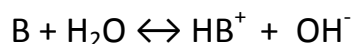


### Expression of equilibrium constant in basic medium

For strong base, such as , NaOH , we never need to write law of chemical equilibrium because the dissociation almost completely. However, is a weak base and its reaction with water is an equilibrium law.

in the general quation:



$$K_a = [HB^+] [OH^-] / [B]$$

**Ex/** What is the pH of a 0.0005 M solution of NaOH at 25 °C ?

**Solution /**



$$[OH^-] = 0.0005 \text{ M} = 5 \times 10^{-4} \text{ M}$$

$$pOH = -\log [OH^-]$$

$$= -\log 5 \times 10^{-4}$$

$$= -\log 5 + 4 \log 10$$

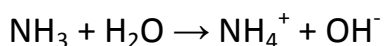
$$= -0.699 + 4$$

$$= 3.301$$

$$pH = 14 - 3.401 = 10.7$$

**Ex/** What is the pH of a 0.1 M NH<sub>3</sub> solution ? K<sub>b</sub> 1.8 x 10<sup>-5</sup>

**Solution /**



$$\begin{array}{ccc} 0.1 & 0 & 0 \end{array}$$

$$\begin{array}{ccc} 0.1 - X & X & X \end{array}$$

$$K_b = [NH_4^+] [OH^-] / [NH_3]$$

$$1.8 \times 10^{-5} = (X)(X) / 0.1 - X$$

$$1.8 \times 10^{-5} = X^2 / 0.1$$

$$X^2 = 1.8 \times 10^{-6}$$

$$X = 1.34 \times 10^{-3} = [OH^-]$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 1.34 \times 10^{-3} = 2.87$$

$$\text{pOH} + \text{pH} = 14$$

$$\text{pH} = 14 - 2.87 = 11.12$$

طريقة اخرى للحل

$$\text{pOH} = 1/2 [\text{pKb} - \log \text{Mb}]$$

$$\text{pKb} = -\log \text{Kb} \quad , \quad \text{Mb} = [\text{OH}^-] = [\text{Base}]$$

$$\text{pOH} = 1/2 [\text{pKb} - \log \text{Mb}]$$

$$= 1/2 [-\log 1.8 \times 10^{-5} - \log 0.1]$$

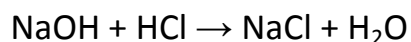
$$= 2.87$$

$$\text{pH} = 14 - 2.87 = 11.12$$

### **Calculation of pH of aqueous solution**

Ex/ What is the pH of the resulting solution when 50 ml 0.1 M NaOH has been added to 75 ml 0.1 M HCl ?

Solution / Each mol of NaOH added neutralizes mole of HCl



$$\text{No. mmol HCl} = 75 \text{ ml} \times 0.1 \text{ mmol / ml} = 7.5 \text{ mmol}$$

$$\text{No. mmol NaOH} = 50 \text{ ml} \times 0.1 \text{ mmol / ml} = 5.0 \text{ mmol}$$

$$\text{No. mmol HCl remaining} = 7.5 - 5.0 = 2.5 \text{ mmol}$$

(unneutralized)

$$\text{Total volume} = 75 \text{ ml} + 50 \text{ ml} = 125 \text{ ml}$$

$$[\text{HCl}] = [\text{H}^+] = \text{no. mmol} / \text{volume ml} = 2.5 \text{ mmol} / 125 \text{ ml} = 0.02 \text{ M}$$

$$\text{pH} = -\log 0.02 = -\log 2 \times 10^{-2} = 1.7$$

Ex/ What is the pH of solution obtained by adding 85 ml 0.1 M NaOH to 75 ml 0.1 M HCl ?

