SECOND LAW OF THERMODYNAMICS

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Limitations of the first law of thermodynamics:- A major limitation of the first law of thermodynamics is that it merely indicates that in any process, there is an exact equivalence between the various forms of energies involved but it provides no information concerning the spontaneity or feasibility of the process, i.e., whether the process is possible or not. For example, the first law does not indicate whether heat can flow from a cold end to a hot end or not. Similarly, the first law does not tell whether a gas can diffuse from low pressure to high pressure or water can itself run uphill etc.

The answers to the above observations are provided by the second law of thermodynamics. However, before we take up different statements of the second law of thermodynamics, it is important to know what we understand by a 'spontaneous process'.
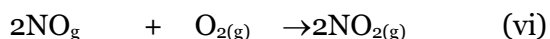
Spontaneity:- Spontaneity means the feasibility of a process i.e., whether the process is possible or not. Let us consider the following two processes:

(i)   Dissolution of sugar in water at room temperature.
(ii)   Burning of coal in air or oxygen

The first process takes place by itself, although it may be slow. The second process cannot take place by itself. It needs initiation i.e., we have to bring a flame near the coal to start its burning. But once it starts burning, it goes on by itself without the help of any external agency. Both the above processes are spontaneous processes. Hence, a spontaneous process may be defined as a process which can take place either of its own or under some initiation or A process which under some given conditions may take place by itself or by initiation independent of the rate is called a spontaneous process or A spontaneous process is simply a process which is feasible. For more clear understanding, a few more examples of the spontaneous processes are as follows:

A. Examples of processes which take place by themselves: (i) Dissolution of common salt in water (ii) Evaporation of water in an open vessel   (iii) Cooling down of a cup of tea (iv) Flow of water down a hill (v) Combination of nitric oxide and oxygen to form nitrogen dioxide
$2NO_g + O_{2(g)} \rightarrow 2NO_{2(g)}$ (vi) Combination of hydrogen and iodine to form hydrogen iodide
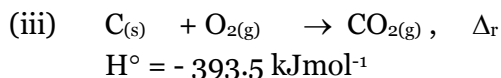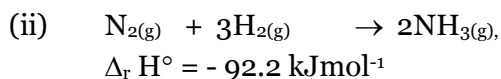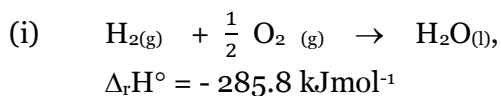$H_{2\,(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
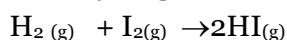
B. Examples of processes which take place on initiation: (i) A candle made up of wax burns only when ignited. (ii) Heating of calcium carbonate to give calcium oxide and dioxide (initiated by heat) : $CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ (iii) Combination of hydrogen and oxygen to form water when initiated by passing an electric spark: $H_{2(g)} + O_{2(g)} \rightarrow H_2O_{(l)}$ (iv) Acetylene burns brightly only upon heating with oxygen: $C_2H_{2(g)} + \frac{5}{2} O_{2(g)} \rightarrow 2CO_{2(g)} + H_2O_{(l)}$
A process which can neither take place by itself nor by initiation is called a non-spontaneous process.   Examples, (i) Flow of water up a hill (ii) Flow of heat from a cold body to a hot body. (iii) Diffusion of gas from low pressure to a high pressure (iv) Dissolution of sand in water.

The driving force for a spontaneous process: Why some processes are spontaneous? Obviously, there must be a force which drives the process or a reaction in a particular direction. This force which is responsible for spontaneity of a process is called the driving force.
Let as now see what is the nature of the driving force?

(1) **Tendency for minimum energy:** It is a common observation that in order to acquire maximum stability, every system tends to have minimum energy. For example, (i) A stone lying at a height has a tendency to fall down so as to have minimum potential energy. (ii) Water flows down a hill to have minimum energy. (iii) A wound watch spring has tendency to unwind itself to decrease its energy to minimum. (iv) Heat flows from hot body to cold body so that heat content of the hot body becomes minimum. Thus all the above process are spontaneous because they have a tendency to acquire minimum energy. Again, let us consider the following exothermic reactions; all of which are spontaneous:

(i) $H_{2(g)} + \frac{1}{2} O_{2\,(g)} \rightarrow H_2O_{(l)}$, $\Delta_r H° = - 285.8$ kJmol^{-1}

(ii) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$, $\Delta_r H° = - 92.2$ kJmol^{-1}

(iii) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$, $\Delta_r H° = - 393.5$ kJmol^{-1}

All these reactions are accompanied by evolution of heat. In other words, the heat content of the products is less than those of the reactants. Hence, one may conclude that a tendency to attain minimum energy, i.e., a negative value of enthalpy change, ΔH, might be responsible for a process or a reaction to be spontaneous or feasible.

