Chapter VI :

I- Helmholtz and Gibbs free energies

1. Introduction :

We can determine the reversibility of the process by looking at the total entropy change. However, total entropy change is not the system property. We need information on the surrounding and that's not very convenient thermodynamically. We need some system properties that can determine the reversibility. The free energy, such as Gibbs free energy and Helmholtz free energy, is the system property. Under a certain limited condition, their sign can be the criteria for the reversibility equivalent to the total entropy change. We derive at two important free energy functions, the Helmholtz free energy (*F, work function*) and the Gibbs free energy (*G*).

2. Helmholtz and Gibbs free energies :

2.1. Free Energy at Constant T and V :

The term '**Helmholtz free energy**' is derived from thermodynamics. It refers to a method of quantifying the amount of work performed by a closed system that retains the same temperature and volume. The maximum amount of work a system is capable of performing throughout a thermodynamic process with a constant temperature is equal to the change in Helmholtz energy for the process.

In a lecture titled "On the Thermodynamics of Chemical Processes" delivered in 1882, the German physicist Hermann von Helmholtz was the first to discover and propose the concept of free energy. The International Union of Pure and Applied Chemistry (IUPAC) suggests that the symbol 'A' and the term 'Helmholtz energy' are derived from the German word for "work," "Arbeit." The symbol of Helmholtz's free energy is F in physics.

Starting with the First Law

$$dU = \delta w + \delta Q$$

At constant temperature and volume we have $\delta w = 0$ and

$$dU = \delta Q$$

Free Energy at Constant T and V

Recall that $dS \geq \delta Q / T$ so we have

$$dU \leq TdS$$

which leads to

$$dU - TdS \leq 0$$

Since T and V are constant we can write this as

$$d(U - TS) \leq 0$$

The quantity in parentheses is a measure of the spontaneity of the system that depends on known state functions.

Definition of Helmholtz Free Energy :

We define a new state function:

$$F = U - TS \text{ such that } dF \leq 0.$$

We call F the Helmholtz free energy.

- At constant T and V the Helmholtz free energy will **decrease** until all possible spontaneous processes have occurred.
- At that point the system will be in equilibrium. The condition for equilibrium is $dF = 0$.

Expressing the change in the Helmholtz free energy we have

$$\boldsymbol{\Delta F = \Delta U - T\Delta S}$$

for an isothermal change from one state to another.

The condition for spontaneous change is that ΔF is less than zero and the condition for equilibrium is that $\Delta F = 0$.

We write

$\Delta F = \Delta U - T\Delta S \leq 0$ (at constant T and V)

- If ΔF is greater than zero a process is not spontaneous. It can occur if work is done on the system, however. The Helmholtz free energy has an important physical interpretation.

Noting the $Q_{rev} = T\Delta S$ we have

$$\Delta F = \Delta U - Q_{rev}$$

According to the first law $\Delta U - Q_{rev} = W_{rev}$ so $\Delta F = W_{rev}$ (reversible, isothermal)

A represents the maximum amount of reversible work that can be extracted from the system.

2.2. Free Energy at Constant T and P :

Gibbs free energy, also known as the **Gibbs function, Gibbs energy, or free enthalpy**, is a quantity that is used to measure the maximum amount of work done in a thermodynamic system when the temperature and pressure are kept constant. Gibbs free energy is denoted by the symbol 'G'. Its value is usually expressed in Joules or Kilojoules. Gibbs free energy can be defined as the maximum amount of work that can be extracted from a closed system.

This property was determined by American scientist Josiah Willard Gibbs in the year 1876 when he was conducting experiments to predict the behaviour of systems when combined together or whether a process could occur simultaneously and spontaneously. Gibbs free energy was also previously known as "available energy." It can be visualised as the amount of useful energy present in a thermodynamic system that can be utilised to perform some work.

Most reactions occur at constant pressure rather than constant volume.

Using the facts that $\delta Q_{rev} \leq TdS$ and $\delta W_{rev} = -PdV$ we have:

$$dU \leq TdS - PdV$$

which can be written $dU - TdS + PdV \leq 0$.

The = sign applies to an equilibrium condition and the < sign means that the process is spontaneous. Therefore:

$$d(U - TS + PV) \leq 0 \text{ (at constant T and P)}$$

We define a state function **$G = U + PV - TS = H - TS$.**

Thus, $dG \leq 0$ (at constant T and P)

The quantity G is called the Gibb's free energy.

