

CHEMICAL THERMODYNAMICS

Spontaneous and Non-spontaneous Processes

Spontaneous Processes: A process which proceeds by itself under specified conditions without the help of any external agency is called spontaneous process. As such all the spontaneous processes are thermodynamically irreversible. A spontaneous process continues till the equilibrium state is reached and it may or may not be instantaneous. In fact, all natural processes are thermodynamically irreversible and spontaneous. Examples are melting of ice above 0°C, dissolution of NaCl in water, mixing of two gases etc.

Non-spontaneous Processes: A process which does not proceed by itself under specified conditions but can be made to occur with the help of an external agency is called non-spontaneous process. Under a given set of conditions, if a process is spontaneous in one direction, it is not spontaneous in the reverse direction.

Enthalpy Change and Spontaneity

Spontaneous processes, in general, tend to achieve a state of minimum energy. Therefore, decrease in enthalpy may be regarded as a criterion for the spontaneity of a process. According to enthalpy criterion, all spontaneous processes should be exothermic ($\Delta H = -ve$). However, there are many endothermic processes ($\Delta H = +ve$) such as evaporation of water, melting of ice and dissolution of NH_4NO_3 in water which occur spontaneously. Thus, decrease in enthalpy cannot be regarded as the sole criterion for predicting the spontaneity of any process.

Concept of Entropy

Entropy is an important thermodynamic property of a system which provides a measure of its degree of disorder or randomness. The greater the molecular disorder of a system, the greater its entropy. Conversely, the more ordered a system, the smaller its entropy. Entropy is a state function and is denoted by 'S'.

Change in Entropy

When heat ' q ' flows reversibly into or out of a system at a temperature ' T ', then there is corresponding increase or decrease of entropy by ' q/T '. Hence, the entropy change is given by

$$\Delta S = \frac{q}{T}$$

Units of entropy: Entropy is expressed in $J K^{-1}$ or $cal K^{-1}$. The unit $cal K^{-1}$ is also called entropy unit (eu).

Standard Entropy Change

The entropy change under standard conditions of 25°C and 1 atm pressure is called standard entropy change and is denoted by ΔS° .

Physical Significance of Entropy

Entropy is a measure of randomness or disorder of a system. For any substance, the molecular order decreases from solid state to liquid state and from liquid state to gaseous state. Accordingly, entropy increases in the order:

$$S_{solid} < S_{liquid} \ll S_{gas}$$

Thus, increase in entropy means change from an ordered to less ordered or disordered form.

Entropy and Spontaneity of Process

The entropy change of universe is given by

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur}$$

All spontaneous processes lead to increase in disorder or randomness and hence entropy increases. So long as a spontaneous process continues, the entropy goes on increasing and reaches the maximum value at equilibrium state after which the entropy does not change. Thus, entropy criteria are as follows:

- If ΔS_{uni} is +ve (i.e., $\Delta S_{uni} > 0$), the process is spontaneous.
- If ΔS_{uni} is -ve (i.e., $\Delta S_{uni} < 0$), the process is non-spontaneous.
- If ΔS_{uni} is zero (i.e., $\Delta S_{uni} = 0$), the process is at equilibrium.

Second Law of Thermodynamics

The first law of thermodynamics is concerned with the conservation of energy during a process. However, it does not help us to predict the feasibility of the process in a given direction. The solution to this problem is provided by second law of thermodynamics.

The statement of second law of thermodynamics is developed in terms of entropy criterion. According to this law, "All spontaneous processes lead to increase in entropy of universe." Since all processes in nature occur spontaneously, the second law can be most generally and concisely stated that "The entropy of the universe (system plus surrounding) is continuously increasing."