Solution /

$$\text{No. mmol HCl} = 75 \text{ ml} \times 0.1 \text{ mmol / ml} = 7.5 \text{ mmol}$$

$$\text{No. mmol NaOH} = 85 \text{ ml} \times 0.1 \text{ mmol / ml} = 8.5 \text{ mmol}$$

$$\text{No. mmol NaOH an excess} = 8.5 - 7.5 = 1.0 \text{ mmol}$$

$$\text{Total volume} = 75 \text{ ml} + 85 \text{ ml} = 160 \text{ ml}$$

$$[\text{NaOH}] = [\text{OH}^-] = \text{no. mmol} / \text{volume ml} = 1.0 \text{ mmol} / 160 \text{ ml} = 6.25 \times 10^{-3} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log 6.25 \times 10^{-3} = 2.21$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.21 = 11.79$$

### **Weak acid plus its salt**

If a salt that contains the same anion is added to solution of a weak acid, the effect is to decrease the concentration of hydronium ion. The salt, completely ionized, increases the concentration of the anion, thereby displacing the chemical equilibrium.

In the titration of a weak acid by a strong base, each mole of base added gives a mole of salt. The effect of this salt must be considered in computing the pH of the solution.

Ex/ What is the pH of an acetic acid solution when 85 ml 0.15 M NaOH have been added to 50 ml 0.1 M HOAc?  $K_a = 1.8 \times 10^{-5}$ ,  $\text{p}K_a = 4.74$



$$\text{No. mmol HOAc} = 50 \text{ ml} \times 0.1 \text{ mmol / ml} = 5.0 \text{ mmol}$$

$$\text{No. mmol NaOH} = 30 \text{ ml} \times 0.15 \text{ mmol / ml} = 4.5 \text{ mmol}$$

$$\text{No. mmol HOAc remaining} = 5.0 - 4.5 = 0.5 \text{ mmol}$$

$$\text{pH} = \text{p}K_a - \log \text{mmoles acid remaining} + \log \text{mmoles salt}$$

$$\text{pH} = 4.74 - \log 0.5 + \log 4.5$$

$$\text{pH} = 4.74 - (-0.3) + 0.65 = 5.7$$

### **Weak base plus salt with common ion**

The treatment is similar to that for the weak acid.

Ex /What is the pH of a solution containing 0.535 gm  $\text{NH}_4\text{Cl}$  in 50ml 0.1M  $\text{NH}_3$  ?  $K_b = 1.8 \times 10^{-3}$

Solution /  $\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^-$

No.mol  $\text{NH}_4\text{Cl} = 0.535 \text{ gm} \times 1\text{mol}/53.5 \text{ gm} = 0.01\text{mol}$

No.mmol =  $0.01 \text{ mol} \times 1000 \text{ mmol} / \text{mol} = 10 \text{ mmol } \text{NH}_4\text{Cl}$

No.mmol  $\text{NH}_3 = 50 \text{ ml} \times 0.1 \text{ mmol} / \text{ml} = 5.0 \text{ mmol}$

$\text{pOH} = \text{pK}_b - \log \text{mmoles base} + \log \text{mmoles salt}$

$\text{pOH} = 4.74 - \log 5.0 + \log 10$

$\text{pOH} = 4.74 - 0.699 + 1.0 = 5.04$

$\text{pH} = 14 - 5.04 = 8.96$

### **salt of weak acid and strong base**

when an equivalent amount of NaOH has been added to a solution of a weak acid (such as HOAc), the solution is not neutral , as it is when an equivalent amount of strong base has been added to a strong acid. The reason is that two bases, the  $\text{OAc}^-$  and the  $\text{OH}^-$  ions, are competing for the protons . At the equivalence point we have added a mole of  $\text{OH}^-$  ion for each mole of HOAc originally present . But, since a small fraction of the total number of protons is still held by the  $\text{OAc}^-$  ion , as undissociated HOAc molecules , we have an excess of  $\text{OH}^-$  ions present.

The pH of the solution is computed from the equilibrium constant of the two competing reaction.

