HETEROGENEOUS EQUILIBRIA

A system is classified as a three-phase system when it involves at least one reactant or product with a physical state distinct from the others. An illustrative example is the reaction:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

In this reaction, calcium carbonate ($CaCO_3$) undergoes a phase change, transitioning from a solid (s) to a combination of solid calcium oxide (CaO) and gaseous carbon dioxide (CO_2). This configuration, encompassing solid and gaseous phases, characterizes the system as a three-phase system.

Another instance is a reaction involving a salt and water:

$$\text{Salt} + H_2O(aq) \rightarrow \text{Salt}(aq)$$

In this case, the salt dissolves in water, leading to a three-phase system. The aqueous state (aq) of the dissolved salt coexists with the solid state of the undissolved salt and the liquid state of water.

These examples highlight the concept of a three-phase system, emphasizing the presence of different physical states within the system, which plays a crucial role in understanding the thermodynamics and dynamics of such chemical processes.

Reaction Quotient and Equilibrium Constant

Consider the following reversible reaction

$$A + B \longrightarrow C + D$$

The reaction quotient (QC) represents the ratio between the product of the active masses of the products and the product of the active masses of the reactants, calculated at a specific point in time.

$\therefore$ $$Q_C = \frac{[C][D]}{[A][B]}$$

The concentration is not necessarily equilibrium concentration.

[At equilibrium $Q_C = K_C$]

Case I

If $Q_C < K_C$ Then: [Reactants] > [Products]

then the system is not at equilibrium

The value of $\frac{[\text{Pioduct}]}{[\text{Readant}]}$ is small

$\therefore$ For establishment of equilibrium the reaction will go in forward direction.

$$[\text{Reactants} \rightarrow \text{Products}]$$

Case II

If $Q_C = K_C$ Then: The system has reached equilibrium, with the concentrations of the species A, B, C, and D all stabilized.

Case III

If $Q_C > K_C$ Then: [Product] > [Reactants]

The system is not at equilibrium.

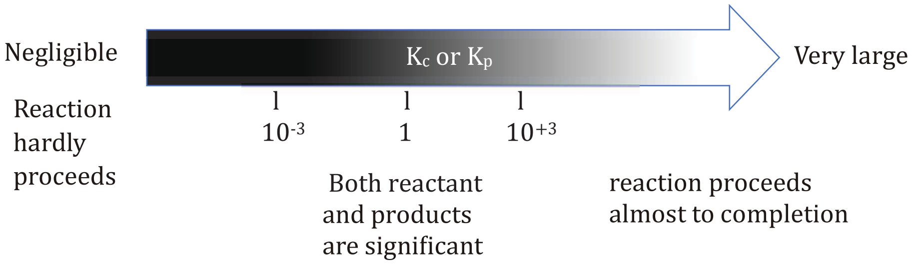
The value of $\frac{[\text{Pioduct}]}{[\text{Reactant}]}$ is large

$\therefore$ For establishment of equilibrium the reaction will go in backward direction.

$$[\text{Products} \rightarrow \text{Reactants}]$$

Predicting The Extent of The Reaction

$$K = \frac{[\text{ Product }]_{eq}}{[\text{ Reactant }]_{eq}}$$



Case-I

When the equilibrium constant, K, is significantly large ($K > 10^3$), the concentration of the product greatly exceeds that of the reactant ([Product] >> [Reactant]). As a result, the concentration of the reactant can be disregarded in comparison to the product. In such instances, the reaction is biased towards the product, and the equilibrium predominantly favors the forward direction over the reverse direction.

Case-II

If K is very small ($K < 10^{-3}$)
[Product] << [Reactant]
Hence concentration of Product can be neglected as compared to the reactant.
In this case, the reaction is reactant favorable.

Ex. The K_p values for three reactions are 10^{-5}, 20 and 300 then what will be the correct order of the percentage composition of the products.

Sol. Since K_p order is $10^{-5} < 20 < 300$ so the percentage composition of products will be greatest for $K_p = 300$.

Applications of Equilibrium Constant

Le-Chatelier's Principle

In accordance with this principle, when a system is in equilibrium and experiences a modification in concentration, pressure, or temperature, it adjusts its equilibrium position to counteract the impact of the change.

(a) **Alteration in Concentration:**

When an equilibrium experiences changes in reactant concentrations, it causes the equilibrium to shift towards the production of products. Conversely, increasing the concentrations of products leads to a shift in favor of reactants.

(b) **Variations in Pressure:**

When pressure is heightened in a system, the volume proportionally decreases, resulting in an increase in the total number of moles per unit volume. According to Le Chatelier's principle, the equilibrium shifts towards the direction where the number of moles decreases. In cases where the number of moles of gases remains unchanged in a reaction, alterations in pressure have no impact on the equilibrium.

In the formation of HI, the number of moles of reactants and products remains unchanged ($\Delta n = 0$). Therefore, changes in pressure or volume do not influence this equilibrium.

(c) Temperature Adjustment:

If the temperature at equilibrium is raised, the reaction proceeds in the direction that absorbs heat. Consequently, an increase in temperature favors the forward reaction in endothermic reactions. Conversely, an increase in temperature promotes the reverse reaction in exothermic reactions.

Units of Equilibrium Constant

The determination of equilibrium constant units, denoted as KC (equilibrium constant based on concentration), involves expressing molar concentrations in terms of mol L^{-1}. Similarly, the units for KP (equilibrium constant based on partial pressures) can be elucidated using partial pressures, measured in Pa, kPa, bar, or atmosphere.

For a practical illustration, consider the units of K_C and K_P for the reaction involving $N_2O_4(g)$ and $2NO_2(g)$:

$$KC = \frac{[NO_2]^2}{[N_2O_2]} = \frac{(mol/L)^2}{mol/L} = \frac{molo}{L}$$

$$KP = \frac{(P^2NO_2)}{(PN_2O_4)} = \frac{(bar^2)}{(bar)} = bar$$

In contemporary discussions, it is noteworthy that K_P and K_C are presently regarded as dimensionless quantities.