CHEM10003 NOTES

Lecture 22 - 24: Chemical Equilibrium

Not all reactions react until completion - some of the reactants often remain unreacted. This is because reactions are allowed to go backwards sometimes.

When the reaction has come to a point where the concentrations of reactants and products aren't changing we can say it has come to equilibrium. The reactions haven't stopped, they are just proceeding at an equal rate in both directions. The total gas pressure will remain constant if gases are involved (and the temperature is constant). The reaction is incomplete in most cases, although some reactions come close to being 100% complete.

Equilibrium constant

$$Equilibrium\ Constant : K_{C\,or\,P} = \frac{[C]^c[D]^d}{[A]^a[B]^b}\ (Units)$$

The equilibrium constant shows us how far the reaction has proceeded towards completion when equilibrium has been reached.

$$Thermodynamics\ Equilibrium\ Constant : K = \frac{\prod (a(products))^{V_P}}{\prod (a(reactants))^{V_R}}\ (No\ Units\,)$$

$$where\ \ a = \frac{P}{P_0} = \frac{P}{1\,bar}\,(for\ gas)\,and\ a = \frac{[A]}{[A]^0} = \frac{[A]}{1\,mol\,dm^{-3}}\,(for\ solutes\ in\ solution)$$

The equilibrium constant is highly affected by temperature and some other conditions. The equilibrium constant can also be written in terms of the partial pressures for gases when there are multiple gases in an equation.

Large values of K indicate that there are more products than reactants so the equilibrium lies towards the right. If K is a small number, then there are large amounts of reactants and very little product at the equilibrium. This means the position of the equilibrium lies towards the reactants side, the left.

Relationship of K_p and K_c

General Relationship:

$$K_P = K_c(RT)^{\Delta n}\ where\ \Delta n = \sum coefficient\ of\ products - \sum coefficient\ of\ reactants$$

In reverse reaction: $K_c{}^* = \dfrac{1}{K_c}$

If reaction is multiplied by n: $K_c{}^* = (K_c)^n$

If reaction is divided by n: $K_c{}^* = (K_c)^{\frac{1}{n}}$

Reaction quotient:

The reaction quotient, Q, represents the concentrations of the reactants and products using the initial values:

- If $Q = K$, then the system is at equilibrium.
- If $Q > K$, then the products are greater than the equilibrium value and the reaction will shift to the left.
- If $Q < K$, then the concentration of products is less than the equilibrium value and reaction will shift to the right.

Homogeneous and Heterogeneous:

Reactions that occur in the same phase are homogeneous however reactions with different phases are heterogeneous. Equilibrium constants also apply for heterogeneous processes.

However, by convention the concentration terms for pure liquids or solids are assigned a value of 1.

Le Chatelier's Principle

Henry Louis Le Chatelier: French chemist who said if an equilibrium system is subjected to change then the system will adjust itself to oppose the change.

These changes include concentration, temperature, and total pressure.

A new equilibrium is established but the equilibrium constant will stay the same, as ratio stays constant.

- Changing concentration: adding more reactant causes the production of more product and vice versa.
- Changing temperature: temperature is the only variable that can change the equilibrium constant:
  - Endothermic: (heat is a reactant) if temperature increases then concentration of reactants decreases so K increases, if temperature decreases then concentration of products decreases and K decreases.
  - Exothermic: (heat is a product) if temperature increases then concentration of products decreases and K decreases, if temperature decreases then reactant decreases and K increases.
  - If the reaction is endothermic then heat counts as a reactant and if the reaction is exothermic then heat counts as a product.
  - So it acts as such when its concentration is increased.

Changing volume: increasing the volume results in more space so when gases are concerned the reaction is likely to move to the side with more separate molecules. Decreasing volume results in a shift to the side with fewer molecules.

Lecture 25 - 26: Acids and Bases

Defining acids and bases

Lewis = A Lewis bases donate pairs of electrons and acids accept pairs of electrons. A Lewis acid is therefore any substance, such as the H+ ion, that can accept a pair of nonbonding electrons.

Bronsted-Lowry = a Bronsted Lowry acid is a proton (H+ atom) donor and a base is a proton acceptor. It allows us to account for bases that are not metal hydroxides. Acid (proton donors) and bases (proton acceptor) always occur together. The generic equation for Bronsted Lowry is:

$$HA\ (aq) + B\ (l) \rightarrow A^-\ (aq) + BH^+\ (aq)$$

Acid Base conjugate base and acid respectively

Amphoteric substances

Water can act as an acid when reacting with NH_3 and as a base when reacting with HCl.

Substances likes water that can act as a both an acid and a base are referred to as amphoteric substances.

Amphiprotic is a broader term describing substances that can both donate and accept protons.

Autoionisation of water = water can undergo autoionization, or self-ionisation, where it undergoes an acid/base reaction with itself. Autoprotolysis: when a proton is transferred between identical molecules.

$H_2O(l) + H_2O(l) \rightarrow OH^-(aq) + H_3O^+(aq)$

Self-ionisation (Autoprotolysis) **of water:**

The equilibrium constant for this is represented by:

$$K_w = [H3O^+][OH^-]$$

At 25 degrees:

$K_w = 1 \times 10^{-14.}$ (In all solutions of acids and bases.)

Increasing the temperature causes the equilibrium constant to increase which demonstrates that the reaction is endothermic.

$[H3O^+] = [OH^-] = 1 \times 10^{-7}$ (In neutral solution)

$[H3O^+] > [OH^-]$ (Acidic Solution)

$[OH^-] > [H3O^+]$ (Basic Solution)