Limitations of the criterion for minimum energy – the above criterion fails to explain the following:

a. A number of reactions are known which are endothermic, i.e., for which ΔH is positive but still they are spontaneous, e.g., (i) Evaporation of water or melting of ice. It takes place by absorption of heat from the surroundings. $H_2O_{(l)} \rightarrow H_2O_{(g)}$, $\Delta_{vap} H° = + 40.8$ kJmol^{-1} $H_2O_{(s)} \rightarrow H_2O_{(l)}$, $\Delta_{fus} H° = + 6.0$ kJ mol^{-1} (ii) Dissolution of salts like NH_4Cl, KCl etc. $NH_4Cl_{(s)} + aq \rightarrow NH_4^+_{(aq)} + Cl^-_{(aq)}$, $\Delta_{sol} H° = + 15.1$kJmol^{-1} (iii) Decomposition of calcium carbonate on heating $CaCO_{3\,(s)} \rightarrow CaO_{(s)} + CO_{2(g)}$ $\Delta_r H° = + 177.8$ kJ mol^{-1} (iv) Decomposition of N_2O_5 at room temperature. $N_2O_{5\,(g)} \rightarrow 4NO_{2\,(g)} + O_{2\,(g)}$, $\Delta_r H° = +219.0$kJmol^{-1}.

b. A number of reactions are known for which ΔH is zero but still they are spontaneous, e.g., (i) Reaction between acetic acid and ethyl alcohol $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightarrow CH_3COOC_2H_{5(l)} + H_2O_{(l)}$ (ii) Expansion of an ideal gas into vacuum. If an insulated vessel containing an ideal gas is connected to an insulated vessel which has been completely evacuated and the stop-cock connecting the two is opened, the expansion is spontaneous but no energy change takes place. This is because energy change can take place either as heat or as work. In this case, as vessels are insulated, q=0. Further, work done, w=$-P_{ext} \times \Delta V$. As $P_{ext} = 0$, therefore, w =0. Hence, by

first law of thermodynamics, $\Delta U = q + w = 0 + 0 = 0$.

c. Even those reactions for which ΔH is negative, rarely proceed to completion even though ΔH remains negative throughout.

d. Reversible reactions also occur. For example, the reaction $H_{2 (g)} + I_{2 (g)} \rightarrow 2HI_{(g)}$ having ΔH = +ve and the reverse reaction, viz., $2HI_{(g)} \rightarrow H_{2(g)} + I_{2 (g)}$ having ΔH = -ve both occur, i.e., are spontaneous. Hence, it may be concluded that the energy factor or enthalpy factor cannot be the sole criterion for predicting the spontaneity or the feasibility of a process. Thus, some other factor must also be involved. This factor is the tendency for maximum randomness.

(2) **Tendency for maximum randomness:** Let us consider a process which is spontaneous but for which $\Delta H = 0$. Since for such a process, energy factor has no role to play, so we shall be able to find out the other factor which makes the process spontaneous. A simple case of such a process is 'mixing of two gases' which do not react chemically. Suppose the two gases are enclosed in bulbs A and B connected to each other by a tube and kept separated by a stop-cock. Now, if the stopcock is opened, the two gases mix completely. The gases which were confined to bulbs A and B separately are no longer in order. Thus, a disorder has come in or in other words, the randomness of the system has increased.

Another excellent example of a spontaneous process for which $\Delta H = 0$ is the spreading of a drop of ink in a beaker filled with water. Thus, it may be concluded that the second factor which is responsible for the spontaneity of a process is the tendency to acquire maximum randomness. This factor helps to explain the spontaneity of the endothermic processes as follows: (i) Evaporation of water takes place because the gaseous water molecules are more random than the liquid water molecules. In other words, the process is spontaneous because it is accompanied by increase of randomness. Similarly, melting of ice is a spontaneous process because liquid state is more random than the solid state. (ii) Dissolution of ammonium chloride is spontaneous because in the solid, the ions are fixed but when they go into the aqueous solution, they are free to move about. In other words, the process is accompanied by an increase of randomness. (iii) Decomposition of solid calcium carbonate is spontaneous because the gaseous CO_2 produced is more random than the solid $CaCO_3$. (iv) Decomposition of N_2O_5 is spontaneous because 2 moles of gaseous N_2O_5 give 5 moles of gaseous products. Hence, the process is accompanied by increase of randomness.

