ACID BASE EQUILIBRIUM

Introduction

- The term acid is “acere”, in Latin language, meaning sour.
- In 17th century the English chemist Robert Boyle grouped the substances as either acids or bases.
- Acids and bases are found in many fruits, vegetables and some household products, like vinegar, apple, oranges, lemons, grapes, soaps, etc.
- To explain the behavior of acids and bases there are many acid-base theories.

1. Acid-Base Theories

1. The Arrhenius Acid-Base Theory

- In 1884, Swedish chemist Svante Arrhenius defined acids as compounds that produce **H^+** ions in aqueous solutions, and bases compounds that produce **OH^-** ions in aqueous solutions.
- This theory was insufficient to explain the acidic or basic properties of some substances such as SO_3 or NH_3.

$$HCl(aq) \longrightarrow Cl^-(aq) + H^+(aq)$$

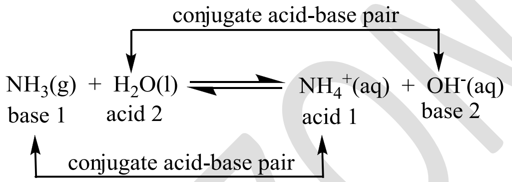
$$HNO_3(aq) \longrightarrow NO_3^-(aq) + H^+(aq)$$

$$NaOH(s) \longrightarrow Na^+(aq) + OH^-(aq)$$

$$Mg(OH)_2(s) \longrightarrow Mg^{+2}(aq) + 2OH^-(aq)$$

2. Bronsted – Lowry Acid-Base Theory

- It was proposed independently by Johannes Nicolaus Brønsted and Thomas Martin Lowry in 1923.
  An acid is defined as any chemical species (molecule or ion) that is able to lose, or "donate" a hydrogen ion (proton), and a base is a species with the ability to gain or "accept" a hydrogen ion (proton)



Example 1

Show the conjugate acid-base pairs in the following reaction.

$CH_3COOH + H_2O \Leftrightarrow CH_3COO^- + H_3O^+$

Solution

CH_3COOH and CH_3COO^- ,

H_2O and H_3O^+ are conjugate acid base pairs

Example 2

Write the conjugate acids of the following bases.

a. OH^- b. CN^- c. ClO^- d. S^{-2}

Solution

a. H_2O b. HCN c. HClO d. HS^-

Example 3

Write the conjugate bases of the following acids.

a. HCO_3^- b. H_3O^+ c. $CH_3NH_3^+$ d. HS^-

Solution

a. CO_3^{-2} b. H_2O c. CH_3NH_2 d. S^{-2}

1. General Properties of Acids

- Are generally sour in taste,
- Are corrosive substances
- Change the color of litmus paper to red,
- React with metals to produce a metal salt and hydrogen gas,
- React with metal carbonates to produce water, CO_2 and a salt,
- React with bases to produce water and a salt, neutralization reaction,
- Conduct electricity.

2. General Properties of Bases

- Are generally bitter in taste,
- Cause slippery feeling to skin,
- Change the color of litmus paper to blue,
- Strong bases are corrosive,
- React with amphoteric metals to produce a metal salt and hydrogen gas,
- React with bases to produce water and a salt,neutralization reaction,
- Conduct electricity.

2. Ionization of Water

- Water is a amphoteric substance, acting as a base against acids and as an acid against bases.

$H_2O(l) + H_2O(l) \Leftrightarrow OH^-(aq) + H_3O^+(aq)$

Equilibrium constant expression for the ionization of water is

$Kw=[H_3O^+]\,[OH^-]$

at 25°C Kw has a value $Kw=1x10^{-14}$;when water is neutral;

$Kw=[H_3O^+]\,[OH^-]=1x10^{-14}$, then $[H_3O^+]= [OH^-]=1x10^{-7}$ M.

