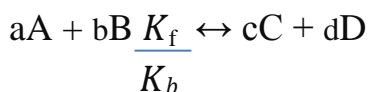


Basic Chemistry

Analytical Chemistry

Chemical Equilibrium:

Keq Equilibrium constant



R_f = rate of forward reaction $R_f = k_f [A]^a [B]^b$

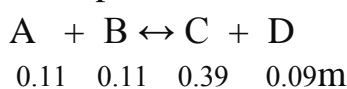
R_b = rate of backward reaction $R_b = k_b [C]^c [D]^d$

at equilibrium $R_f = R_b$

$$K_f [A]^a [B]^b = K_b [C]^c [D]^d \quad K_f K_b = \frac{[C]^c [D]^d}{[A]^a [B]^b} = Keq$$

Calculation of equilibrium constant

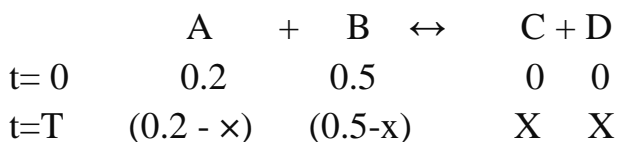
Example: calculate the keq. for reaction



$$Keq = \frac{[C][D]}{[A][B]} = \frac{(0.11)^2}{0.09 \cdot 0.39} = 0.35$$

Ex: calculate the concentration of reactants and products Equilibrium concentration

$[A] = 0.2M$, $[B] = 0.5M$, $Keq = 0.3$



$$Keq = 0.3 = \frac{(x^2)}{((0.2-x)(0.5-x))}$$

$$0.3 = \frac{x * x}{0.01 - 0.5x - 0.2x + x^2}$$

$$x^2 = 0.3(0.10 - 0.7x + x^2)$$

$$x^2 = 0.03 - 0.21x + 0.3x^2$$

$$x^2 - 0.3x^2 + 0.21x - 0.03 = 0$$

$$0.7x^2 + 0.21x - 0.03 = 0$$

$$x = \frac{b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$x = \frac{-0.21 \pm \sqrt{0.0441 + 0.0840}}{1.4} = \frac{-0.21 \pm \sqrt{0.1281}}{1.4}$$

X = 0.11M the concentration of C and D

0.2 - X = 0.2 - 0.11 = 0.09 is the concentration of A

0.5 - 0.11 = 0.39 is the concentration of B

Le - Chatelier's Principle

When a stress is applied on a system at equilibrium, the system will shift to direction which decrease the effect of stress.

Factors affect chemical equilibrium

1- Temperature

Endothermic reaction $\Delta H = +ve$

Exothermic reaction $\Delta H = -ve$

the change in the equilibrium constant (K_1 at temperature T_1 and K_2 at temperature T_2) can be predicted by the Clausius-Clapeyron equation:

$$\ln \frac{K_1}{K_2} = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

This is because the number and the energy of collisions among the reacting species increase with increasing temperature. The rates of many endothermic reactions increase about two- to three fold for every 10°C rise in temperature.

$A + B \leftrightarrow C + D \rightarrow \Delta H = +ve$ endothermic

An increase \uparrow in temp will shift the reaction to forward direction

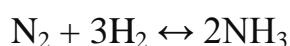
While \downarrow decrease in temp will shift the reaction to backward direction

2- Effect of pressure (for gases):

Pressure can have a large influence on the position of chemical equilibrium for reactions.

For solutions, pressure effects are usually negligible. occurring in the gaseous phase.

An increase in pressure favors a shift in the direction that results in a reduction in the volume of the system, for example, when one volume of nitrogen reacts with three volumes of hydrogen to produce two volumes of ammonia. But for reactions occurring in solutions



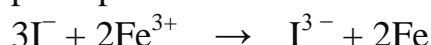
Increase in pressure shift the reaction forward (product)

Decrease in pressure shift the reaction backward (reaction)

3-Effect of concentration:

The value of an equilibrium constant is independent of the concentrations of the re-
Changes in concentration do not affect the equilibrium constant. They do affect the position of the equilibrium. actants and products.

However, the position of equilibrium is very definitely influenced by the concentrations. The direction of change is readily predictable from Le Chatelier's ^ principle. Consider the reaction of iron(III) with iodide:



If the four components are in a state of equilibrium, as determined by the equilibrium constant, addition or removal of one of the components would cause the equilibrium to reestablish itself. For example, suppose we add more iron(II) to the solution. According to Le Chatelier's principle, the reaction will shift to the left to relieve ^ the stress. Equilibrium will eventually be reestablished, and its position will still be defined by the same equilibrium constant.

Increase in (reactants) or decrease (products) will shift the reaction forward.

Catalyst

Catalyst affect the rate of reaction don't affect the eq. constant or (eq) position.

- Increase the rate of reaction, decrease the time of reaction.