Limitation of the criterion for maximum randomness:- It is important to mention here that just as the energy factor (ΔH) cannot be the sole criterion for determining the spontaneity of a process, similarly, the randomness factor also cannot be the sole criterion for the spontaneity of a process. This is obvious from the fact that if the randomness factor were the only criterion, then the processes like liquefaction of a gas or solidification of a liquid would not have been feasible, since these were accompanied by decrease of randomness. Thus, it may be concluded that the overall tendency for a process to be

spontaneous will depend upon both the factors.

Overall tendency as the driving force for a process: The overall tendency for a process to occur depends upon the resultant of the following two tendencies:

  (i) Tendency for minimum energy
  (ii) Tendency for maximum randomness

The resultant of the above two tendencies which gives the overall tendency for a process to occur is called the driving force of the process.

Hypothetical process: To understand the conditions under which the process will be spontaneous or non-spontaneous, let us consider a hypothetical process $A \rightarrow B$. Suppose 'E' represents the tendency for minimum energy, 'R' represents the tendency for maximum randomness and 'D' represents the overall tendency (i.e., the driving force) which is the resultant of E and R. Then the following different possibilities arise:

Type 1:   When the net driving force is in the forward direction

 (i) E$\rightarrow$ (ii) E$--\rightarrow$ (iii) E$\leftarrow$

   R$\rightarrow$ R$\leftarrow$ R$--\rightarrow$

   D$--\rightarrow$ D$-\rightarrow$ D$-\rightarrow$

   (D = E + R)   (D = E − R)   (D = R − E)

  (i) Both E and R favour the forward process. The net driving force is very large and favours the forward process.
  (ii) E favours R opposes but E> R so that the net driving force, though small, favours the forward process.
  (iii) E opposes and R favours but R>E, so that the net driving force is again in the forward direction.

In all the above three cases, since the driving force is in the forward direction, therefore, under any of the above conditions, the process will be spontaneous. Further, it may be noted that whereas processes (i) and (ii) are exothermic, the process (iii) is endothermic.

Type 2:   When the net driving force is in the backward direction

 (i)   E$\leftarrow$ (ii) E$\rightarrow$ (iii) E$\leftarrow--$

    R$\leftarrow$ R$\leftarrow--$ R$\rightarrow$

    D$\leftarrow--$ D$\leftarrow-$ D$\leftarrow-$

   (D = E + R)   (D = E - R)   (D = R-E)

  (i)   Both E and R oppose
  (ii) E favours and R opposes but R>E
  (iii) E opposes and R favours but E>R

Type 3:   When the net driving force is zero

Type 4: E favours, R opposes but E=R

    E$\rightarrow$; R$\leftarrow$; D =0

Type 5: E opposes, R favours but E=R

    E$\leftarrow$; R$\rightarrow$; D=0

In all the above five cases (Type 2 and Type 3), the process is non-spontaneous. Further, whereas processes (i), (iii) and (v) are endothermic, the processes (ii) and (iv) are exothermic.

In the light of the above discussion, let us now explain the spontaneity of a few processes, e.g.,

1. Evaporation of water. $H_2O_{(l)} \rightarrow H_2O_{(g)}$, $\Delta H = +44$kJ mol^{-1} .
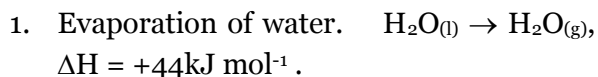
    In this process, E opposes (process being endothermic), R favours (because gas is more random   than liquid). Since the

process is known to be spontaneous, hence R must be greater than E (R>E).

2. Dissolution of NH_4Cl in water. $NH_4Cl_{(s)}$ + aq $\rightarrow$ $NH_4^+_{(aq)}$ + $Cl^{-1}_{(aq)}$, ΔH = + 15.1 kJ mol^{-1} in this process, E opposes and favours. Here again, the spontaneity of the process is explained by suggesting that R>E.

3. Reaction between H_2 and O_2 to form H_2O. $H_{2(g)}$ + $\frac{1}{2}$ $O_{2\,(g)}$ $\rightarrow$ $H_2O_{(l)}$, ΔH = - 286.2 kJmol^{-1}. Here, E favours (the reaction being exothermic) but R opposes (because liquid is less random than the gases). However, since the process is experimentally known to be spontaneous, we must have E>R.

4. Decomposition of $CaCO_3$ on heating: $CaCO_{3\,(s)}$ $\rightarrow$ $CaO_{(s)}$ + $CO_{2(g)}$, ΔH = +177.8 kJmol^{-1}. Here, E opposes but R favours. Thus , to explain the spontaneity of the process, we must have R>E.

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