# Principles of Chemical Engineering

## Reaction Engineering

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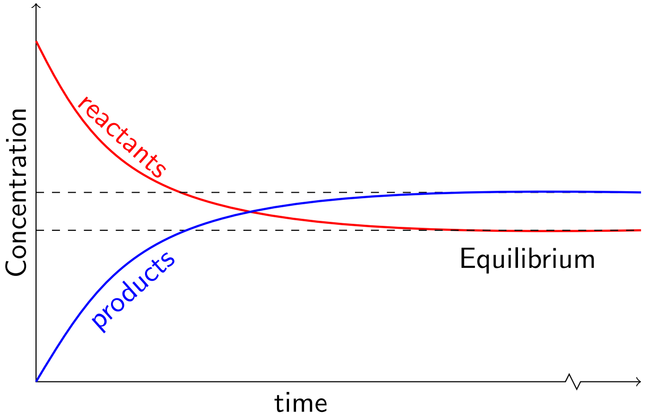
# Syllabus Contents

Chemical Equilibrium - LeChatelier's Principle

In a chemical reaction, chemical equilibrium is a state in which the rate of the forward reaction equals the rate of the backward reaction. In other words, there is no net change in concentrations of reactants and products.

At equilibrium, the quantities of everything present in the mixture remain constant, although the reactions are still continuing. This is because the rates of the forward and the back reactions are equal. Chemical equilibrium is also called dynamic equilibrium.

# Concentration at Equilibrium



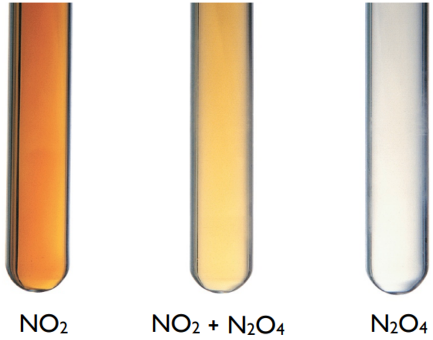

Once the concentration of both the reactants and the products stops showing change, chemical equilibrium is achieved.

# Equilibrium Reaction - Example

$$\underset{\text{reddish-brown gas}}{2\,NO_2} \rightleftharpoons \underset{\text{colorless gas}}{N_2O_4}$$

Starting with $NO_2$ gas in a sealed transparent container at room temperature, we can see the decrease in intensity of brown color, with time. This indicates the start and progress of the reaction of $NO_2$ to $N_2O_4$.

# Equilibrium Reaction - Example (contd..)




Even after a long time of reaction, the contents of the container would not turn to colorless. This indicates that the reaction is not going for completion. The contents remain at the same color for a long time, indicating the attainment of equilibrium.

- Conversion of $SO_2$ to $SO_3$:

$$SO_2 + \frac{1}{2}\,O_2 \rightleftharpoons SO_3$$

- Ammonia from $N_2$ and $H_2$:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

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.

Le Chatelier's principle can be used to predict the behavior of a reacting system due to changes in pressure, temperature, or concentration.

According to Le Chateliers principle, adding additional reactant to a system will shift the equilibrium to the right, towards the side of the products. By the same logic, reducing the concentration of any product will also shift equilibrium to the right.

The converse is also true. If we add additional product to a system, the equilibrium will shift to the left, in order to produce more reactants. Or, if we remove reactants from the system, equilibrium will also be shifted to the left.

Given this reaction at equilibrium:

$$N_2 + 3\,H_2 \rightleftharpoons 2\,NH_3$$

In which direction—toward reactants or toward products—does the reaction shift if the equilibrium is stressed by each change?

- [(i)] $H_2$ is added.
- [(ii)] $NH_3$ is added.
- [(iii)] $NH_3$ is removed.

**Solution:**

- [(i)] If $H_2$ is added, there is now more reactant, so the reaction will shift toward products to reduce the added $H_2$.
- [(ii)] If $NH_3$ is added, there is now more product, so the reaction will shift toward reactants to reduce the added $NH_3$.
- [(iii)] If $NH_3$ is removed, there is now less product, so the reaction will shift toward products to replace the product removed.

- Pressure changes do not markedly affect the solid or liquid phases. However, pressure strongly impacts the gas phase.
- Le Chatelier's principle implies that a pressure increase shifts an equilibrium to the side of the reaction with the fewer number of moles of gas, while a pressure decrease shifts an equilibrium to the side of the reaction with the greater number of moles of gas.
- If the number of moles of gas is the same on both sides of the reaction, pressure has no effect.

What is the effect on this equilibrium if pressure is increased?

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)$$

**Solution:**
According to Le Chateliers principle, if pressure is increased, then the equilibrium shifts to the side with the fewer number of moles of gas. This particular reaction shows a total of 4 mol of gas as reactants and 2 mol of gas as products, so the reaction shifts toward the products side.

High pressure favors the forward reaction, i.e., the production of ammonia.

- If the temperature is increased the equilibrium will shift to favour the reaction which will reduce the temperature. The endothermic reaction is favoured.

- If the temperature is decreased the equilibrium will shift to favour the reaction which will increase the temperature. The exothermic reaction is favoured.

# Le Chatelier's Principle (contd..)

## Effect of Temperature

$$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g) \qquad \Delta H_{\text{forward rxn}} = -92 \text{ kJ/mol}$$

- **An increase in temperature:**
  Favours the endothermic reaction because it takes in energy. The reverse reaction is endothermic, so the reverse reaction is favoured. The yield of ammonia ($NH_3$) will decrease.
- **A decrease in temperature:**
  Favours the exothermic reaction because it releases energy. The forward reaction is exothermic, so the forward reaction is favoured. The yield of $NH_3$ will increase.

# Le Chatelier's Principle (contd..)

## Effect of Catalyst

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