In a system at constant T and P, the Gibb's energy will **decrease** as the result of spontaneous processes until the system reaches equilibrium, where $dG = 0$.

Comparing Gibbs and Helmholtz

- Comparing the Helmholtz and Gibb's free energies we see that $F(V,T)$ and $G(P,T)$ are completely analogous except that F is valid at constant V and G is valid at constant P.

We can see that

$$G = F + PV$$

which is exactly analogous to

$$H = U + PV$$

the relationship between enthalpy and internal energy.

For chemical processes we see that $\Delta G = \Delta H - T\Delta S \leq 0$ (at constant T and P)

$\Delta F = \Delta U - T\Delta S \leq 0$ (at constant T and V)

- *G and F* allows to predict the evolution of a system between different states. Consider two different states (A and B) of a system for which we can calculate F and G. We will show that when

$G_b - G_a$ *or* $F_b - F_a < 0$	the system in state A can spontaneously reach state B thus producing work.
$G_b - G_a$ *or* $F_b - F_a > 0$	the system in state A can not spontaneously reach state B.
$G_b - G_a$ *or* $F_b - F_a = 0$	state A is in equilibrium with state B.

3- Changes of Gibbs free energy for Pure compound :

Starting with Gibb's function :

$$G = H - TS$$

$$dG = dH - TdS - SdT, \quad H = U + PV$$

$$dG = (dU + PdV + VdP) - TdS - SdT$$

$$dU = \delta Q + \delta W = TdS - PdV$$

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

$$\Rightarrow \mathbf{dG = VdP - SdT} \ldots\ldots\ldots\ldots\ldots(\mathbf{1})$$

If T is constant :

$$dG = VdP$$

If P is constant :

$$dG = -SdT$$

4- Changes of Helmholtz free energy for Pure compound :

Starting with free enthalpy function :

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dU = \delta Q + \delta W = TdS - PdV$$

$$dF = TdS - PdV - TdS - SdT$$

$$\Rightarrow \mathbf{dF} = -\mathbf{PdV} - \mathbf{SdT} \ldots\ldots\ldots\ldots\ldots.(\mathbf{2})$$

If T is constant :

$$dF = -PdV$$

If V is constant :

$$F = -SdT$$

5- The change in Gibbs free energy (ΔG) for a chemical reaction :

The change in Gibbs free energy (ΔG) for a chemical reaction at constant temperature (T) and pressure can be calculated:

5.1.Using ΔG = ΔH - TΔS formula :

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

ΔG = change in Gibbs free energy for the reaction (kJ mol^{-1})

ΔH = enthalpy change for the reaction (kJ mol^{-1})

T = temperature of the reaction (K)

ΔS = change in entropy for the reaction (kJ K^{-1} mol^{-1})

- For a reaction in which the reactants and products are present in their standard states (state at 298.15 K and atmospheric pressure):

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

$\Delta G°$ = change in standard Gibbs free energy for the reaction (kJ mol^{-1})

$\Delta H°$ = standard enthalpy change(2) for the reaction (kJ mol^{-1})

T = temperature of the reaction (K)

$\Delta S°$ = change in standard absolute entropy(3) for the reaction (kJ K^{-1} mol^{-1})

- **A chemical reaction is spontaneous if :**
- (a) entropy change of the *entire universe* is positive ($\Delta S_{total} = +$):

$$\Delta S_{total} > 0$$

- (b) change in Gibbs free energy for the *chemical system* is negative ($\Delta G_{system} = -$):

$$\Delta G_{system} < 0$$

- **A chemical reaction is nonspontaneous (not spontaneous) if :**
- (a) entropy change of the *entire universe* is negative ($\Delta S_{total} = -$):

$$\Delta S_{total} < 0$$

- (b) change in Gibbs free energy for the *chemical system* is positive ($\Delta G_{system} = +$):

$$\Delta G_{system} > 0$$

Let's take, for example, a reaction that we know occurs spontaneously at 298.15 K and atmospheric pressure, the chemical reaction in which hydrogen in its standard state, hydrogen gas ($H_{2(g)}$) and oxygen in its standard state,

oxygen gas ($O_{2(g)}$), react under standard conditions, 298.15 K and atmospheric pressure, to produce water in its standard state, liquid water ($H_2O_{(l)}$). You may have experienced this spontaneous chemical reaction yourself by producing some hydrogen gas in the lab then using a heat source like a lit taper to increase the kinetic energy of the gas molecules giving them sufficient energy to successfully collide to produce products (water molecules) in a self-sustaining reaction, that is, a spontaneous reaction that also produces an audible "pop" (which is why it is usually called the "pop test" for hydrogen gas). The balanced chemical equation for this reaction is given below:

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$$

If we are given the following information:

$\Delta H°(\text{reaction}) = -285.8 \text{ kJ mol}^{-1}$

$\Delta S°(\text{reaction}) = -163.5 \text{ J K}^{-1} \text{ mol}^{-1}$

We can calculate ΔG°(reaction) because we know the conditions under which the reaction occurs, that is:

$T = 298.15 \text{ K}$

However, first we need to convert the entropy change in $\text{J K}^{-1} \text{ mol}^{-1}$ to $\text{kJ K}^{-1} \text{ mol}^{-1}$:

$\Delta S°(\text{reaction}) = -163.5 \text{ J K}^{-1} \text{ mol}^{-1} = -163.5 \text{ K}^{-1} \text{ mol}^{-1} \div 1000 \text{ kJ}^{-1} = -0.1635 \text{ kJ K}^{-1} \text{ mol}^{-1}$

Now we can substitute the values for ΔH°(reaction), T (K), and ΔS°(reaction) into the equation for calculating standard Gibbs free energy change for the reaction:

$$\begin{aligned}\Delta G°(\text{reaction}) &= \Delta H°(\text{reaction}) \quad - T\Delta S°(\text{reaction}) \\ &= -285.8 \text{ kJ mol}^{-1} - (298.15 \ \times -0.1635 \text{ kJ mol}^{-1}) \\ &= -285.8 \text{ kJ mol}^{-1} - (-48.75 \text{ kJ mol}^{-1}) \\ &= -285.8 \text{ kJ mol}^{-1} + 48.75 \text{ kJ mol}^{-1} \\ &= -237.1 \text{ kJ mol}^{-1}\end{aligned}$$

ΔG° for the spontaneous reaction in which hydrogen gas and oxygen gas combine to produce liquid water under standard conditions is $-237.1 \text{ kJ mol}^{-1}$.

Let us now consider a reaction that we know is NOT spontaneous, such as the decomposition of liquid water to produce hydrogen gas and oxygen gas.

You may have set an experiment up in the laboratory in which you pass an electric current through water and separately collect and test for hydrogen gas ($H_{2(g)}$) and oxygen gas ($O_{2(g)}$). This reaction is said to be nonspontaneous because if you turn off the electricity the chemical reaction stops occurring. If this reaction were spontaneous it would continue going after you turn off the electricity.

The balanced chemical equation for this nonspontaneous decomposition of water under standard conditions (298.15 K and atmospheric pressure) is geven below:

$$H_2O_{(l)} \rightarrow H_{2(g)} + \tfrac{1}{2}O_{2(g)}$$

If we are given the following information we can calculate ΔG° for this reaction:

Substance	**$\Delta H_f°$ (kJ mol^{-1})**	**ΔS° (J K^{-1} mol^{-1})**
$H_{2(g)}$	0	130.6
$O_{2(g)}$	0	205.1
$H_2O_{(l)}$	−285.8	69.9

First, calculate the standard enthalpy change for the reaction, $\Delta H°$(reaction), in kJ mol^{-1} using the standard heat of formation ($\Delta H_f°$) for each reactant and product as shown below:

$$\begin{aligned}\Delta H°(\text{reaction}) &= \Sigma\Delta H_f°(\text{products}) &&- \Sigma\Delta H_f°(\text{reactants})\\ &= [\Delta H_f°(H_{2(g)}) + ½ \times \Delta H_f°(O_{2(g)})] &&- [\Delta H_f°(H_2O_{(l)})]\\ &= [0 + (½ \times 0)\ ] &&- [-285.8]\\ &= 0 &&+ 285.8\end{aligned}$$

$$\Delta H°(\text{reaction}) = +285.8 \text{ kJ mol}^{-1}$$

Next, calculate the standard absolute entropy change for the reaction, $\Delta S°$(reaction), in J K^{-1} mol^{-1} using the tabulated standard absolute entropies of each reactant and product as shown below:

