SPONTANEITY IN TERMS OF FREE ENERGY CHANGE

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(a) **Deriving the criteria from entropy consideration**: It has already been explained that the total entropy change for a system which is not isolated from the surroundings is given by-

$\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$ .... (i)

Consider a process (or a reaction) being carried out at constant temperature and pressure. Suppose the heat is lost by the surroundings and gained by the system. If the heat lost by the surroundings is represented by q_p ($_p$ indicating that the process is being carried out at constant pressure) then by definition of entropy change

$\Delta S_{surroundings} = -q_p/T$ .... (ii)

(minus sign before q_p indicates that the heat is lost by the surroundings). Further, we know that at constant pressure

$q_p = \Delta H$ ....(iii)

Substituting this value in equation (ii), we get

$\Delta S_{total} = \Delta S_{system} - \dfrac{\Delta H}{T}$ ....(iv)

Using the symbol ΔS in place of ΔS_{system} , we can write equation (iv) as

$\Delta S_{total} = \Delta S - \dfrac{\Delta H}{T}$ ....(v)

Multiplying throughout by T, we get

$T\Delta S_{total} = T\Delta S - \Delta H$ ....(vi)

But, for a change taking place at constant temperature and pressure,

$\Delta G = \Delta H - T\Delta S$.......................... (vii)

Substituting this value in equation (vi), we get

$T\Delta S_{total} = -\Delta G$ or $\Delta G = -T\Delta S_{total}$ .... (viii)

But in terms of total entropy change, it has already been explained that if ΔS_{total} is positive, the process is spontaneous. If ΔS_{total} is zero, the process is in equilibrium, and if ΔS_{total} is negative, the direct process is non-spontaneous; the reverse process may be spontaneous.

Putting these results in equation (viii), it can be concluded that the criteria in terms of free energy change for the spontaneity of the process will be as follows:

(i)   If ΔG is negative, the process will be spontaneous.

(ii)   If ΔG is zero, the process is in equilibrium.

(iii)   If ΔG is positive, the direct process is non-spontaneous; the reverse process may be spontaneous.

An important advantage of free energy criteria over the entropy criteria lies in the fact that the former requires free energy change of the system only whereas the latter requires the total entropy change for the system and the surroundings.

(b) **Deriving the criteria from Gibbs energy equation**

The Gibbs energy equation is given by $\Delta G = \Delta H - T\Delta S$. This equation combines in itself both the factors which decide the spontaneity of a process, namely, (i) the energy factor, ΔH (ii) the entropy factor, $T\Delta S$. Thus, ΔG is the resultant of the energy factor (i.e., tendency for minimum energy) and the entropy factor (i.e., the tendency for maximum randomness). Depending upon the signs of ΔH and $T\Delta S$ and their relative magnitudes, the following different possibilities arise:

1. When both ΔH and $T\Delta S$ are negative, i.e., energy factor favours the process but randomness factor opposes it, then (i) If $\Delta H > T\Delta S$ the process is spontaneous and ΔG is negative. (ii) If $\Delta H < T\Delta S$, the process is non-spontaneous and ΔG is positive. (iii) If $\Delta H = T\Delta S$, the process is in equilibrium and ΔG is zero.

2. When both ΔH and $T\Delta S$ are positive, i.e., energy factor opposes the process but randomness factor favours it. Then (i) If $\Delta H > T\Delta S$, the process is non-spontaneous and ΔG is positive. (ii) If $\Delta H < T\Delta S$, the process is

spontaneous and ΔH is negative. (iii) If $\Delta H = T\Delta S$, the process is in equilibrium and ΔG is zero.

3. When ΔH is negative but $T\Delta S$ is positive, i.e., energy factor as well as the randomness factor favour the process. The process will be highly spontaneous and ΔG will be highly negative.

4. When ΔH is positive but $T\Delta S$ is negative, i.e., energy factor as well as the randomness factor oppose the process. The process will be highly non-spontaneous and ΔG will be highly positive.

To sum up, the criteria for spontaneity of a process in terms of ΔG is as follows:

(i) If ΔG is negative, the process is spontaneous.

(ii) If ΔG is zero, the process does not occur or the system is in equilibrium.

(iii) If ΔG is positive, the process does not occur in forward direction. It may occur in the backward direction.

Effect of temperature on the spontaneity of a process:

The spontaneity of a process depends upon (i) the energy factor (ΔH), and (ii) the randomness/ entropy factor ($T\Delta S$). The magnitude of the first factor does not change much with temperature but the second factor changes appreciably with change of temperature. Hence, the resultant $\Delta G = \Delta H - T\Delta S$ would change with temperature and so would the spontaneity of the process, e.g.,

(a) For endothermic reaction: ΔH is always positive, i.e., this factor opposes the process. If $T\Delta S$ is negative, this factor will also oppose the process and process will be non-spontaneous. However, if $T\Delta S$ is positive (so that it favours the process), then the process can if magnitude of the factor $T\Delta S$ is greater than the magnitude of ΔH. The reaction is then said to be entropy driven. The magnitude of the factor, $T\Delta S$ is affected by temperature as follows:

(b) If the temperature is very low such that $T\Delta S < \Delta H$ slightly in magnitude, ΔG will be positive and hence the process will be non-spontaneous.