A quantitative statement of the second law is that for any spontaneous process,

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur} > 0$$

Explanation: Let us consider a spontaneous flow of heat ' q ' from a system at higher temperature ' T_{sys} ' to the surrounding at lower temperature ' T_{sur} '. Then changes in entropies of system and surrounding are given as follows:

$$\Delta S_{sys} = -\frac{q}{T_{sys}}$$

$$\Delta S_{sur} = +\frac{q}{T_{sur}}$$

Now, the total entropy change of universe (system + surrounding) is given by

$$\Delta S_{uni} = \Delta S_{sys} + \Delta S_{sur}$$

$$\text{Or, } \Delta S_{uni} = \frac{q}{T_{sur}} - \frac{q}{T_{sys}}$$

$$\text{Or, } \Delta S_{uni} = q \left(\frac{1}{T_{sur}} - \frac{1}{T_{sys}} \right)$$

$$\therefore \Delta S_{uni} = q \left(\frac{T_{sys} - T_{sur}}{T_{sys} T_{sur}} \right)$$

Since, $T_{sys} > T_{sur}$, $\Delta S_{uni} > 0$. This is second law.

Other Statements of Second Law

1. **Kelvin statement:** The thermodynamic efficiency of heat engine is less than unity. The thermodynamic efficiency of a heat engine is defined as the fraction of heat converted into work. It is denoted by η and is given by
$$\eta = \frac{\text{work done}}{\text{heat absorbed}}$$
2. **Clausius statement:** The spontaneous flow of heat is always unidirectional and occurs from higher temperature body to lower temperature body.

Entropy Change During Phase Transition

The enthalpy change during any physical transformation is given by the formula:

$$\Delta S_t = S_f - S_i = \frac{\Delta H_t}{T_t}$$

Where, ' S_i ' and ' S_f ' are the entropies of initial state and final state respectively, ' ΔH_t ' is the enthalpy of transition and ' T_t ' is the constant temperature at which transition takes place.

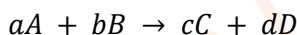
Examples:

- Entropy**
1. ~~Enthalpy~~ of fusion, $\Delta S_{fus} = S_l - S_s = \frac{\Delta H_{fus}}{T_m}$
 2. ~~Enthalpy~~ of vaporization, $\Delta S_{vap} = S_g - S_l = \frac{\Delta H_{vap}}{T_b}$
 3. ~~Enthalpy~~ of sublimation, $\Delta S_{sub} = S_g - S_s = \frac{\Delta H_{sub}}{T_{sub}}$

Here, ' T_m ' and ' T_b ' refer to melting and boiling points respectively.

Entropy Change in Chemical Reaction

For a general reaction of the type



the entropy change is given by the formula:

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

$$\text{Or, } \Delta S = (cS_C + dS_D) - (aS_A + bS_B)$$

Where S_A , S_B , S_C and S_D are the molar entropies of A, B, C and D respectively. Under standard states we can write

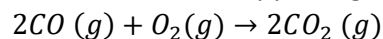
$$\Delta S^\circ = \sum S^\circ_{products} - \sum S^\circ_{reactants}$$

$$\text{Or, } \Delta S^\circ = (cS^\circ_C + dS^\circ_D) - (aS^\circ_A + bS^\circ_B)$$

Numerical Problems

1. Calculate the change in entropy for converting rhombic sulphur to monoclinic sulphur. Enthalpy of transition at 95.5°C is $+353.8 \text{ J mol}^{-1}$. [Ans: $0.96 \text{ J K}^{-1} \text{ mol}^{-1}$]
2. The latent heat of fusion of ice is 336 J g^{-1} . Calculate the molar entropy of ice at its normal melting point. [Ans: $22.15 \text{ J mol}^{-1} \text{ K}^{-1}$]

3. Calculate the standard entropy change for the following reaction:



Given that the standard entropies (S°) of CO, O₂ and CO₂ are 197.6 J K⁻¹ mol⁻¹, 205.03 J K⁻¹ mol⁻¹ and 213.6 J K⁻¹ mol⁻¹ respectively. [Ans: -173.03 J K⁻¹]

Concept of Gibbs Free Energy

Gibb's free energy or simply free energy is an important thermodynamic property of a system which provides a measure of its capacity to do useful work. It is denoted by 'G' and defined mathematically by the equation:

$$G = H - TS$$

Where, 'H' and 'S' are enthalpy and entropy of the system respectively. Since 'H', 'T' and 'S' are all state functions, 'G' is must also be a state function. Hence, change in 'G' is given by

$$\Delta G = G_2 - G_1$$

$$\text{Or, } \Delta G = (H_2 - T_2 S_2) - (H_1 - T_1 S_1)$$

$$\text{Or, } \Delta G = (H_2 - H_1) - (T_2 S_2 - T_1 S_1)$$

$$\therefore \Delta G = \Delta H - (T_2 S_2 - T_1 S_1)$$

At constant temperature, $T_1 = T_2 = T$ (say). Therefore,

$$\Delta G = \Delta H - T(S_2 - S_1)$$

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

This equation is known as Gibb's – Helmholtz equation.