$$\begin{aligned}\Delta S°(\text{reaction}) &= \Sigma\Delta S°(\text{products}) &&- \Sigma\Delta S°(\text{reactants})\\ &= [\Delta S°(H_{2(g)}) + ½ \times \Delta S°(O_{2(g)})] &&- [\Delta S°(H_2O_{(l)})]\\ &= [(1 \times 130.6) + (\ ½ \times 205.1)] &&- [1 \times 69.9]\\ &= [130.6 + 102.55] &&- [69.9]\\ &= 233.15 &&- 69.9\\ &= +\ 163.25 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

After that, convert $\Delta S°$(reaction) from J K^{-1} mol^{-1} to kJ K^{-1} mol^{-1} so that the units are consistent with those for the $\Delta H°$(reaction) term as shown below:

$$\begin{aligned}\Delta S°(\text{reaction}) &= +\ 163.25 \text{ K}^{-1} \text{ mol}^{-1} \quad \div 1000 \text{ kJ}^{-1}\\ &= +\ 0.1633 \text{ kJ K}^{-1} \text{ mol}^{-1}\end{aligned}$$

Finally, calculate $\Delta G°$(reaction) in kJ mol^{-1} at standard temperature (T = 298.15 K) and pressure by substituting these values for $\Delta H°$(reaction), T (reaction in K) and $\Delta S°$(reaction) into the equation for the change in Gibbs free energy of the chemical system as shown below:

$$\begin{aligned}\Delta G°(\text{reaction}) &= \Delta H°(\text{reaction}) &&- T\Delta S°(\text{reaction})\\ &= +285.8 &&- (298.15 \times 0.1633)\\ &= +285.8 &&- 48.69\\ &= +237.1 \text{ kJ mol}^{-1}\end{aligned}$$

$\Delta G°$ for the nonspontaneous reaction in which liquid water decomposes under standard conditions to produce hydrogen gas and oxygen gas is +237.1 kJ mol^{-1}.

If a chemical reaction is spontaneous, then $\Delta G_{\text{reaction}}$ is negative, $\Delta G < 0$

If a chemical reaction is nonspontaneous, then $\Delta G_{\text{reaction}}$ is positive, $\Delta G > 0$

5.2.Using ΔG°_{f} :

Tabulated values of standard free energies of formation allow chemists to calculate the values of ΔG° for a wide variety of chemical reactions rather than having to measure them in the laboratory. The standard free energy of formation (ΔG°_{f}) of a compound is the change in free energy that occurs when 1 mol of a substance in its standard state is formed from the component elements in their standard states. By definition, the standard free energy of formation of an element in its standard state is zero at 298.15 K. One mole of Cl_2 gas at 298.15 K, for example, has $\Delta G^{\circ}_{f} = 0$.

Using standard free energies of formation to calculate the standard free energy of a reaction is analogous to calculating standard enthalpy changes from standard enthalpies of formation using the familiar "products minus reactants" rule:

$$\Delta G^{\circ}_{R} = \sum n_p \left(\Delta G^{\circ}_{f}\right)_{products} - \sum n_R \left(\Delta G^{\circ}_{f}\right)_{Reactants}$$

where n_p and n_R are the stoichiometric coefficients of each product and reactant in the balanced chemical equation. A very large negative ΔG° indicates a strong tendency for products to form spontaneously from reactants; it does not, however, necessarily indicate that the reaction will occur rapidly. To make this determination, we need to evaluate the kinetics of the reaction.

Example :

Calculate ΔG° for the reaction of isooctane with oxygen gas to give carbon dioxide and water. Use the following data:

- ΔG°_{f}(isooctane) = −353.2 kJ/mol,
- $\Delta G^{\circ}_{f}(CO_2)$ = −394.4 kJ/mol, and
- $\Delta G^{\circ}_{f}(H_2O)$ = −237.1 kJ/mol. Is the reaction spontaneous as written?

