

COMMON ION EFFECT:

Let AB to the weak electrolyte. Considering its dissociation,



and applying law of mass action we have

$$K = \frac{[A^+][B^-]}{[AB]}$$

The equilibrium constant, K , has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution. It will increase the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increase, i.e., the equilibrium will shift to the left hand side.

In other words, the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion. This is termed as common ion effect. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or $NaOH$ to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH_4^+ or OH^- .

As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

Example 6: The ionization constant of HCN is 4×10^{-10} . Calculate the concentration of hydrogen ions in 0.2 M solution of HCN containing 1 mol L^{-1} of KCN ?

Solution: The dissociation of HCN is represented as



Applying law of mass action,

$$K_a = \frac{[H^+][CN^-]}{[HCN]} \text{ or } [H^+] = \frac{K_a [HCN]}{[CN^-]}$$

In presence of strong electrolyte, the total CN^- concentration comes from KCN which undergoes complete dissociation. It is further assumed that dissociation of HCN is very-very small and the concentration of HCN can be taken as the concentration of undissociated HCN .

Thus, $[HCN] = 0.2 \text{ M}$ and $[CN^-] = 1 \text{ M}$

Putting these values in the expression

$$[H^+] = (K_a [HCN])/([CN^-]) = (4 \times 10^{-10} \times 0.2)/1 = 8 \times 10^{-11} \text{ mol L}^{-1}$$

[Note: When KCN is not present, the $[H^+]$ concentration is equal to \sqrt{CK} i.e., $\sqrt{(0.2 \times 4 \times 10^{-10})} = 8.94 \times 10^{-8} \text{ mol L}^{-1}$. This shows that concentration of H^+ ions falls considerably when KCN is added to HCN solution.

Example 7: Determine the concentration of hydroxyl ions in 0.4 M NH_4OH solution having (i) no ammonium chloride, (ii) 5.35 g of NH_4Cl in a litre of the solution. Ionization constant of NH_4OH is 1.8×10^{-5} .

Solution: (i) Let 'a' be the degree of dissociation of NH_4OH in absence of NH_4Cl .

$$a = \sqrt{(K_b/c)}$$

$$\begin{aligned} \text{So, } [OH^-] &= C a = \sqrt{(K_b c)} = \sqrt{(1.8 \times 10^{-5} \times 0.4)} \\ &= 2.68 \times 10^{-3} \text{ mol L}^{-1} \end{aligned}$$

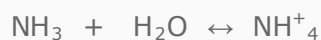
(ii) In presence of NH_4Cl

$$[NH_4^+] = 5.35/53.5 = 0.1M \text{ and } [NH_4OH] = 0.4M$$

$$\begin{aligned} \text{So, } [OH^-] &= (K_b [NH_4OH])/[NH_4^+] = (1.8 \times 10^{-5} \times 0.4)/0.1 \\ &= 7.2 \times 10^{-5} \text{ mol L}^{-1} \end{aligned}$$

Example 8: When 0.100 mole of ammonia, NH_3 , is dissolved in sufficient water to make 1.0 L solution, the solution is found to have a hydroxide ion concentration of $1.34 \times 10^{-3} M$. Calculate K_b for ammonia.

Solution:



$$\text{At equilibrium } (0.100 - 1.34 \times 10^{-3}) M \quad 1.34 \times 10^{-3} M$$

$$= 0.09866 M \quad + \quad OH^-$$

$$1.34 \times 10^{-3} M$$

$$K_b = [NH_4^+][OH^-]/[NH_3] = (1.34 \times 10^{-3} \times 1.34 \times 10^{-3})/0.09866$$

$$= 1.8199 \times 10^{-5}$$