3. The pH Scale

- pH is a measure of the acidity or basicity of a solution.
- It is defined as the cologarithm of the concentration of dissolved hydrogen ions (H^+).
- It varies between 0 to 14.
- Indicators are used to determine the acidity level of solutions.

$$pH = -\log\left[H^+\right] \text{ or } \left[H^+\right] = 10^{-pH}$$

Similarly for $[OH^-]$ ion *pOH* can be expressed as;

$$pOH = -\log\left[OH^-\right] \text{ or } \left[OH^-\right] = 10^{-pOH}$$

- For pure water at 25°C,

$[H^+]= 1x10^{-7}$ M and $[OH^-]= 1x10^{-7}$ M

$[H^+]= 1x10^{-7}$ M and $[OH^-]= 1x10^{-7}$ M.

$pH=-\log(1x10^{-7}) = 7$ and $pOH=-\log(1x10^{-7}) = 7$

$$pH + pOH = 14$$

- The pH value of a solution gives an idea about the condition of a solution as follows;

if pH<7.0 solution is acidic,
if pH= 7.0 solution is neutral,
if pH >7.0 solution is basic.

Example 4

Calculate the pH and pOH of the solutions given below.

a. A solution with a $[H^+]$ of $1x10^{-3}$ M.
b. A solution with a $[OH^-]$ of $1x10^{-3}$ M.
c. A solution with a $[H^+]$ of $5x10^{-7}$ M.

A solution with a $[OH^-]$ of $8x10^{-11}$ M.

Example 5

A sample of vinegar has a pH of 3. Calculate the pOH, $[H^+]$, and $[OH^-]$.

Example 6

Lemon juice has a hydrogen ion concentration of $4x10^{-3}$M. Calculate the pH, and pOH, and $[OH^-]$. (log 4 = 0.6)

Example 7

Fill the following table for each of the solution.

Solution	$[H^+]$	$[OH^-]$	pH	pOH
0.05 M NaOH				
0.05 M H_2SO_4				
0.05 M $Ca(OH)_2$				

4. Strength of Acids and Bases

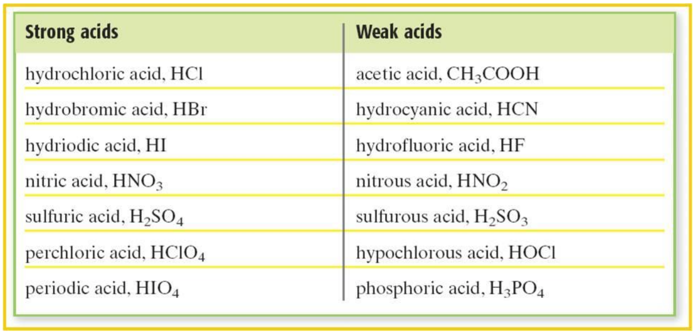
Acid Strength

- Acids are classified as weak or strong according to their degree of dissociation in water.
- Weak acids ionizes reversibly to form H_3O^+ ion in small extent. Usually fewer than 1 percent.
- Its solution does not conduct electricity well.

$$HA(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Ka is acid dissociation constant referring the measure of an acid's strength.
- If $Ka<1.10^{-3}$, acid is generally said to be weak.
- If $Ka=1$ to 1.10^{-3}, acid is accepted as moderate.
- If Ka>1 , acid is strong.

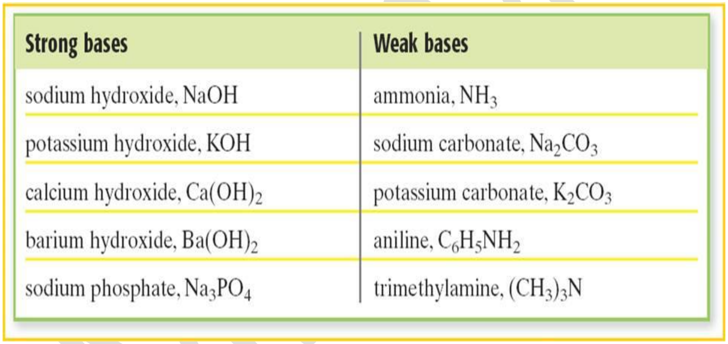


Strong acids	Weak acids
hydrochloric acid, HCl	acetic acid, CH_3COOH
hydrobromic acid, HBr	hydrocyanic acid, HCN
hydriodic acid, HI	hydrofluoric acid, HF
nitric acid, HNO_3	nitrous acid, HNO_2
sulfuric acid, H_2SO_4	sulfurous acid, H_2SO_3
perchloric acid, $HClO_4$	hypochlorous acid, HOCl
periodic acid, HIO_4	phosphoric acid, H_3PO_4