Solution :

The balanced chemical equation for the reaction is as follows:

$$C_8H_{18(l)} + 252\ O_{2(g)} \rightarrow 8\ CO_{2(g)} + 9\ H_2O_{(l)}$$

We are given ΔG°_{f} values for all the products and reactants except O_2(g). Because oxygen gas is an element in its standard state, ΔG°_{f} (O_2) is zero. Using the "products minus reactants" rule,

$$\Delta G_R^\circ=[8\Delta G^\circ_f\,(\mathrm{CO2})+9\Delta G^\circ_f\,(\mathrm{H_2O})]-[1\Delta G^\circ_f\,(\mathrm{C_8H_{18}})+252\Delta G^\circ_f\,(\mathrm{O_2})]=[(8\ \mathrm{mol})(-394.4\ \mathrm{kJ/mol})+(9\ \mathrm{mol})(-237.1\ \mathrm{kJ/mol})]-[(1\ \mathrm{mol})(-353.2\ \mathrm{kJ/mol})+(252\mathrm{mol})(0\ \mathrm{kJ/mol})]$$

$$\Delta G_R^\circ = -4935.9\ \mathrm{kJ}\ (\text{per mol of } \mathrm{C_8H_{18}})$$

Because ΔG° is a large negative number, there is a strong tendency for the spontaneous formation of products from reactants (though not necessarily at a rapid rate). Also notice that the magnitude of ΔG° is largely determined by the ΔG°_f of the stable products: water and carbon dioxide.

Calculated values of ΔG° are extremely useful in predicting whether a reaction will occur spontaneously if the reactants and products are mixed under standard conditions. We should note, however, that very few reactions are actually carried out under standard conditions, and calculated values of ΔG° may not tell us whether a given reaction will occur spontaneously under nonstandard conditions. What determines whether a reaction will occur spontaneously is the free-energy change (ΔG) under the actual experimental conditions, which are usually different from ΔG°. If the ΔH and $T\Delta S$ terms for a reaction have the same sign, for example, then it may be possible to reverse the sign of ΔG by changing the temperature, thereby converting a reaction that is not thermodynamically spontaneous, having $K_{eq} < 1$, to one that is, having a $K_{eq} > 1$, or vice versa. Because ΔH and ΔS usually do not vary greatly with temperature in the absence of a phase change, we can use tabulated values of ΔH° and ΔS° to calculate ΔG° at various temperatures, as long as no phase change occurs over the temperature range being considered.

In the absence of a phase change, neither ΔH nor ΔS vary greatly with temperature.

Summary

Gibbs Free Energy is the thermodynamic quantity of a system that is the energy available to do work. It is used to determine whether or not a reaction is spontaneous. Simply put, spontaneous processes are those that occur 'naturally,' and nonspontaneous processes are those that do not. What I mean by 'naturally' is that a reaction will occur in a system without the net influx of free energy from the surroundings. For example, ice at 10°C and 1atm will melt spontaneously whereas ice at -10°C and 1atm will not.

What we observe is that during a spontaneous process a system will 'use up' some of its free energy and therefore the change in Gibbs free energy is negative ($\Delta G<0$) for a spontaneous process. Likewise the change in Gibbs free energy is positive ($\Delta G>0$) for a nonspontaneous process and requires the input of free energy from the surroundings. Finally, the change in Gibbs free energy is zero ($\Delta G=0$) for a reaction that has reached equilibrium. These are summarized in the table below.

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MEANING OF ΔG VALUES

$\Delta G<0$	Spontaneous
$\Delta G>0$	Nonspontaneous
$\Delta G=0$	At Equilibrium

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

The change in Gibbs free energy (ΔG) for a system depends upon the change in enthalpy (ΔH) and the change in entropy (ΔS) according to the following equation:

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

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

The relationship holds true under standard conditions or under non-standard conditions. We can take away a few generalizations regarding when a reaction will be spontaneous (i.e. when $\Delta G<0$).

A negative value for ΔH and a positive value for ΔS both contribute toward achieving a negative value for ΔG and a spontaneous reaction. And for a reaction to even have a chance of being spontaneous at least one of these (negative ΔH or positive ΔS) must be true.

The first term in the calculation of ΔG is ΔH, the enthalpy change, and for many reactions/conditions this is the dominant term in the equation. This is why we often anticipate that most exothermic reactions (negative ΔH) will be spontaneous and most endothermic reactions (positive ΔH) will not, but we cannot say this with absolute certainty.

The second term in the calculation of ΔG is $-T\Delta S$. ΔS is typically significantly smaller than ΔH explaining why ΔH is often the dominant term in the equation. But temperature is also a part of this term and this term, and ΔS specifically, have an increasing importance as the temperature is increased.

