and surrounding and total entropy change for exothermic and endothermic reactions:-

1. **For exothermic reactions:**

(a) In exothermic reactions, the randomness and hence entropy increases so that ΔS_{sys} is positive. The heat given out by the reaction is absorbed by the surrounding. Hence the disorder of the surrounding also increases. The total entropy change is highly positive. Hence, the reactions are highly spontaneous.



Exothermic Process
$\Delta S_{surr} > 0$

(b) In some exothermic reactions, the entropy of the system may decrease for example- in the condensation of gas or solidification of a liquid. Heat evolved is very high that it greatly increases the disorder of the surrounding and the overall entropy change (ΔS_{total}) is again positive.

In oxidation of magnesium:- $2Mg + O_2(g) \rightarrow 2MgO$, $\Delta S_{reaction} = -217 Jk^{-1}mol^{-1}$

$\Delta H_{reaction} = -1202K\ Jmol^{-1}$, this heat is absorbed by the surrounding at 25°C .

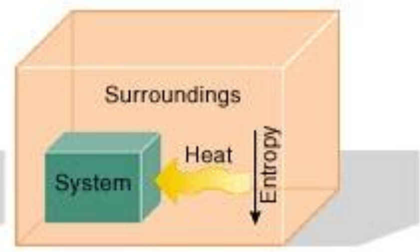
$\Delta S_{surrounding} = -\frac{-1202 \times 1000\ J\ mol-1}{298K} = 4034 JK^{-1}mol^{-1}$

$\Delta S_{total} = -217 JK^{-1}mol^{-1} + 4034 JK^{-1}mol^{-1} = 3817\ JK^{-1}mol^{-1}$

ΔS_{total} is positive, the reaction is spontaneous.

2. **For endothermic reactions:**

In endothermic reactions, heat is absorbed by the reactants while it is lost by the surroundings. The disorder of the surrounding decreases i.e., (ΔS_{surr} is negative).The disorder of the reactants may increase. When the entropy of the system increases enough to overcome the decrease in entropy of the surrounding then overall entropy change is positive. Hence the reaction will be spontaneous.



Entropy change during phase transition: The change of matter from one state to another state is called phase transition. (i) Solid to liquid (melting point at definite temp.) (ii) Liquid to vapour (boiling point at definite temp.)

The entropy change $\Delta S = \frac{q\ rev.}{T}$, q_{rev} = heat absorbed or evolved, T= Temperature

Entropy of fusion: It may be defined as: “The entropy change when 1 mole of the solid substance changes into liquid form at its melting point”. For example: when ice melts i.e Water (s) → water (l)

$S_{\text{water}} - S_{\text{ice}} = \Delta S_{\text{fus}} = \Delta_{\text{fus}} H^o / T_f$, where $\Delta_{\text{fus}} H^o$ = enthalpy of fusion and T_f = fusion temperature (Melting point)

Numerical: The standard enthalpy of fusion $\Delta_{\text{fus}}H°$ at 273K and 1 bar pressure for water is 6.0 KJmol^{-1}. Calculate the entropy of fusion of ice.

Solution: $H_2O\,(s) \rightarrow H_2O\,(l)$
$\Delta_{\text{fus}} H° = +6.0$ KJmol^{-1} T = 273K

$$\Delta S_{\text{fus}} = \frac{q\ fus}{T} = \frac{\Delta H°}{T} = \frac{6.0 \times 1000\ J\ mol{-1}}{273} = 21.98\ JK^{-1}mol^{-1}$$

Entropy of vaporization: It is defined as “The entropy change when 1 mole of a liquid changes into vapours at the boiling point.” The entropy of vaporization for a liquid at its boiling point is:
$\Delta_{\text{vap}} S = \Delta_{\text{vap}} H / T_b$, $\Delta_{\text{vap}} H°$ is the standard enthalpy of vaporization and T_b is the boiling point.

Numerical: Calculate the entropy of vaporization for water. The enthalpy change for the transition of liquid water to steam is 40.8KJ mol^{-1} at 373K.

Solution: $\Delta_{\text{vap}} S° = \frac{\Delta\ vap\ H}{T}$

$\Delta_{\text{vap}} H° = 40.8$KJ mol^{-1} and T = 373K

$$\Delta_{\text{vap}} S° = \frac{40.8 \times 1000\ J\ mol{-1}}{373K} = 109.4\ JK^{-1}mol^{-1}$$

Entropy of sublimation: Sublimation is a direct conversion of a solid into its vapour.

Entropy of sublimation may be defined as: “The entropy chane when 1 mole of a solid changes into vapour at a particular temperature.”

$$\Delta_{\text{Sub}} S° = \frac{\Delta\ Sub\ H}{T}$$

Δ_{Sub} H = Standard enthalpy of sublimation

T = Temperature

$\Delta_{\text{Sub}} H = (\Delta_{\text{fus}}H + \Delta_{\text{vap}}H)$

Entropy change in processes not involving any phase transformation: In these processes entropy also increases when the number of molecules of products is greater than the number of molecules of reactants.
e.g.

$2\,SO_3\,(g) \rightarrow 2SO_2\,(g) + O_2\,(g)$
$PCl_5\,(g) \rightarrow PCl_3\,(g) + Cl_2\,(g)$
$N_2O_4 \rightarrow 2NO_2\,(g)$

GIBBS FREE ENERGY: This is another thermodynamic quantity that helps in predicting the spontaneity of a process. Gibbs energy of the system is defined as “the maximum amount of energy available to a system during a process that can be converted into useful work". It is a measure of capacity of a system to do useful work. It is denoted by G .

