1   Definition

When the rate of the forward and backward reaction is equal and the concentration of the reactants and products remain constant. Physical equilibrium occurs between two phases of the same substance and chemical equilibrium occurs between reactants and products undergoing a chemical change.

$$N_2O_4 \, (g) \rightleftharpoons 2\,NO_2 \, (g) \tag{1}$$

The forward rate of the reaction is given as $K_f[N_2O_4]$ and the rate of the reverse reaction is given as $K_r[NO_2]^2$. Because at equilibrium, the rate of the forward is equal to the rate of the reverse, therefore K_{eq} is given as:

$$\frac{K_f}{K_r} = K_{eq} = \frac{[NO_2]^2}{[N_2O_4]} \tag{2}$$

2   Characteristics of Equilibrium

1. **Equilibrium is dynamic:** The reaction has not stopped when equilibrium is achieved, but the forward and reverse reaction are occurring at the same rate.

2. **Equilibrium is Achieved in a Closed System:** A closed system cannot exchange matter with the surroundings, so equilibrium is achieved where no reactants or products will be lost to the surroundings.

3. **Constant Concentration of Reactants and Products:** Because the rate of the forward and reverse reaction are constant, hence the rate of the forward and reverse reaction is also constant.

4. **Macroscopic Properties are Constant:** Macroscopic properties of the chemicals such as color and density do not change as they depend on the concentration of the reactants/products.

5. **Equilibrium can be Achieved from Both Directions:** The same equilibrium mixture will result under the same conditions, no matter whether the reaction started with more products or reactants.

3 Equilibrium Constant (K_{eq})

The Equilibrium Constant denoted by the symbol (K_{eq}) is a dimensionless quantity and is only temperature dependent for a specific reaction and for a given reaction $aA + bB \rightleftharpoons cC + dD$, the equilibrium constant value is given as:

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{3}$$

The value of the equilibrium constant also provides information about the extent of the reaction. However, it does not indicate how fast the system will achieve equilibrium.

1. **If $K_{eq} >> 1$:** The reaction is considered to go almost to completion, and there are predominately products rather than reactants

2. **If $K_{eq} << 1$:** The reaction is considered to hardly proceed, and there are predominately reactants rather than products

When a reaction is reversed, the K_{eq} value is inverted (K_{eq}^{-1}. If the concentration of the coefficient are multiplied by a factor of n, then the equilibrium constant is also raised to a factor of n ($K_{eq}{}^n$. If a reaction is multi-step, the resulting overall reaction is the product of the individual equilibrium constant values ($K_{eq} = [K_1] \times [K_2] \times [K_3]$).

4 Reaction Quotient (Q)

The Reaction Quotient (Q) measures the relative amount of reactant and products present in a reaction at a particular time before equilibrium has been achieved. To find the Q value, simply substitute the formula for K_{eq} but with non-equilibrium concentrations.

$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \tag{4}$$

The reaction quotient provides information on the direction in which the reaction will proceed.

1. **If $Q < K_{eq}$:** The reaction proceeds to the right to form products until the equilibrium has been reached.

2. **If** $Q = K_{eq}$**:** The system is currently at equilibrium.

3. **If** $Q > K_{eq}$**:** The reaction proceeds to the right to form reactants until the equilibrium has been reached.

5   Le Chatelier's Principle

Le Chatelier's Principle states that system at equilibrium when subjected to a change (concentration, pressure, temperature), will respond in a way as to minimize the effects of the change.

5.1   Concentration Change

If the concentration of a particular reactant is increased, the equilibrium will shift to the opposite side of where the concentration has been increased. However, this does not affected the K_c value.

5.2   Pressure Change (Gas-Phase Equilibrium Only)

If the partial pressure of the gas is increased or the volume is decreased, the reaction shifts towards the side with less gaseous molecules to decrease the pressure and similarly the K_c value remains unchanged.

5.3   Temperature Change

If the reaction is exothermic, the heat can be considered as a product in the forward reaction. Hence it will shift to the reactants (because the reverse reaction is endothermic) and this will cause a change in the K_c value.

5.4 K_c Temperature Dependence

Changing the temperature of the reaction unlike changing the concentration and pressure changes the rate of the forward and reverse reactions, and therefore changing the K_c value. As provided by the Arrhenius Equation in the previous unit ($k = Ae^{\frac{-E_a}{RT}}$), because the forward and reverse reaction has different activation energy, changing the temperature affects the rate of the forward and reverse reaction differently and hence changing the K_c value.

1. **Endothermic reaction:** The K_c value will increase.

2. **Exothermic reaction:** The K_c value will decrease.

