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:

$$B + H_2O \leftrightarrow HB^+ + OH^-$$

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

Ex/ What is the pH of a 0.0005 M solution of NaOH at 25 ^oC ?

Solution / $NaOH \rightarrow Na^+ + OH^-$

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

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

$= - \log 5 \text{ x } 10^{-4}$

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

$= -0.699 + 4$

$=3.301$

$pH = 14 – 3.401 = 10.7$

Ex/ What is the pH of a 0.1 M NH_3 solution ? K_b 1.8 x 10^{-5}

Solution / $NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

0.1	0	0
0.1 – X	X	X

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

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

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

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

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

pOH = -log [OH^-] = - log 1.34 x 10^{-3} = 2.87

pOH + pH = 14

pH 14 – 2.87 = 11.12

طريقة اخرى للحل

pOH 1/2 [pKb – log Mb]

pKb = -log Kb , Mb = [OH^-] = [Base]

pOH = 1/2 [pKb – log Mb]

= 1/2 [-log 1.8 x 10^{-5} – log 0.1]

=2.87

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

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

No.mmol HCl = 75 ~~ml~~ x 0.1 mmol / ~~ml~~ = 7.5 mmol

No.mmol NaOH = 50 ml x o.1 mmol / ml = 5.0 mmol

No.mmol HCl remaining = 7.5 – 5.0 = 2.5 mmol

(unneutralized)

Total volume = 75 ml + 50 ml = 125 ml

[HCl]= [H^+] = no.mmol / volume ml = 2.5 mmol / 125 ml = 0.02 M

pH -log 0.02 = - log2 x 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 /

No.mmol HCl = 75 ml x 0.1 mmol / ml = 7.5 mmol

No.mmol NaOH = 85 ml x o.1 mmol / ml = 8.5 mmol

No.mmol NaOH an excess =8.5 - 7.5 = 1.0 mmol

Total volume = 75 ml + 85 ml = 160 ml

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

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

pH = 14 – 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, increase 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 ?Ka = 1.8×10^{-5} , pKa = 4.74

Solution / $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

No.mmol HOAc= 50 ~~ml~~ x 0.1 mmol / ~~ml~~ = 5.0 mmol

No.mmol NaOH = 30 ~~ml~~ x o.15 mmol / ~~ml~~ = 4.5 mmol

No.mmol HOAc remaining = 5.0 – 4.5 = 0.5 mmol

pH = pKa – log mmoles acid remaining + log mmoles salt

pH = 4.74 – log 0.5 +log 4.5

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 containing0.535 gm NH_4Cl in 50ml 0.1M NH_3 ? Kb = 1.8×10^{-3}

Solution / $NH_3 + H2O \leftrightarrow NH_4^+ + OH^-$

No.mol NH_4Cl = 0.535 gm x 1mol/53.5 gm = 0.01mol

No.mmol = 0.01 ~~mol~~ x 1000 mmol / ~~mol~~ = 10 mmol NH_4Cl

No.mmol NH_3 =50 ~~ml~~ x o.1 mmol / ~~ml~~ = 5.0 mmol

pOH = pKb – log mmoles base + log mmoles salt

pOH = 4.74 – log 5.0 +log 10

pOH = 4.74 -0.699 +1.0 = 5.04

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 OAc^- and the OH^- ions, are competin g for the protons . At the equivalence point we have added a mole of 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 OAc^- ion , as undissociated HOAc molecules , we have an excess of 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 ?Ka = 1.8×10^{-5}

Solution /

pH = 1/2 (pKw + pKa + log Ms)

pKw = - log Kw = - log 1×10^{-14} = 14

pKa = - log Ka = -log 1.8×10^{-5} 4.74

Ms = [salt] = no of moles salt / total volume

No.mmol HOAc = 50 ml x 0.1 mmol / ml = 5.0 mmol

At equivalent point:

mmoles of acid = mmols of base

no.mmolNaOH = 50 ml x 0.1 mmol / ml = 5.0 mmol

Total volume =(50 + 50)ml = 100 ml

Ms = 5.0 mmol / 100 ml = 0.05 M

pH = 1/2 (pKw + pKa + log Ms)

