Acid – base equilibria and PH of solutions

An acid is a substance that furnishes protons or H_+ ions and a base a substance that accepts protons. In classical terminology the acid HA dissociates in aqueous solution according to the equation

$$HA=H^+ + A^-$$

And a base MOH dissociates to give M^+ $^-OH_-$ ions. The reaction of HA with MOH is

$$MOH=M^+ + OH^-$$

And a base MOH dissociates to give M_+ $+OH_-$ ions. The reaction of HA with MOH is

$$HA +MOH = MA + H_2O$$

This reaction goes more or less to completion because the H_2O molecule is only slightly dissociated. To understand the limitations of acid-base titrations and the selection of proper indicators for such titrations, the student must understand the equilibrium relations involved in neutralization reactions.

Equilibrium constant :

A chemical reaction is at equilibrium when the rates of the forward and the concentrations of the reacting components are related by the equilibrium constant equation. For the reaction

$aA + bB \leftrightarrow cC + dD$

We have the relation

$Ke = [D]^d [C]^c / [A]_a [B]_b$

In which the square brackets indicate the molar concentrations of the reacting species, and each molar concentration is raised to a power that is the coefficient of that substance in the chemical equation. The constant Ke is known as the equilibrium constant. Conventionally the products of the reaction are written in the numerator of the expression.

The equilibrium constant is experimentally determined for every reaction by measuring the concentrations of the reacting species after a condition of equilibrium has been attained. The constant is valid only at the temperature at which the determination is made, a change in temperature will change the equilibrium concentrations, there by changing the numerical value of Ke.

Factors effecting the equilibrium state:

Temperature , Pressure , Concentration, Time, Volume and Catalyst.

pH and Hydrogen ion concentration

Pure water dissociates slightly, forming equivalent amounts of hydronium and hydroxide ions , according to the equation

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

The H^+ ion formed by dissociation of one H_2O molecule unites with another H_2O molecule to form an hydronium ion. At room temperature the concentration of H_3O^+ and OH^- ions in pure water are each 1×10^{-7} molar.

The equilibrium expression for dissociation of water is :

$$Ke = [H_3O^+] [OH^-] / [H_2O]^2$$

Since $[H_2O]$ is constant, we have

$$[H_2O^+] [OH^-] = Kw$$

The constant Kw is evaluated by substituting known numerical values for the concentrations of the ions and solving this gives

$$Kw = (1 \times 10^{-7}) (1 \times 10^{-7}) = 1 \times 10^{-14}$$

This is the value for the constant at 25 ^{0}C .

The obvious simple solution is to use a related function , known as pH, to express hydronium ion concentrations .The function pH is defined by the equation

$$pH = - \log [H_3O^+]$$

which also gives corresponding values for the concentration of OH^- ion pOH, defined by

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

It will be noted that the sum pH +pOH is always 14 when the solution is at room temperature

$$pH + pOH = 14$$

Ex/ What is the pH of a solution in which the hydronium ion concentration is 0.0002 M ?

Solution / $[H_3O^+] = M = 2 X 10^{-4}$

$pH =- \log [H_3O^+]$

$= -\log (2 x 10^{-4}) = - \log 2 + 4 \log 10$

$= -0.30 + 4$

$= 3.7$

Ex/The pH of a solution is 5.40. What is the concentration hydronium ion?

Solution /

$pH = 5.40$

$pH = - \log [H_3O^+]$

$[H_3O^+] = 10^{-Ph} = 10^{- 5.4} = 10^{-6} x 10^{+0.6}$

$= 3.98 x 10^{-6} \approx 4 x 10^{-6}$

Ex/ What is the OH^- concentration in 0.001 M of HCl solution? What is the H^+ concentration derived from the dissociates of the solvent ?

Solution / $Kw = [H^+] [OH^-]$

$1 X 10^{-14} = (0.001)[OH^-]$

$[OH^-] = 1 X 10^{-14} / 1 X 10^{-3} = 1 x 10^{-11}M$

$H_2O \leftrightarrow H^+ + OH^-$

$[OH^-] = [H^+] = 1 X 10^{-11}$

Ex/ What are the concentration of H^+ and OH^- in 0.0030 M solution of $Ba(OH)_2$?