We can summarize the following regarding when a reaction is spontaneous :

If ΔH is Negative and ΔS is Positive

If ΔH is negative and ΔS is positive, ΔG will always be negative and the reaction is spontaneous at all temperatures.

If ΔH is Positive and ΔS is Negative

If ΔH is positive and ΔS is negative, ΔG will never be negative and a reaction will not be spontaneous at any temperature, or you could say that the reverse reaction is spontaneous at all temperatures.

If ΔH and ΔS are Both Negative

If ΔH and ΔS are both negative, ΔG will only be negative below a certain threshold temperature and we say that the reaction is only spontaneous at 'low temperatures.'

If ΔH and ΔS are Both Positive

If ΔH and ΔS are both positive, ΔG will only be negative above a certain threshold temperature and we say that the reaction is only spontaneous at 'high temperatures.'

These four possibilities are summarized in the following table:

ΔH^o	ΔS^o	$-T\Delta S^o$	CONDITIONS FOR SPONTANEITY
-	+	-	Spontaneous at All Temperatures
+	-	+	Nonspontaneous at All Temperatures
-	-	+	Spontaneous at Low Temperatures
+	+	-	Spontaneous at High Temperatures

6. The Relationship between ΔH and ΔS :

There is a relationship between ΔH and ΔS for a system at one of its phase change temperatures, (melting/freezing or boiling point) students are often required to know. Take for example boiling water at 100°C. At the boiling temperature you actually have liquid and gaseous water in equilibrium with each other. As for any system at equilibrium ΔG = 0 leading to the following derivation:

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

$$0 = \Delta H - T\Delta S$$

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

$$\Delta S = \Delta H/T$$

It is from this last expression that undergraduate students are presented with equations that relate the freezing temperature to the ΔH and ΔS of fusion and the boiling temperature to the ΔH and ΔS of vaporization:

$$\Delta S^{\circ}_{fus} = \Delta H^{\circ}_{fus}/T_{fus},\ \Delta S^{\circ}_{vap} = \Delta H^{\circ}_{vap}/T_b$$

One could also rearrange the equation to solve for temperature which could be used to solve for a freezing or boiling point. And for reactions in which ΔH and ΔS are either both negative or both positive this expression could also be used to solve for the threshold temperature below which or above which a reaction would be spontaneous.

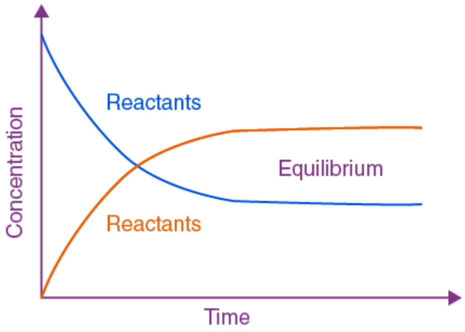
One thing to keep in mind for calculations involving any of these equations is that ΔG and ΔH values are often reported in kJ/mol whereas ΔS values are typically reported in J/K·mol. Make sure to convert so that all units are the same (both kJ or both J...either way) before performing any calculations. Finally, all temperatures should be in Kelvin (the absolute scale) when performing calculations.

II- Chemical Equilibrium

1. Introduction :

Chemical equilibrium refers to the state of a system in which the concentration of the reactant and the concentration of the products do not change with time, and the system does not display any further change in properties.

When the rate of the forward reaction is equal to the rate of the reverse reaction, the state of chemical equilibrium is achieved by the system. When there is no further change in the concentrations of the reactants and the products due to the equal rates of the forward and reverse reactions, the system is said to be in a state of dynamic equilibrium.



State of Chemical Equilibrium

A graph with the concentration on the y-axis and time on the x-axis can be plotted. Once the concentration of both the reactants and the products stops showing change, chemical equilibrium is achieved.