Ex / What is the pH at the equivalence point when 50 ml 0.1 M NaOH is titrated with 0.1 M NaOH ?  $K_a = 1.8 \times 10^{-5}$

Solution /

$\text{pH} = 1/2 (\text{pK}_w + \text{pK}_a + \log M_s)$

$\text{pK}_w = - \log K_w = - \log 1 \times 10^{-14} = 14$

$\text{pK}_a = - \log K_a = -\log 1.8 \times 10^{-5} = 4.74$

$M_s = [\text{salt}] = \text{no of moles salt} / \text{total volume}$

$\text{No. mmol HOAc} = 50 \text{ ml} \times 0.1 \text{ mmol} / \text{ml} = 5.0 \text{ mmol}$

At equivalent point:

$\text{mmoles of acid} = \text{mmoles of base}$

$\text{no. mmol NaOH} = 50 \text{ ml} \times 0.1 \text{ mmol} / \text{ml} = 5.0 \text{ mmol}$

$\text{Total volume} = (50 + 50) \text{ ml} = 100 \text{ ml}$

$M_s = 5.0 \text{ mmol} / 100 \text{ ml} = 0.05 \text{ M}$

$\text{pH} = 1/2 (\text{pK}_w + \text{pK}_a + \log M_s)$

$= 1/2 (14 + 4.74 + \log 0.05)$

$= 8.71$

The general expression for the concentration of  $\text{OH}^-$  ion in a solution of a salt of a weak acid and strong base is

$$[\text{OH}^-] = \sqrt{\frac{C_s K_w}{K_a}}$$

$$[\text{H}^+] = \sqrt{\frac{K_w K_a}{C_s}}$$

Where  $C_s$  is the salt concentration, neglecting the small amount which **reacts**.

### **Salt of weak base with strong acid**

The equilibrium expression is treated exactly the same as for a weak acid

Ex / What is the pH of a solution containing 10 mmol  $\text{NH}_4\text{Cl}$  in a volume of 100 ml?  $K_b = 1.8 \times 10^{-5}$

Solution /

$\text{pH} = 1/2 (\text{pK}_w - \text{pK}_b - \log M_s)$

$M_s = [\text{salt}] = \text{no. moles salt} / \text{total volume} = 10 \text{ mmol} / 100 \text{ ml} = 0.1 \text{ M}$

$\text{pH} = 1/2 (14 - 4.74 + 1) = 5.13$

$$\begin{aligned}
 [\text{H}^+] &= \sqrt{[\text{CS}] \frac{K_w}{K_b}} \\
 &= \sqrt{\frac{0.1 \times 10^{-14}}{1.8 \times 10^{-5}}} = \sqrt{\frac{1 \times 10^{-10}}{1.8}} \\
 &= 0.7 \times 10^{-5}
 \end{aligned}$$

$$\begin{aligned}
 \text{pH} &= -\log [\text{H}^+] = -\log [0.7 \times 10^{-5}] \\
 &= -\log 0.7 + 5\log 1 \\
 &= -(-0.127 - 5) = 5.127
 \end{aligned}$$

### **Buffers solution**

A buffer solution is one that contains a weak acid and its salt or a weak base and its salt. The name is based on the fact that an acid or base added to a buffer solution causes less change in pH than an acid or base added to pure water or to an unbuffered solution. To illustrate the buffer effect, we shall consider a solution containing acetic acid and a salt, sodium acetate or ammonium hydroxide and ammonium chloride.

Expression of the general equation for buffer solution is:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

### **calculation of the pH of buffer solution**

Ex / What is the pH of a solution that is 0.40 M in formic acid and 1.00 M in sodium formate ?  $K_b = 1.8 \times 10^{-4}$



$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\text{pK}_a = -\log 1.8 \times 10^{-4} = 3.75$$

$$\text{pH} = 3.75 + \log 1.00 / 0.40$$

$$= 3.75 + 0.39 = 4.14$$

Ex / Calculate the pH change that takes place when a 1.0 mole of HCl is added to 5.0 m each of acetic acid and sodium acetate?  $K_a = 1.8 \times 10^{-5}$

Solution / Befor addation

$$\begin{aligned} \text{pH}_1 &= \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]} \\ &= 4.74 + \log 5.0 / 5.0 \\ &= 4.74 \end{aligned}$$