Solution /

$$Ba(OH)_2 \rightarrow Ba^{+2} + 2OH^-$$

$$Kw = [OH^-]\,[H^+]$$

$$1 \times 10^{-14} = (2 \times 0.003)\,[H^+]$$

$$[H^+] = 1 \times 10^{-14} / 6 \times 10^{-3} = 1.6 \times 10^{-12}$$

$$[OH^-]\ 2 \times 0.003 = 6 \times 10^{-3}$$

Ex / A sample of blood found to have a pH 3.80. What were the H^+ and OH^- concentration in the blood?

Solution /

$$pH = -\log [H^+]$$

$$3.8 = -\log [H^+]$$

$$[H^+] = 10^{-3.8}$$

$$= 10^{-4} \times 10^{+0.2} = 1.58 \times 10^{-4}$$

$$= 1.6 \times 10^{-4}$$

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

$$[OH^-] = 1 \times 10^{-14} / 1.6 \times 10^{-4} = 6.25 \times 10^{-11}$$

Expression of equilibrium constant in acidic medium

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

Ex / What is the pH of a 0.005 M solution of HCl at 25ºC ?

Solution /

$$HCl \rightarrow H^+ + Cl^-$$

$$[H^+] = 0.005\ M = 5 \times 10^{-3} M$$

$$pH = -\log [H^+] = -\log 5 \times 10^{-3}$$

$$pH = -[\log 5 + \log 10^{-3}]$$

$= -0.7 + 3$

$pH = 2.7$

Ex / What is the pOH of a 2×10^{-4} M solution of HNO_3 ?

Solution / $HNO_3 \rightarrow H^+ + NO_3^-$

$[H^+] = 2 \times 10^{-4} M$

$pH = -\log [H^+] = -\log 2 \times 10^{-4}$

$= -[\log 2 + \log 10^{-4}]$

$= -0.3 + 4 = 3.7$

$pH + pOH = pKw = 14$

$pOH = 14 - pH = 14 - 3.7 = 10.3$

Expression of equilibrium constant for a weak acid in aqueous solution in the general quation:

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

$$Ka = [H_3O^+] [A^-] / [HA] [H_2O]$$

$[H_2O]$ = constant

$$HA \leftrightarrow H^+ + A^-$$

$$Ka = [H^+] [A^-] / [HA]$$

Ka = acid dissociation constant for weak acid

Ex / Express the acid dissociation constant for weak acid HF is dissolved in water ?

Solution /

$$HF \leftrightarrow H^+ + F^-$$

$$Ka = [H^+] [F^-] / [HF]$$

Ex / / What is the pH of 0.02M solution of acetic acid ? $Ka = 1.8 \times 10^{-5}$

Solution / $CH_3COOH \leftrightarrow CH_3COO^- + H^+$

0.02 0 0

$$0.02 - X \qquad X \qquad X$$

$$Ka = [CH_3COO^-] [H^+] / [CH_3COOH]$$

$$1.8 \text{ X } 10^{-5} = (X)(X) / (0.02 - X)$$

Neglects

$$X^2 = 36 \times 10^{-8}$$

$$X = 6 \times 10^{-4} \text{ M} = [H^+]$$

$$pH \ - \log [H^+] = -\log 6 \times 10^{-4} = -0.78 + 4 = 3.22$$

ملاحظة : يهمل (×) في الحالة التي يكون فيها ثابت تفكك الحامض الضعيف (Ka) يساوي

10^{-5}, 10^{-6}......فما دون

طريقة اخرى للحل

$$pH = 1/2 \, (pKa - \log Ma)$$

$$pKa = -\log Ka \qquad , Ma = [H^+] = [\text{ Acid}]$$

$$pH = 1/2 \, (-\log Ka - \log Ma)$$

$$= 1/2 \, (-\log 1.8 \times 10^{-5} - \log 0.02)$$

$$= 1/2(4.47 + 1.7) = 3.22$$

Example 1 : Calculate the PH of a $2*10^{-3}M$ of hydrochloric acid solution.