Physical Significance of Free Energy

From first law of thermodynamics, we have

$$q = \Delta E + w \quad \dots\dots\dots (1)$$

Where, w is the work done by the system. A part of the work done by the system may be the mechanical work of expansion ($P\Delta V$) and the other part may be the useful work (w_{useful}) obtainable from the system. Thus, we can write

$$w = P\Delta V + w_{\text{useful}} \quad \dots\dots\dots (2)$$

From equations (1) and (2), we get

$$q = \Delta E + P\Delta V + w_{\text{useful}}$$

$$\text{Or, } q = \Delta H + w_{\text{useful}} \quad \dots\dots\dots (3)$$

From entropy concept, we know

$$\Delta S = \frac{q}{T}$$

$$\text{Or, } q = T\Delta S \quad \dots\dots\dots (4)$$

From equations (3) and (4), we get

$$T\Delta S = \Delta H + w_{\text{useful}}$$

$$\text{Or, } \Delta H - T\Delta S = -w_{\text{useful}}$$

$$\text{Or, } \Delta G = -w_{\text{useful}}$$

$$\text{Or, } -\Delta G = w_{\text{useful}} \quad \dots\dots\dots (5)$$

Thus, decrease in free energy is equal to the net useful work that can be obtained from a reversible process taking place at constant temperature and pressure.

Free Energy and Spontaneity of Process

Let us consider a process involving transfer of heat 'q' between system and surrounding at constant temperature and pressure. Then, we have

$$q_{\text{sys}} = -q_{\text{sur}}$$

The entropy change of the surrounding is given by

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T} = -\frac{q_{\text{sys}}}{T}$$

At constant pressure, $q_{\text{sys}} = \Delta H_{\text{sys}}$. Therefore,

$$\Delta S_{\text{sur}} = -\frac{\Delta H_{\text{sys}}}{T}$$

The total entropy change of universe is given by

$$\Delta S_{\text{uni}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$$\text{Or, } \Delta S_{\text{uni}} = \Delta S_{\text{sys}} - \frac{\Delta H_{\text{sys}}}{T}$$

$$\text{Or, } \Delta S_{\text{uni}} = \frac{T\Delta S - \Delta H}{T}$$

$$\text{Or, } \Delta S_{\text{uni}} = \frac{-(\Delta H - T\Delta S)}{T}$$

$$\text{Or, } \Delta S_{\text{uni}} = -\frac{\Delta G}{T}$$

$$\therefore \Delta G = -T\Delta S_{\text{uni}}$$

For a spontaneous process, ΔS_{uni} should be positive and accordingly, ΔG should be negative i.e., free energy must decrease. So long as a spontaneous process continues, the free energy goes on decreasing and reaches the minimum value at equilibrium state after which the free energy does not change. Thus, free energy criteria are as follows:

- If ΔG is $-ve$ (i.e., $\Delta G < 0$), the process is spontaneous.
- If ΔG is $+ve$ (i.e., $\Delta G > 0$), the process is non-spontaneous.
- If ΔG is zero (i.e., $\Delta G = 0$), the process is at equilibrium.

The advantage of predicting spontaneity in terms of ΔG is that it refers to the system only, whereas prediction of spontaneity in terms of ΔS_{uni} involves both the system and the surrounding.