(i) If the temperature is moderate such that $T\Delta S > \Delta H$ slightly in magnitude, ΔG will be slightly negative. Hence, the process will be spontaneous but slow.

(ii) If the temperature is high, $T\Delta S$ will be much greater than ΔH in magnitude so that ΔG is highly negative. Hence, the process will not only be spontaneous but fast. Thus, an endothermic reaction which may be non-spontaneous at low temperature may become spontaneous at high temperature. This is the reason why endothermic reactions are carried out at high temperature.

(c) For exothermic reactions: ΔH is always negative, i.e., this factor always favours the process. Thus, if $T\Delta S$ is positive, this factor will also favour the process and the process will always be spontaneous. However, if $T\Delta S$ is negative (so that it opposes the process), then the process can occur only if the magnitude of ΔH is very large so that ΔG is negative. The reaction is then said to be enthalpy driven. Alternatively, the spontaneity of the reaction is affected by temperature as follows:

(i) If the temperature is so high that $T\Delta S > \Delta H$ in magnitude, ΔG will be positive and the process will be spontaneous.

(ii) If the temperature is made so low that $T\Delta S < \Delta H$ in magnitude, ΔG will be the process will be negative and the process will be spontaneous. Thus, an exothermic reaction which may be non-spontaneous at high temperature may become spontaneous at low temperature.

Depending upon the signs of ΔH and ΔS and the value of temperature, the various possible results may be summed up as follows:

SIGN OF ΔH	SIGN OF ΔS	VALUE OF TEMPERATURE (T)	SPONTANEITY
−	+	Any	Spontaneous
+	−	Any	Non-spontaneous
−	−	Low	Spontaneous
−	−	High	Non-spontaneous
+	+	Low	Non-spontaneous
+	+	High	Spontaneous

EXAMPLE: Enthalpy and entropy changes of a reaction are 40.63 kJ mol⁻¹ and 108.8 JK⁻¹ mol⁻¹ respectively. Predict the feasibility of the reaction at 27°C.

Solution: Here, we are given

$\Delta H = 40.63$ kJ mol⁻¹ = 40630 J mol⁻¹

$\Delta S = 108.8$ JK⁻¹ mol⁻¹

$T = 27°C = 27+273 = 300$ K

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

$= 40630$ J mol⁻¹ $- 300$K $\times$ 108.8 JK⁻¹ mol⁻¹

$= 7990$ J mol⁻¹

Since ΔG comes out to be positive (i.e., $\Delta G > 0$) the reaction is not feasible in the forward direction.

Standard free energy change of a reaction ($\Delta G°$reaction) and standard free energy of formation ($\Delta_r G°$):

Standard free energy change of a reaction is defined as the change in free energy which takes place when the reactants in the standard state (1 atm., 298K) are converted into the products in their standard state.

Just as the enthalpy of a reaction can be calculated from the standard enthalpies of formation ($\Delta_f H°$), taking the standard enthalpies of formation of the elements as zero, the free energy change during a process (or a reaction) can be calculated in a similar way from the standard free energy of formation ($\Delta_f G°$) of the different reactants and products involved, taking standard free energy of formation of the elements as zero i.e.,

for any process or reaction,

$\Delta_r G°$ = [Sum of the standard free energy of formation of products] − [Sum of standard free energy of formation of reactants]
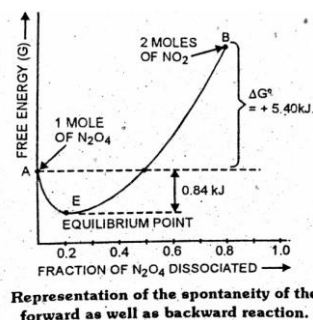
$= \Sigma \Delta_f G°$(Products) $- \Sigma \Delta_f G°$(Reactants)

Standard free energy of formation of a compound is defined as the energy change which takes place when one mole of the compound is formed from its elements taken in their standard states. Similar to standard enthalpy of formation ($\Delta_f H°$), the standard free energy of formation ($\Delta_f G°$) of elementary substances is taken as zero.

Free energy change and chemical equilibrium: We know that a reaction is spontaneous if ΔG is negative.

Now, in a reversible reaction, the forward as well as backward reaction takes place. This means that ΔG is negative for the forward as well as for backward reaction. Let us now see how it happens.