Solution:

since Hcl is astrong electrolyte and it is completely ionized.

$[H^+] = 2*10^{-3} M$

$PH = -Log[H^+] = -Log(2*10^{-3}) = \underline{\underline{2.7}}$

Example 2 : Calculate the PoH and the PH of a $5*10^{-2}M$ solution of NaOH.

Solution :

$[OH^-] = 5*10^{-2} M$

$PoH = -Log[OH^-] = -Log(5*10^{-2}) = \underline{\underline{1.3}}$

$PH + PoH = 14$

$\therefore \quad PH = 14 - 1.3 = \underline{\underline{12.7}}$

Example 3 : Calculate the hydrogen ion concentration of a solution with pH = 9.67.

Solution:

$PH = -Log[H^+] = 9.67$

$[H^+] = 10^{-9.67} = \underline{\underline{2.14*10^{-10}}} M$

Acid – Base strength:

When an acid or base is dissolved in water, it will dissociate or ionize. The degree of ionization depends on the strength of the acid. A "strong" electrolyte is completely dissociated, while a "weak" electrolyte is partially dissociated. Hence, a weak acid has a relatively smell dissociation constant (Ka), whereas a strong of an acid has a Large dissociation constant.

Similarly, a strong base has a Larg (K_b) and a weak base has small (K_b).

A list of some common strong and weak electrolytes are shown in the following table.

strong Electrolytes	Weak Electrolytes
Hcl, HI	acetic acid CH_3COOH, $HCOOH$ formic acid
$HClO_4$, HBr	HF, HNO_2, HCN hydrocyanic acid
H_2SO_4	H_2S, H_2SO_3
HNO_3	NH_3, C_6H_5OH phenol
NaOH, KOH	$C_6H_5NH_2$ aniline
$Ba(OH)_2$, LiOH	N_2H_4CO Urea

Example 1: calculate the PH of a 0.05 M solution of acetic acid? $Ka = 1.8*10^{-5}$

Solution:

The acetic acid dissociates according to the equation:

$$\underset{0.05-x}{HOAC} = \underset{x}{H^+} + \underset{x}{OAC^-}$$

$$Ka = \frac{[H^+][OAC^-]}{[HOAC]}$$

Let concentration of $H^+ = x$

conc. of $OAC^- = x$

conc. of HOAC undissociation $= 0.05 - x$

$$\frac{x^2}{0.05-x} = 1.8*10^{-5}$$

$0.05 - x \simeq 0.05$ (that x is negligible in comparison with 0.05)

$$\frac{x^2}{0.05} = 1.8*10^{-5} \Rightarrow x^2 = 9*10^{-7} \Rightarrow x = 9.49*10^{-4}\ M = [H^+]$$

$$PH = -Log[H^+] = -Log[9.49*10^{-4}] = \underline{\underline{3.02}}$$

The generalized approximate equation for the dissociation of a weak acid is:

$$\boxed{[H^+] = \sqrt{Ka \cdot C}}$$

where:

C: is the concentration of the weak acid.

Example 2: what is the pH of a 0.1 M NH_3 Solution ?

$K_b = 1.75*10^{-5}$

Solution:

$$NH_3 + H_2O = NH_4^+ + OH^-$$

$$\underset{0.1-x}{} \qquad \qquad \underset{x}{} \qquad \underset{x}{}$$

$$\frac{x^2}{0.1-\underset{\text{negligible}}{\boxed{x}}} = 1.75*10^{-5} \Rightarrow x^2 = 1.75*10^{-6} \Rightarrow x = 1.32*10^{-3} M = [OH^-]$$

$$POH = -Log[OH^-] = -Log(1.32*10^{-3}) = 2.87$$

$$PH = 14 - POH = \underline{11.12}$$

The generalized approximate equation for the dissociation of a weak base is:

$$\boxed{[OH^-] = \sqrt{K_b \cdot C}}$$