Base Strength

- Strength of bases are also similar to acids.
- $B(aq) + H_2O(l) \Leftrightarrow BH^+(aq) + OH^-(aq)$
- Kb is base dissociation constant referring the measure of an base's strength.

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$



Strong bases	Weak bases
sodium hydroxide, NaOH	ammonia, NH_3
potassium hydroxide, KOH	sodium carbonate, Na_2CO_3
calcium hydroxide, $Ca(OH)_2$	potassium carbonate, K_2CO_3
barium hydroxide, $Ba(OH)_2$	aniline, $C_6H_5NH_2$
sodium phosphate, Na_3PO_4	trimethylamine, $(CH_3)_3N$

Example 8

Write the K_a or K_b expressions of the following weak acids and bases.

a. HF
b. NH_3
c. H_2CO_3
d. H_3PO_4

Example 9

A 9.4 g sample of the acid HA, is dissolved in 500 mL of solution, has a $[H^+] = 1.10^{-4}$ M. If the molecular weight of the acid is 188 g/mol, calculate;

a. molarity of the acid solution,
b. the [A-],
c. the value of K_a for HA.

Solution

a. $n = \frac{9.4}{188} = 0.05mol,\ M = \frac{0.05mol}{0.5L} = 0.1M$

b.	$HA(aq) + H_2O(l) \Leftrightarrow$	$H_3O^+(aq)$ +	$A^-(aq)$
Initial:	0.1 M	-	-
Change:	-1.10^{-4} M	$+1.10^{-4}$ M	$+1.10^{-4}$ M
At Equilib:	$0.1- 1.10^{-4}$ M	1.10^{-4} M	$1. 10^{-4}$ M

c. $K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{1.10^{-4} \times 1.10^{-4}}{0.1-1.10^{-4}} = 1x10^{-7}$

Example 10

A solution of nitrous acid, HNO_2, contains 1.41 g of HNO_2 in 10 L water and has a pH of 3. What is the dissociation constant of the acid? And percent dissociation of the acid. (H:1, N:14, O:16)

Solution

$n = \frac{1.41g}{47g/mol} = 0.03mol,\ M = \frac{0.03mol}{10L} = 0.003M$

$pH = 3 = -\log[H^+] \Rightarrow [H^+] = 10^{-3} = 0.001M$

	$HNO_2(aq)$ + $H_2O(l)$ ⇔	$H_3O^+(aq)$ +	$NO_2^-(aq)$
Initial:	0.003 M	-	-
Change:	-0.001 M	+0.001 M	+0.001 M
At Equilib:	0.002 M	0.001 M	0.001M

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{0.001 \times 0.001}{0.002} = 5x10^{-4}$$

$$\text{Percent dissociation} = \frac{[NO_2^-]}{[HNO_2]} x100 = \frac{0.001}{0.003} x100 = 33.3\%$$

Example 11

What molarity of NH_3 solution provides a pH value of 11? ($K_b = 2x10^{-5}$)

Solution

$if\ pH = 11$ then $pOH = 14 - 11 = 3$

$pOH = 3 = -\log[OH-] = 10^{-3} = 0.001M$

	$NH_3(aq)$ + $H_2O(l)$ ⇔	$OH^-(aq)$ +	$NH_4^+(aq)$
Initial:	x M	-	-
Change:	-0.001 M	+0.001 M	+0.001 M
At Equilib:	x-0.001 M	0.001 M	0.001M

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 2x10^{-5} = \frac{0.001 \times 0.001}{x - 0.001}$$

$x = 0.051M \quad \Rightarrow \quad [NH_3] = 0.051M$

Relationship Between K_a and K_b

K_a and K_b of a conjugate acid-base pair has the following relationship;

$K_a \times K_b = K_w = 1.10^{-14}$

Example 12

What is the K_b value of F^- ion if it has a K_a value of $7.2x10^{-4}$?