6 Catalyst

The addition as a catalyst does not shift the position of the equilibrium or change the yield of either the forward or the reverse reaction. Because they lower activation energy for both the forward and the reverse reaction, the catalyst speeds up the forward and reverse reaction in equal proportions an enables a mixture to achieve equilibrium faster. They also do not change the values of the equilibrium constant.

7 Industrial Processes

The following two industrial processes are common in our day to day lives and is important to know how they work as well as the stresses implemented to improve efficiency.

7.1 Haber Process

The Haber process is an industrial process to produce ammonia (NH_3) and is given by the following chemical equation.

$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2\,NH_3\,(g)\ \Delta H = -93\,kJ/mol \tag{5}$$
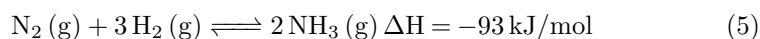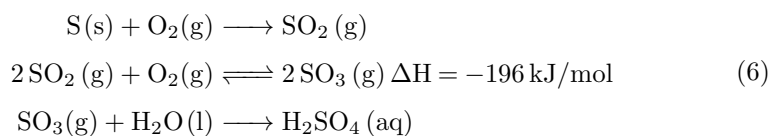
The reaction is sped up and the yield is improved by using the following stresses on the equilibrium equation.

1. **Concentration:** The produced NH_3 is removed as ti is formed to shift the equilibrium to the products and increase the yield.

2. **Pressure:** The process is conducted under high pressure (20000kPa) to shift towards the side with less moles hence improving the NH_3 yield.

3. **Temperature:** The forward reaction is endothermic and hence a low temperature would favour the yield of the products. However, at lower temperature, the reaction occurs too slowly to be feasible industrially and hence the process usually occurs at 450ºC.

4. **Catalyst:** The process usually uses an Iron catalyst (Fe) and small amounts of Aluminum (Al), Magnesium Oxide (MgO) and Rubidium (Ru).

7.2 Contact Process

The contact process involves three simple reaction as seen below and is used to manufacture sulfuric acid (H_2SO_4 (aq)).

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$
$$2\,SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)\ \Delta H = -196\,\text{kJ/mol} \tag{6}$$
$$SO_3(g) + H_2O(l) \longrightarrow H_2SO_4(aq)$$

The industrial process is improved using the following stresses:

1. **Pressure:** The pressure of the reaction is kept really high (200kPa) to cause the equation to shift to the products because it has fewer moles of gaseous molecules.

2. **Temperature:** The forward reaction is endothermic and favours a lower temperature but again the temperature is maintained at 450 ^{o}C to ensure that the reaction is not too slow.

3. **Catalyst:** The most common catalyst used in this reaction is Vanadium (V) Oxide (V_2O_5).

8   Ice Tables (Initial-Change-Equilibrium)

ICE Tables can be used to determine the concentration of the reactants and products at equilibrium. This is achieved in the following three steps.

1. Write the balance chemical equation.

2. Write the ICE Table with the initial concentration, change in concentration denoted by a factor of x and the equilibrium concentration.

3. Write the expression for K_c from the balanced chemical equation and substitute the equilibrium concentration values to solve for x.

8.1 Approximation for Small K_{eq}

If the K_eq value is very small ($K_{eq} << 1$), the reaction is hardly proceeding and the reactants predominate at equilibrium, therefore $[\text{reactant}]_{\text{initial}} \approx [\text{reactant}]_{\text{equilibrium}}$. the value of x in this case is extremely small and subtracting x from the initial concentration will not greatly impact the calculated equilibrium concentration value. Therefore, it can be assumed that $x << 1$ to avoid using the quadratic formula if percent ionization is less than 5% or $\frac{[\text{initial}]}{K_{eq}} > 500$

9 Gibbs Free Energy and Equilibrium

The Gibbs Free Energy value ΔG^{θ} under standard conditions (STP) can be used to predict the spontaneity of a reaction and the position of the equilibrium.

1. $\Delta G > 0$: Because the Gibbs Free Energy is positive, then the forward reaction is non-spontaneous and the reactants are favoured.

2. $\Delta G < 0$: Because the Gibbs Free Energy is negative, then the forward reaction is spontaneous and the products are favoured.

The equilibrium constant can also be determined based off the Gibbs Free Energy of the reaction as given by the following formula where ΔG is the Gibbs Free Energy change of the reaction, R is the gas constant (8.31J/mol K), the T is the absolute temperature of the reaction (given in Kelvins) and the K is the equilibrium constant.

$$K = e^{\frac{-\Delta G}{RT}}$$
$$\Delta G = -RT \ln(K) \tag{7}$$

Starting with pure reactants or pure products, the free energy decreases as the reaction moves towards equilibrium.

1. **Exergonic:** $\Delta G_{\text{reactants}} > \Delta G_{\text{products}}$

2. **Endergonic:** $\Delta G_{\text{reactants}} < \Delta G_{\text{products}}$