2. Types of Chemical Equilibrium :

There are two types of chemical equilibrium Homogeneous Equilibrium and Heterogeneous Equilibrium:

2.1. Homogenous Chemical Equilibrium :

In this type, the reactants and the products of chemical equilibrium are all in the same phase. Homogenous equilibrium can be further divided into two types:

Reactions in which the number of molecules of the products is equal to the number of molecules of the reactants. For example,

- **$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$**
- **$N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$**

Reactions in which the number of molecules of the products is not equal to the total number of reactant molecules. For example,

- **$2SO_2$ (g) + O_2 (g) ⇌ $2SO_3$ (g)**
- **$COCl_2$ (g) ⇌ CO (g) + Cl_2 (g)**

2.2. Heterogeneous Chemical Equilibrium :

In this type, the reactants and the products of chemical equilibrium are present in different phases. A few examples of heterogeneous equilibrium are given below:

- **CO_2 (g) + C (s) ⇌ 2CO (g)**
- **$CaCO_3$ (s) ⇌ CaO (s) + CO_2 (g)**

Thus, the different types of chemical equilibrium are based on the phase of the reactants and products.

3. Equilibrium Constant :

The equilibrium constant of a chemical reaction (usually denoted by the symbol K) provides insight into the relationship between the products and reactants when a chemical reaction reaches equilibrium. For example, the equilibrium constant of concentration (denoted by K_c) of a chemical reaction at equilibrium can be defined as the ratio of the concentration of products to the concentration of the reactants, each raised to their respective stoichiometric coefficients. It is important to note that there are different types of equilibrium constants that provide relationships between the product. For the hypothetical reaction:

$$aA + bB \rightleftharpoons cC + dD$$

the equilibrium constant expression is written as :

$$K_C = \frac{[C]^c.[D]^d}{[A]^a.[B]^b}$$

4. Thermodynamics and equilibrium chemical :

Using the fundamental equations for the state function (and its natural variables):

$$dG = VdP - SdT$$

If T is constant :

$$dG = VdP$$

According to the Law of Ideal Gases:

$$V = \frac{nRT}{P}$$

Of which:

$$dG = nRT\frac{dP}{P}$$

at the standard conditions, integration be from P0 = 1 atm to P

$$G - G_0 = nRTlnP$$

Concerning the chemical reaction :

$$aA + bB \leftrightarrow cC + dD$$

- Writing Anthalpy phrase for reactants and products :

For reactants :

$$G_1 = G_1^{\circ} + RT(alnP_A + blnP_B)$$

For products :

$$G_2 = G_2^{\circ} + RT(clnP_C + dlnP_D)$$

$$\Delta G = \Delta G^{\circ} + RTln\frac{P_C^c . P_D^c}{P_A^a . P_B^b}$$

at equilibrium*:*

$$\Delta G = 0 \Rightarrow G_1 = G_2$$

$$\Delta G^{\circ} + RTlnK_P = 0$$

Where :

$$K_P = \frac{P_C^c . P_D^c}{P_A^a . P_B^b}$$

$$\Rightarrow \Delta \boldsymbol{G}^{\circ} = \boldsymbol{-RTlnK_P}$$

K_P called partial pressure equilibrium, this equation applies to all reactions involving gases. In the case of solutions:

$$\Delta G^{\circ} = -RT\ln K_c$$

5. Relationship between kc and kp :

Consider the following reversible reaction:

$$aA + bB \leftrightarrow cC + dD$$

The equilibrium constant for the reaction is expressed in terms of the concentration (mole/litre):

$$\Rightarrow K_C = \frac{[C]^c.[D]^d}{[A]^a.[B]^b}$$

If the equilibrium involves gaseous species, then the concentrations are replaced by partial pressures of the gaseous substances. The equilibrium constant in terms of partial pressures is:

$$K_P = \frac{P_C^c.P_D^c}{P_A^a.P_B^b}$$

Where **P_A, P_B, P_C and P_D** represent the partial pressures of the substance A, B, C and D, respectively. If gases are assumed to be ideal, then according to the ideal gas equation:

pV = nRT or p = nRT/V

For X gas concentration in mixture :

$$PV = nRT, \qquad [X] = \frac{n}{V} = \frac{P_X}{RT}$$

Where P_X is the partial pressure of the X gas :

$$P_X = [X]RT$$

Substituting for pressure, in terms of concentration:

$$P_A = [A]\ RT;\ P_B = [B]\ RT;\ P_C = [C]\ RT \text{ and } P_D = [D]\ RT$$

Substituting these values in expression for Kp:

$$K_P = \frac{P_C^c.P_D^c}{P_A^a.P_B^b} = \frac{[C]^c(RT)^c.[D]^d(RT)^d}{[A]^a(RT)^a.[B]^b(RT)^b}$$

$$K_P = \frac{[C]^c.[D]^d}{[A]^a.[B]^b}.(RT)^{(c+d)-(a+b)}$$

$$\Rightarrow \boldsymbol{K_P = K_C.(RT)^{\Delta n}}$$

Where, △n = (c+d) – (a+b), number of moles of gaseous products – number of moles of gaseous reactants in the balanced chemical reaction.