Catalysts are very important to the analytical chemist in a number of reactions for analytical uses that are normally too slow to be analytically useful. An example is the use of an of enzyme catalysts. osmium tetroxide catalyst to speed up the titration reaction between arsenic(III) and cerium(IV), whose equilibrium is very favorable but whose rate is normally too slow to be useful for titrations. The measurement of the change in the rate of a kinetically slow reaction in the presence of a catalyst can actually be used for determining the catalyst concentration. The same reaction between arsenic(III) and cerium(IV) is catalyzed also by iodide and the measurement of this reaction rate (through the disappearance of the yellow cerium(IV) color) constitutes the basis for what used to be the most widely used (and is still frequently used) method for measuring iodine, also called the Sandell-Kolthoff method.

Gibbs free energy and equilibrium constant

Enthalpy (ΔH): The content of heat.

Entropy (ΔS): The measurement of randomness (disorder)

Any system tend to be at lower energy (ΔH) and higher disorder (ΔS),

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

Gibbs free energy combine between ΔH and ΔG

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ at constant condition (} 25^\circ\text{C, 1 atm)}$$

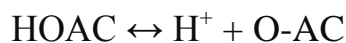
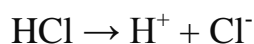
$$\Delta G = -RT \ln \text{keq.}$$

$$- 2.303 = RT \log \text{keq.}$$

$$R = 8.314 \text{ J.K}^{-1}.\text{mol}^{-1}$$

where R is the gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$). Hence, if we know the standard A large equilibrium constant results from a large negative free energy change for the reaction in question. free energy of a reaction, we can calculate the equilibrium constant. Obviously, the larger ΔG° (when negative), the larger will be K. Note that while ΔG° and ΔG give information about the spontaneity of a reaction, they say nothing about the rate at which it will occur. The reaction between hydrogen and oxygen to form water has a very large negative free energy change associated with it. But at room temperature, in the absence of a catalyst (or a spark!), these gases may coexist together for years without observable reaction.

Acid – Base Equilibrium



$$\text{Keq} = \text{Ka} = \frac{(\text{H}^+)(\text{OAC}^-)}{(\text{HOAC})}$$



$[\text{H}_2\text{O}] = \text{constant taken as 1}$

$$K = [\text{H}^+][\text{OH}^-] = K_w = 1 \times 10^{-14}$$

For pure water $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$

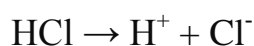
$$\text{pH} = -\log [\text{H}^+] = 7$$

$$\text{pH} = -\log [\text{H}^+] = 7$$

acidic basic

← 7 →

Ex: $1 \times 10^{-3} \text{ M}$ solution of HCl. What is the concentration of $[\text{H}^+]$, pH?



$$[\text{H}^+] = 1 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log [\text{H}^+] = -\log (1 \times 10^{-3})$$

$$-(3-) = \log 10 = 3 \times 1 = 3$$

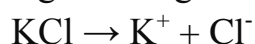
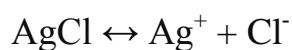
$$\text{pH} = 3$$

Ex : pH of a solution is 9.67, what is $[H^+]$

$$[H^+] = 10^{-9.67}$$

$$10^{-10} \times 10^{+0.33} = 2.13 \times 10^{-10}$$

Effect of common Ion on Solubility

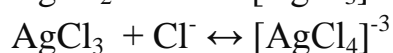
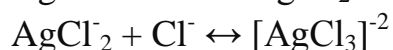


←

Shift the reaction to backward direction
(formation of precipitate)

So, the presence of common ion decreases the solubility of slightly soluble salts. While the large excess of common ion increases the solubility of slightly soluble salts by formation of soluble complex.

Excess in Cl^- ion:



Also if the common ion is silver:

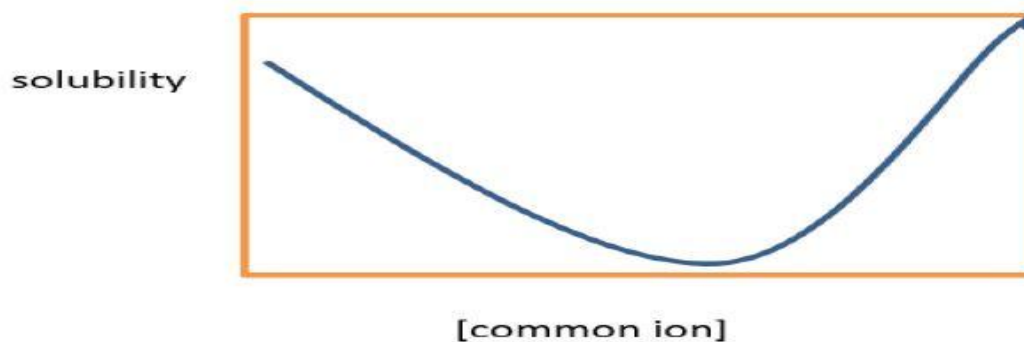
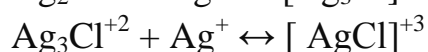
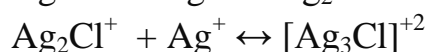
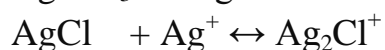
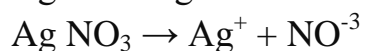
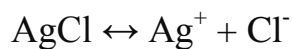


Figure: The relation between the solubility and the concentration of common ion