To understand free energy changes taking in reversible reactions, let us consider the following reaction: N_2O_4 (g) $\leftrightarrow$ 2 NO_2 (g). The standard free energy change ($\Delta G°$) for this reaction is + 5.40 kJ mol⁻¹. Since $\Delta G°$ is positive, one might predict that N_2O_4 in its standard state (at 298 K and 1 bar pressure) would not dissociate into NO_2 at all and that the reverse reaction (i.e., formation of N_2O_4 from NO_2) would go to completion. However, both these predictions are incorrect. The reaction is reversible and we know that the reversible reactions tend to go to equilibrium and not to completion. Moreover, the forward as well as the backward reaction should be spontaneous.

Representation of the spontaneity of the forward as well as backward reaction.

The free energy of the system in which the above reaction occurs at 298 K and 1 atmosphere is plotted against the fraction of N_2O_4 dissociated. In the figure, point A represents the standard free energy of one mole of N_2O_4, point B represents the standard free energy of two moles of NO_2 and the other points between A and B on the curve represents the free energies of mixtures of N_2O_4 and NO_2.

The free energy curve exhibits a minimum at the equilibrium point E, where 16.6% of the N_2O_4 is dissociated. The difference between the standard free energy of two moles of NO_2 (point B) and the standard free energy of the one mole of N_2O_4 (point A), $\Delta G°$ for the reaction is +5.40 kJ. However, as shown in figure, the free energy of the reaction mixture at the equilibrium point (E) is less than either of the pure reactant (A) or the product (B). In the present example, the point E is lower by 0.84kJ than the point A. This means that when 1 mole of N_2O_4 changes into the equilibrium mixture, the value of $\Delta G° = -0.84$kJ.

Similarly, when 2 moles of NO_2 change into the equilibrium mixture, the values of $\Delta G° = -5.40 + (-0.84) = -6.24$ kJ. Thus, in both the cases, the values of $\Delta G°$ are negative and hence both the processes (i.e., forward reaction as well as backward reaction) are spontaneous.

Relationship between standard free energy and equilibrium constant: The free energy change of the reaction in any state ΔG, (when equilibrium has not been attained) is related to the standard free energy change of the reaction, $\Delta G°$ (which is equal to the difference in free energies of formation of the products and reactants both in their standard states) and is given by the equation,

$\Delta_r G = \Delta_r G° + RT \ln Q$ ……………… (i)

where Q is the reaction quotient, it is equal to Q_p if the reactants and products are gaseous and equal to Q_c if they are in the solution.

When equilibrium is attained, there is no further free energy change, i.e., $\Delta G = 0$ and Q become equal to K (equilibrium constant). Hence, the above equation becomes

$0 = \Delta_r G° + RT \ln K$ or $\Delta_r G° = -RT \ln K$ …(ii)
Or $\Delta_r G° = -2.303\ RT \log K$ ……………….. (iii)

Example: Calculate the standard free energy change for the reaction $4NH_3$ (g) + $5O_2 \rightarrow 4NO$ (g) + $6H_2O$ (l). Given that the standard free energies of formation ($\Delta_f G°$) for NH_3 (g), NO (g) and H_2O (l) are -16.8, $+86.7$ and -237.2 kJ mol^{-1} respectively. Predict the feasibility of the above reaction at the standard state.

Solution: Here, we are given
$\Delta_f G° (NH_3) = -16.8$ kJ mol^{-1}
$\Delta_f G° (NO) = +86.7$ kJ mol^{-1}
$\Delta_f G° (H_2O) = -237.2$ kJ mol^{-1}
$\therefore \Delta_r G° = \Sigma\Delta_f G°$ (products) $- \Sigma\Delta_f G°$ (reactants)
$\quad = [4 \times \Delta_f G° (NO) + 6 \times \Delta_f G° (H_2O)] - [4 \times \Delta_f G° (NH_3) + 5 \times \Delta_f G° (O_2)]$
$\quad = [4 \times (86.7) + 6 \times (-237.2)] - [4 \times (-16.8) + 5 \times 0]$
$\quad = -1009.2$ kJ
Since $\Delta_r G°$ is negative, the process is feasible.

Example: Calculate $\Delta_r G°$ for conversion of oxygen to ozone $3/2\ O_2$ (g) $\rightarrow O_3$ (g) at 298 K, if K_p for this conversion is 2.47×10^{-29}

Solution: $\Delta_r G° = -2.303\ RT \log K_p$

$= -(2.303)(8.314 JK^{-1}\ mol^{-1})(298K) \log (2.47 \times 10^{-29})$

$= 163229\ Jmol^{-1} = 163.2\ kJmol^{-1}$ [For standard condition, T

$= 298K$, and $\log(2.47 \times 10^{-29})$

$= -29 + 0.3927 = -28.6073$]

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