Significance of Gibb's – Helmholtz Equation: $\Delta G = \Delta H - T\Delta S$

Gibb's – Helmholtz equation gives the interplay of enthalpy factor (ΔH) and entropy factor (ΔS) in predicting the spontaneity of a process as shown in the following table:

Table: Significance of Gibb's – Helmholtz equation

| ΔH | ΔS | $\Delta G (= \Delta H - T\Delta S)$ | Nature of process |
|------------|------------|-------------------------------------|-------------------|
| + | – | + (at all T) | Non – spontaneous |
| + | + | + (at low T) | Non – spontaneous |
| + | + | – (at high T) | Spontaneous |
| – | + | – (at all T) | Spontaneous |
| – | – | – (at low T) | Spontaneous |
| – | – | + (at high T) | Non – spontaneous |

Effect of Temperature on Spontaneity of Chemical Reaction

The effect of temperature on spontaneity of a chemical reaction can be explained with the help of Gibb's-Helmholtz equation:

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

1. For endothermic reactions, $\Delta H = +ve$

- If ΔS is $-ve$, ΔG is always $+ve$ and hence the reaction is non-spontaneous at all temperatures.
- If ΔS is $+ve$, following two cases arise:
 - At low temperature, $T\Delta S < \Delta H$ in magnitude so that ΔG is $+ve$ and the reaction is non-spontaneous.
 - At high temperature, $T\Delta S > \Delta H$ in magnitude so that ΔG is $-ve$ and the reaction is spontaneous.

Thus, an endothermic reaction which is non-spontaneous at low temperature may become spontaneous at high temperature.

2. For exothermic reactions, $\Delta H = -ve$

- If ΔS is $+ve$, ΔG is always $-ve$ and hence the reaction is spontaneous at all temperatures.
- If ΔS is $-ve$, following two cases arise:
 - At low temperature, $T\Delta S < \Delta H$ in magnitude so that ΔG is $-ve$ and the reaction is spontaneous.
 - At high temperature, $T\Delta S > \Delta H$ in magnitude so that ΔG is $+ve$ and the reaction is non-spontaneous.

Thus, an exothermic reaction which is non-spontaneous at high temperature may become spontaneous at low temperature.

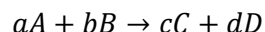
3. If $\Delta H = T\Delta S$, ΔG is zero and the reaction is at equilibrium.

Standard Free Energy Change

The free energy change under standard conditions of 25°C and 1 atm pressure is called standard free energy change. It is denoted by ΔG° and is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

For a general reaction of the type



the standard free energy change is also given by

$$\Delta G^\circ = \sum \Delta G_f^\circ(\text{Products}) - \sum \Delta G_f^\circ(\text{Reactants})$$

$$\text{Or, } \Delta G^\circ = \{c\Delta G_f^\circ(C) + d\Delta G_f^\circ(D)\} - \{a\Delta G_f^\circ(A) + b\Delta G_f^\circ(B)\}$$

Where, $\Delta G_f^\circ(A)$, $\Delta G_f^\circ(B)$, $\Delta G_f^\circ(C)$ and $\Delta G_f^\circ(D)$ are standard free energy of formation of A, B, C and D respectively.

Note:

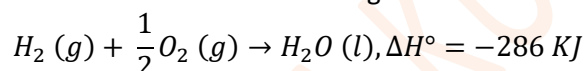
1. ΔG_f° values for elementary substances are taken to be zero.
2. The standard free energy change (ΔG°) is related to the equilibrium constant (K) by the equation

$$\Delta G^\circ = -RT \ln K$$

$$\text{Or, } \Delta G^\circ = -2.303RT \log K$$

Numerical Problems

1. Calculate ΔG° for the following reaction:



Given that absolute entropies (S°) at 298 K are: $H_2(g) = 130.6$, $O_2(g) = 204.9$ and $H_2O(l) = 70 \text{ J K}^{-1} \text{ mol}^{-1}$. [Ans: -237.4 KJ]

2. Enthalpy and entropy changes of a reaction are $40.63 \text{ KJ mol}^{-1}$ and $108.8 \text{ J K}^{-1} \text{ mol}^{-1}$ respectively. Predict the feasibility of the reaction at 27°C. [Ans: $\Delta G = +7.99 \text{ KJ mol}^{-1}$, not feasible]
3. Calculate the temperature above which the reduction of lead oxide to lead in the following reaction becomes spontaneous:



Given: $\Delta H = 108.4 \text{ KJ mol}^{-1}$ and $\Delta S = 190 \text{ J K}^{-1} \text{ mol}^{-1}$. [Ans: 570.5 K]