Solution

F^- ion is conjugate base of HF. Then, $K_w = 1.10^{-14} = K_b x\ 7.2x10^{-4}$

$K_b = 1.39x10^{-11}$

5. Neutralization

The reaction between an acid and a base to form salt and water is called neutralization. Indeed it is the reaction between H^+ ion and OH^- ion to form water

$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$

The nature of the particular acid and base involved in a reaction determines the acidity or basicity of the resulting solution.

strong acid + strong base → neutral solution
strong acid + weak base → acidic solution
weak acid + strong base → basic solution
weak acid + weak base → acidic or basic solution
depends upon K_a and K_b values.

Example 13

What will be the pH of the resulting solution which is prepared by mixing 40 mL of 0.3 M NaOH solution and 60 mL and 0.4 M HBr solution?

Solution

$HBr(aq) + NaOH(aq) \rightarrow NaBr(aq) + H_2O(l)$
0.4 M 0.3 M
60 mL 40 mL

$n_{NaOH} = V \times M = 0.06 \times 0.4 = 0.024 mol$

$n_{HBr} = 0.04 \times 0.3 = 0.012 mol$

After neutralization 0.024 – 0.012 = 0.012 mol NaOH remains Unreacted which makes resulting solution basic and volume of the solution is 60 + 40 = 100 mL.

$$M_{NaOH} = \frac{n}{V_T} = \frac{0.012}{0.1} = 0.12M,\ pOH = -\log[OH^-] = -\log(0.12) = 0.92$$

$pH = 14 - 0.92 = 13.08$

Example 14

A 6.4 g impure sample of NaOH is completely neutralized by 50 mL of 0.4 M HCl. Calculate the percentage purity by mass of NaOH in the sample?

Solution

Because the complete neutralization had occurred mole numbers of H^+ and OH^- ions are equal. Therefore moles of NaOH and HCl are equal.

$n_{NaOH} = n_{HCl} = V \times M = 0.05 \times 0.4 = 0.02 mol$

$m_{NaOH} = n \times MM = 0.02 \times 40 = 0.8g$ neutralized

$$\%\text{purity NaOH} = \frac{0.8}{6.4} = 12.5\%$$

Example 15

A 0.5 g impure sample of a diprotic acid, which is 90% by mass is completely neutralized by 50 mL of 0.2 M KOH solution. Find the molecular weight of the acid?

Solution

Because the complete neutralization had occurred mole numbers of H^+ and OH^- ions are equal.

$n_{KOH} = 0.05 \times 0.2 = 0.01 mol$ then, $n_{H^+} = n_{OH^-} = 0.01 mol$

$$n_{H_2A} = \frac{n_{H^+}}{2} = \frac{0.01}{2} = 0.005 mol, \text{ because acid is diprotic.}$$

$$m_{H_2A} = 0.5 \times \frac{90}{100} = 0.45g, n = \frac{m}{MM} \Rightarrow MM = \frac{0.45}{0.005} = 90g/mol$$

6. Titration

- Titration is a process for analyzing the amount of acid or base in a solution.
- In titration the solution whose volume and concentration are known is called **titrant** or **standard solution**.
- The neutralization point is known as an **equivalence point** or **end-point**. It is monitored by using an acid or a base indicator.

Example 16

A 0.1 M of 50 mL HCl solution is titrated with 0.1 M NaOH solution. Calculate the pH of the final solutions in each of the following cases and draw a curve showing pH versus volume of NaOH added.

a. In the original acid solution.
b. After 10 mL of NaOH solution has been added.
c. After 49 mL of NaOH solution has been added.
d. After 50 mL of NaOH solution has been added.
e. After 60 mL of NaOH solution has been added.