Mathematically: $G = H - TS$, $H =$ heat content, $T =$ absolute temperature, $S =$ entropy of the system. For isothermal process we have: $G_1 = H_1 - TS_1$ (for the initial state), $G_2 = H_2 - TS_2$ (for the final state)
$\therefore G_2 - G_1 = (H_2 - H_2) - T(S_2 - S_1)$, $\Delta G = G_2 - G_1$ is the change in Gibbs free energy of the system. $\Delta H = H_2 - H_1$ is the enthalpy change, $\Delta S = S_2 - S_1$ is the entropy change,
$\therefore \Delta G = \Delta H - T\Delta S$
This equation is known as Gibbs Helmholtz equation or Gibbs energy equation.

Free energy change and non- mechanical work (useful work): In addition to predicting the spontaneity of a process, another important aspect of Gibbs energy is its relationship to the useful work (other than pressure- volume work) that can be obtained from the system. Hence, Gibb's free energy is defined as "The thermodynamic quantity of a system the decrease in whose value during a process is equal to the maximum possible useful work that can be obtained from the system." This result may be derived as follows:

The relationship between heat absorbed by a system q, the change in its internal energy ΔU, and the work done by the system is given by the equation of the first law of thermodynamic, i.e.,

$$q = \Delta U + w_{\text{expansion}} + w_{\text{non- expansion}} \;\text{.........(i)}$$

Under constant pressure condition, the expansion work is given by PΔV

$$\therefore q = \Delta U + P\Delta V + w_{\text{non-expansion}}$$

$$= \Delta H + w_{\text{non-expansion}} \quad (\text{because } \Delta U + P\Delta V = \Delta H) \;\text{.......... (ii)}$$

For a reversible change taking place at a constant temperature,

$$\Delta S = \frac{q\,rev}{T} \text{ or } q_{rev} = T\Delta S \;\text{...................(iii)}$$

Substituting the value of q from equation (iii) in equation (ii)

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

$$\text{Or} \quad \Delta H - T\Delta S = -w_{\text{non-expansion}} \;\text{...................(iv)}$$

For a change taking place under conditions of constant temperature and pressure,

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

substituting this value in eqn. (iv) above, we get

$$\Delta G = -w_{\text{non-expansion}} \;\text{..............................(v)}$$

Thus, free energy change can be taken as a measure of work other than the work of expansion. For most changes, the work of expansion cannot be converted to other useful work, whereas the non-expansion work is convertible to useful work.
Rearranging equation (v), we may write :

$$-\Delta G = w_{\text{non-expansion}} = w_{\text{useful}} \;\text{............ (vi)}$$

Hence, the decrease in free energy of the system during any change, ΔG, is a measure of the useful or net work derived during the change. It may, therefore, be generalized that the free energy, G, of a system is a measure of its capacity to do useful work. It is a part of the energy of the system which is free for conversion to useful work and is, therefore, called free energy. It can be shown that the free energy change is equal to the maximum possible useful work that can be obtained from a process (for a reversible change at constant T and P). Hence, we can write

$$-\Delta G = w_{\max} \;\text{......... (vii)}$$

Thus, a spontaneous process can be utilized to do useful work. The greater the change in Gibbs energy, greater is the amount of work that can be obtained from the process. If the work involved is the electrical work as in the case of galvanic cells, then as electrical work =n FE, the above relationship is written as $-\Delta G = n FE$, where n = number of electrons involve in the cell reaction, E = EMF of the cell , F = Faraday If all the reactants and products of the cell reaction are in their standard states, i.e., 298K and 1 atm pressure, the above relationship is written as

$$-\Delta G^\circ = n\,FE^\circ \text{ ....(viii)}$$

Where, ΔG° = standard free energy change and E° = standard EMF of the cell.

In a fuel cell, it is found that the heat evolved (ΔH) is not completely converted into energy, i.e., useful work (given by ΔG).The ratio $\Delta G/\Delta H$ is called the efficiency of the fuel cell. Thus, Efficiency of a fuel cell = $\frac{\Delta G}{\Delta H}$

Assignment :

(1) When potassium chloride is dissolved in water (A) entropy increases (B) entropy decreases (C) entropy increases and then decreases (D) free energy increases.

(2) For a reversible process at equilibrium, the change in entropy may be expressed as:
(A) $\Delta S = Tq_{rev}$ (B) $\Delta S = \frac{q\,rev}{T}$ (C) $\Delta S = -\frac{\Delta H}{T}$ (D) $\Delta S = \Delta G$.

(3) For a spontaneous reaction, ΔG should be: (A) positive (B) negative (C) equal to zero (D) may be positive or negative.

(4) Which of the following processes is accompanied by decrease in entropy?
(A) Evaporation of water (B) Sublimation of dry ice (C) Melting of ice (D) Condensing steam.

(5) Free energy is related to enthalpy and changes in entropy as: (A) $\Delta G = \Delta H - T\Delta S$
(B) $\Delta G = T\Delta S - \Delta H$ (C) $\Delta G = \frac{\Delta H - \Delta S}{T}$ (D) $\Delta G = \Delta H + T\Delta S$

Answer 1 (A) 2. (B) 3. (B) 4. (D) 5. (A)