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

= 8.71

The general expression for the concentration og OH^- ion in a solution of a salt of a weak acid and strong base is

$$[OH^-] = \sqrt{\frac{Cs\ Kw}{Ka}}$$

$$[H^+] = \sqrt{\frac{Kw\ Ka}{Cs}}$$

Where Cs 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 aweak acid

Ex / What is the pH of a solution containing 10mmol NH_4Cl in a volume of 100ml ? Kb = 1.8×10^{-5}

Solution /

pH = 1/2 (pKw - pKb - log Ms)

Ms = [salt] = no.moles salt / total volume = 10 mmol / 100 ml = 0.1 M

pH = 1/2(14-4.74 +1)=5.13

$[H^+] = \sqrt{[Cs]\frac{Kw}{Kb}}$

$$= \sqrt{\frac{0.1\ x\ 10^{-14}}{1.8\ x\ 10^{-5}}} = \sqrt{\frac{1\ x\ 10^{-10}}{1.8}}$$

$= 0.7 \times 10^{-5}$

pH = - log $[H^+]$ = - log $[0.7 \times 10^{-5}]$

= -log 0.7 + 5log1

= -(-0.127 -5) = 5.127

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 un buffered 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:

$$pH = pKa + \log\frac{[salt]}{[acid]}$$

$$pOH = pKb + \log\frac{[salt]}{[base]}$$

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 ? Kb = 1.8×10^{-4}

Solution / $HCOOH + H_2O \longrightarrow H_3O^+ + HCOO^-$

$$pH = pKa + \log\frac{[salt]}{[acid]}$$

pKa = -log 1.8×10^{-4} = 3.75

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? Ka=1.8 x 10^{-5}

Solution / <u>Befor addation</u>

$$pH_1 = pKa + \log\frac{[salt]}{[acid]}$$

$$= 4.74 + \log 5.0 / 5.0$$

$$= 4.74$$

After addation HCl

$$pH_2 = pKa + \log \frac{salt-[\overset{+}{H}]}{acid+[\overset{+}{H}]}$$

$$= 4.74 + \log \frac{5-1}{5+1} = 4.58$$

Δ pH = $pH_2 - pH_1$

= 4.58 – 4.74 =- 0.16

Ex / Amixture of NH_3Cl and 1.0 M NH_3 solution is prepared to give a buffer of pH 9.0. What quantities of each are required ? if we use 100 ml NH_3 solution , Kb = 1.8 x 10^{-5}

Solution / pH + pOH = 14

pOH = 14 – pH = 14 – 9.0 = 5

$[OH^-] = 10^{-Poh} = 10^{-5}$

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

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

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

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

nb = 1.0 mmol / ml x 100 ml = 100 mmol

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

Weight = 180 mmol x 53.5 mg / mmol = 9600 mg = 9.6 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_3 ? pKb = 4.74 , Kb = 1.8 x 10^{-5}

Solution / before add.

$$pOH = pKb + \log \frac{[salt]}{[bast]}$$

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

pH_1 = 14 – 4.92 = 9.08

After addation 0.0500 M NaOH

[NH3] = (0.20×400+0.0500×100)/500 = 85.0/500 = 0.170 M

[NH4Cl] = (0.30×400-0.0500×100)/500 = 115.0/500 = 0.230 M

pOH = 4.74 + log 0.230/0.170

= 4.74 + 0.13 = 4.87

pH2 = 14 – 4.87 = 9.12

ΔpH =pH2 – pH1 = 9.12 – 9.08 = 0.04

b- After addation 0.0500M Hcl

[NH3] = (0.20×400-0.0500×100)/500 = 75.0/500 = 0.150 M

[NH4Cl] = (0.30×400+0.0500×100)/500 = 125.0/500 = 0.250 M

pOH = 4.74 + log 0.250/0.150

=4.74 + 0.22 = 4.96

pH2 = 14 – 4.96 =9.04

ΔpH = pH2 – pH1 = 9.04 – 9.08 = -0.04