Solution

a. $[H^+] = 0.1M$, then $pH= -\log(0.1) = 1$

$$b.\ n_{HCl} = n_{H^+} = M \times V = 0.01 \times 0.05 = 0.005 mol$$

$$n_{NaOH} = n_{OH^-} = 0.1 \times 0.01 = 0.001 mol$$

Since 0.001 mol H^+ is neutralized

0.005-0.001=0.004 mol H^+ remains.

Total volume becomes 50 + 10 =60 mL=0.06L

$$[H+] = \frac{0.004}{0.06} = 0.067M \text{ then } pH = -\log 0.067 = 1.17$$

$$c.\ n_{HCl} = n_{H^+} = M \times V = 0.01 \times 0.05 = 0.005 mol$$

$$n_{NaOH} = n_{OH^-} = 0.1 \times 0.049 = 0.0049 mol$$

Since 0.0049 mol H^+ is neutralized

0.005-0.0049=0.0001mol H^+ remains.

Total volume becomes 50 + 49 =99 mL=0.099L

$$[H+] = \frac{0.0001}{0.099} = 0.001M \text{ then } pH = -\log 0.001 = 3$$

$$d.\ n_{HCl} = n_{H^+} = M \times V = 0.01 \times 0.05 = 0.005 mol$$

$$n_{NaOH} = n_{OH^-} = 0.1 \times 0.05 = 0.005 mol$$

Since $n_{H^+}=n_{OH^-}$ complete neutralization occurs,

and solution becomes neutral, $pH = 7$

$$e.\ n_{HCl} = n_{H^+} = M \times V = 0.01 \times 0.05 = 0.005 mol$$

$$n_{NaOH} = n_{OH^-} = 0.1 \times 0.06 = 0.006 mol$$

$$n_{OH^-} \rangle n_{H^+}$$

Since 0.005 mol H^+ is neutralized

0.006-0.005=0.001mol OH^- remains.

Total volume becomes 50 + 60 =110 mL=0.11L

$$[OH^-] = \frac{0.001}{0.11} = 0.009M \text{ then } pOH = -\log 0.009 = 2.04$$

$$pH = 14 - 2.04 = 11.96$$

7. Hydrolysis

- Hydrolysis is the general term of the chemical reactions of anions with water.
- Salts of weak acids and bases hydrolyze in aqueous solutions.
- For example NaF is a salt formed from strong base and weak acid.

$F^- + H_2O \Leftrightarrow HF + OH^-$ $\quad K_b = \frac{[HF][OH^-]}{[F^-]}$

K_b is dissociation constant of the weak base

- For the salts produced from weak acid and weak bases;
  if $K_a>K_b$, then salt is acidic.
  if $K_a<K_b$, then salt is basic.

Example 17

What is the pH of 0.1 M $NaNO_2$ solution?
(Ka for $HNO_2=5.10^{-4}$)

Solution

In the salt NO_2^- ion is weak acid anion, thus it hydrolyzes.

	$NO_2^- + H_2O \Leftrightarrow$	HNO_2	OH^-
Initial	0.1 M	-	-
Change	-x	+x	+x
At equil	0.1-x M	x M	x M

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{5\times10^{-4}} = \frac{x.x}{0.1} \Rightarrow x = 1.41\times10^{-6}M$$

$$[OH^-] = x = 1.41\times10^{-6}M, pOH = -\log(1.41\times10^{-6})$$

$$pOH = 5.85 \Rightarrow pH = 14 - 5.85 = 8.15$$

Example 18

Calculate the mass of sodium acetate, CH_3COONa, that must be dissolved in water to make a 0.5 L solution which has a pH value of 9? K_a for $CH_3COOH = 1.8x10^{-5}$ and CH_3COONa=82 g/mol.

Solution

In the salt CH_3COO^- ion is weak acid anion, thus it hydrolyzes.