$$\Delta n = \sum (n)_{products(gaz)} - \sum (n)_{Reactants(gaz)}$$

6. The van 't Hoff Equation :

We can use Gibbs-Helmholtz to get the temperature dependence of K *:*

We have :

$$lnK_P = -\frac{\Delta G^\circ}{RT}$$

$$\frac{dlnK_P}{dT} = -\frac{1}{R} \times d\left(\frac{\Delta G^\circ}{T}\right)\Big/ dT \dots\dots\dots\dots\dots (1)$$

But :

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

$$\frac{\Delta G^\circ}{T} = \frac{\Delta H^\circ}{T} - \Delta S^\circ$$

$$\frac{d\left(\frac{\Delta G^\circ}{T}\right)}{T} = -\frac{\Delta H^\circ}{T^2}$$

with compensation in (1) we find*:*

$$\boldsymbol{\frac{dlnK_P}{dT} = -\frac{1}{R}.\frac{\Delta H^\circ}{T^2}}$$

This equation is known as ***Vant'Hoff*** equation

- We see that whether K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative. If temperature is changed little enough that ΔH_o can be considered constant, we can translate a K value at one temperature into another by integrating the above expression, we get a similar derivation as with melting point depression:

$$\ln K(T_2)/K(T_1) = -\Delta H_o/R(1/T_2 - 1/T_1)$$

- If more precision is required we could correct for the temperature changes of ΔH^o by using heat capacity data.
- How K increases or decreases with temperature is linked to whether the reaction enthalpy is positive or negative.

7. Factors Affecting Chemical Equilibrium :

According to ***Le-Chatelier's*** principle, if there is any change in the factors affecting the equilibrium conditions, the system will counteract or reduce the effect of the overall transformation. This principle applies to both chemical and physical equilibrium.
There are several factors like temperature, pressure and concentration of the system that affect equilibrium. Some important factors affecting chemical equilibrium are explained below.

7.1. Change in Concentration :

- The concentration of the reactants or products added is relieved by the reaction, which consumes the substance that is added.
- The concentration of reactants or products removed is relieved by the reaction, which is in the direction that replenishes the substance which is removed.
- When the concentration of the reactant or product is changed, there is a change in the composition of the mixture in chemical equilibrium.

7.2. Change in Pressure :

Change in pressure happens due to the change in the volume. If there is a change in pressure, it can affect the gaseous reaction as the total number of gaseous reactants and products are now different. According to Le Chatelier’s principle, in heterogeneous chemical equilibrium, the change of pressure in both liquids and solids can be ignored because the volume is independent of pressure.

7.3. Change in Temperature :

The effect of temperature on chemical equilibrium depends upon the sign of ΔH of the reaction and follows Le-Chatelier’s Principle.

- As temperature increases, the equilibrium constant of an exothermic reaction decreases.
- In an endothermic reaction, the equilibrium constant increases with an increase in temperature.

Along with the equilibrium constant, the rate of reaction is also affected by the change in temperature. As per Le Chatelier’s principle, the equilibrium shifts towards the reactant side when the temperature increases in the case of exothermic reactions; for endothermic reactions, the equilibrium shifts towards the product side with an increase in temperature.

7.4. Effect of a Catalyst :

A catalyst does not affect the chemical equilibrium, it only speeds up a reaction. In fact, the catalyst equally speeds up the forward as well as the reverse reaction. This results in the reaction reaching its equilibrium faster.

The same amount of reactants and products will be present at equilibrium in a catalysed or non-catalysed reaction. The presence of a catalyst only facilitates the reaction to proceed through a lower-energy transition state of reactants to products.

7.5. Effect of Addition of an Inert Gas :

When an inert gas like argon is added to a constant volume, it does not take part in the reaction, so the equilibrium remains undisturbed. If the gas added is a reactant or product involved in the reaction, then the reaction quotient will change.