After addation HCl

$$\begin{aligned} \text{pH}_2 &= \text{pK}_a + \log \frac{\text{salt} - [\text{H}^+]}{\text{acid} + [\text{H}^+]} \\ &= 4.74 + \log \frac{5-1}{5+1} = 4.58 \end{aligned}$$

$$\Delta \text{pH} = \text{pH}_2 - \text{pH}_1$$

$$= 4.58 - 4.74 = -0.16$$

Ex / A mixture of  $\text{NH}_4\text{Cl}$  and 1.0 M  $\text{NH}_3$  solution is prepared to give a buffer of pH 9.0. What quantities of each are required ? if we use 100 ml  $\text{NH}_3$  solution ,  $K_b = 1.8 \times 10^{-5}$

Solution /  $\text{pH} + \text{pOH} = 14$

$$\text{pOH} = 14 - \text{pH} = 14 - 9.0 = 5$$

$$[\text{OH}^-] = 10^{-\text{pOH}} = 10^{-5}$$

$$[\text{OH}^-] = K_b \times \frac{nb}{ns}$$

$$10^{-5} = 1.8 \times 10^{-5} \times \frac{nb}{ns}$$

$$\frac{nb}{ns} = \frac{10^{-5}}{1.8 \times 10^{-5}}$$

$$\frac{nb}{ns} = \frac{1}{1.8} \Rightarrow \frac{ns}{nb} = 1.8$$

$$nb = 1.0 \text{ mmol / ml} \times 100 \text{ ml} = 100 \text{ mmol}$$

$$\frac{ns}{100 \text{ mmol}} = 1.8 \Rightarrow ns = 1.8 \times 100 \text{ mmol} = 180 \text{ mmol}$$

$$\text{Weight} = 180 \text{ mmol} \times 53.5 \text{ mg / mmol} = 9600 \text{ mg} = 9.6 \text{ gm}$$

Ex / Calculate the pH change that takes place when a 100.0 ml portion  
 (a) 0.0500 M NaOH and (b) 0.0500 M HCl is added to 400.0 ml of  
 the buffer solution that contains 0.3M ammonium chloride and 0.2 M  
 NH<sub>3</sub> ? pK<sub>b</sub> = 4.74 , K<sub>b</sub> = 1.8 x 10<sup>-5</sup>

Solution / before add.

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pOH} = 4.74 + \log \frac{0.3}{0.2} = 4.92$$

$$\text{pH}_1 = 14 - 4.92 = 9.08$$

After addition 0.0500 M NaOH

$$[\text{NH}_3] = (0.20 \times 400 + 0.0500 \times 100) / 500 = 85.0 / 500 = 0.170 \text{ M}$$

$$[\text{NH}_4\text{Cl}] = (0.30 \times 400 - 0.0500 \times 100) / 500 = 115.0 / 500 = 0.230 \text{ M}$$

$$\text{pOH} = 4.74 + \log 0.230 / 0.170$$

$$= 4.74 + 0.13 = 4.87$$

$$\text{pH}_2 = 14 - 4.87 = 9.12$$

$$\Delta \text{pH} = \text{pH}_2 - \text{pH}_1 = 9.12 - 9.08 = 0.04$$

b- After addition 0.0500M HCl

$$[\text{NH}_3] = (0.20 \times 400 - 0.0500 \times 100) / 500 = 75.0 / 500 = 0.150 \text{ M}$$

$$[\text{NH}_4\text{Cl}] = (0.30 \times 400 + 0.0500 \times 100) / 500 = 125.0 / 500 = 0.250 \text{ M}$$

$$\text{pOH} = 4.74 + \log 0.250 / 0.150$$

$$= 4.74 + 0.22 = 4.96$$

$$\text{pH}_2 = 14 - 4.96 = 9.04$$

$$\Delta \text{pH} = \text{pH}_2 - \text{pH}_1 = 9.04 - 9.08 = -0.04$$