	$CH_3COO^- + H_2O \Leftrightarrow$	CH_3COOH	OH^-
Initial	a M	-	-
Change	-x	+x	+x
At equil	a -x M	x M	x M

solution

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1.8\times10^{-5}} = \frac{x.x}{a}$$

$$\frac{x.x}{a} = 0.56x10^{-9}, \quad pH = 9 \Rightarrow pOH = 14 - 9 = 5$$

$$[OH^-] = 1.10^{-5}M \Rightarrow x = 1.10^{-5}M$$

$$\frac{1.10^{-5}x1.10^{-5}}{a} = 0.56x10^{-9} \Rightarrow a = 0.18M$$

$$0.18 = \frac{n}{0.5L} \Rightarrow n = 0.09mol \text{ of } CH_3COONa$$

$$m = 0.09x82 = 7.38g \text{ of } CH_3COONa$$

8. Buffer Solutions

- A buffer solution is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid.
- It has the property that the pH of the solution changes very little when a small amount of acid or base is added to it.
- Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. Such as pH of blood, to maintain pH stability carbonic acid-bicarbonate buffer system is used.

- In a simple buffer solution there is an equilibrium between a weak acid, HA, and its conjugate base, A^-.

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

  The acid dissociation constant for a weak acid, HA, is defined as

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

- Simple manipulation with logarithms gives the Henderson-Hasselbalch equation, which describes pH in terms of pKa.

$$pH = pKa + \log\frac{[A^-]}{[HA]}$$

Example 19

Calculate the pH of a buffer solution prepared by mixing 500 mL of 0.1 M NaF and 500 mL of 0.02 M HF?
(K_a for HF =$6.7x10^{-4}$)

Solution

$$pH = pKa + \log\frac{[F^-]}{[HF]} \text{ and pKa=-log(6.7x10}^{-4}) = 3.17$$

$$pH = pKa + \log\frac{[F^-]}{[HF]} = 3.17 + \log\frac{0.1}{0.02} = 3.87$$

Example 20

0.15 mol of sodium acetate(CH_3COONa) and 0.1 mol acetic acid (CH_3COOH) are added to enough water to make 1 L buffer solution. If K_a for CH_3COOH = $1.8x10^{-5}$)

a. What is the pH of the solution?
b. What will be the pH of the solution if 0.01 mol HNO_3 is added?
c. What will be the pH of the solution if 0.01 mol NaOH is added?

Solution

$$CH_3COOH + H_2O \Leftrightarrow CH_3COO^- + H_3O^+$$

Initial	0.1 M	0.15 M	-
Change	-x	+x	+x
At equil	0.1-x M	0.15 + x M	x M

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8x10^{-5} = \frac{(0.15)\times(x)}{(0.1)}$$

$$x = 1.2\times10^{-5}M$$

$$pH = -\log(1.2\times10^{-5}) = 4.92$$

b. From 0.01 mol HNO_3 , 0.01 mol H_3O^+ ion is produced and it combines with CH_3COO^- ion to produce 0.01 mol CH_3COOH.

$$CH_3COOH + H_2O \Leftrightarrow CH_3COO^- + H_3O^+$$

In buffer	0.1 M	0.15 M	$1.2x10^{-5}$ M
Addition		+0.01M	
Changes	+0.01 M	-0.01 M	-0.01 M
In final buffer	0.11 M	0.14 M	x M

$$K_a = 1.8x10^{-5} = \frac{(0.14)\times(x)}{(0.11)} \Rightarrow x = 1.4\times10^{-5}M$$

$$pH = -\log(1.4\times10^{-5}) = 4.85$$

c. From 0.01 mol NaOH , 0.01 mol OH^- ion is produced and it combines with CH_3COOH to produce 0.01 mol CH_3COO^-.

$$CH_3COOH + H_2O \Leftrightarrow CH_3COO^- + H_3O^+$$

In buffer		0.1 M	0.15 M	$1.2x10^{-5}$ M
Addition	+0.01		-	-
Changes	-0.01 M	+0.01 M	x M	
In final buffer		0.09 M	0.16 M	x M

$$K_a = 1.8x10^{-5} = \frac{(0.16)\times(x)}{(0.09)} \Rightarrow x = 1.1\times10^{-5}M$$

$$pH = -\log(1.1\times10^{-5}) = 4.99$$