Acid-Base Equilibria & pH Calculations Analytical Chemistry

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Acid – Base Equilibrium

Acid-base reactions, in which protons are exchanged between donor molecules (acids) and acceptors (bases), form the basis of the most common kinds of equilibrium problems which you will encounter in almost any application of chemistry. In order to thoroughly understand the material in this unit, you are expected to be familiar with the following topics which were covered in the separate unit Introduction to Acid-Base Chemistry[1]:

- The Arrhenius concept of acids and bases
- The Brønsted-Lowry concept, conjugate acids and bases
- Strong vs. weak acids and bases
- Definition of pH and the pH scale

Arrhenius Theory

An **Arrhenius acid** is any species that increases the concentration of H^+ in aqueous solution. An **Arrhenius base** is any species that increases the concentration of OH^- in aqueous solution[2].

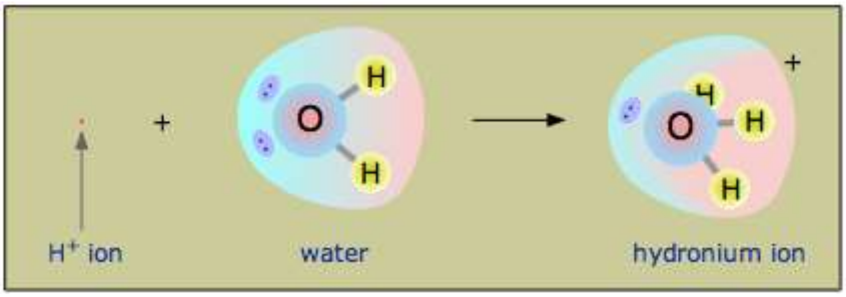
Brønsted- Lowry Theory

In the **Brønsted-Lowry** definition, **acids** are proton donors, and **bases** are proton acceptors. Note that these definitions are interrelated. Defining a base as a proton acceptor means an acid must be available to provide the proton. For example, in reaction below acetic acid, CH3COOH, donates a proton to ammonia, NH_3, which serves as the base [3].

$$\mathbf{CH_3COOH_{(aq)} + NH_{3(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + NH_4^+{}_{(aq)}}$$

The acetate ion considered as a conjugate base (which is strong because weaker the acid means stronger the conjugate base), the ammonium ion is the conjugate acid for the ammonia (the base).

As you should know from introduction to acids and bases, the +1 electric charge of the tiny proton (a bare hydrogen nucleus) is contained in such a miniscule volume of space that the resulting charge density is far too large to enable its independent existence in solution; it will always attach to, and essentially bury itself in, the non-bonding orbitals of a solvent. Thus in aqueous solution, what we commonly represent as the "hydrogen ion" H^+ is more accurately described as the hydronium ion H_3O^+**.** [2]



Strong and Weak Acids

Acids can be very different in a very important way. Consider HCl(aq). When HCl is dissolved in H_2O, it completely dissociates into H^+(aq) and Cl^-(aq) ions; all the HCl molecules become ions:

$$\mathbf{HCl \rightarrow H^+_{(aq)} + Cl^-_{(aq)} \qquad 100\%}$$

Any acid that dissociates 100% into ions is called a strong acid. If it does not dissociate 100%, it is a weak acid. **CH3COOH** is an example of a weak acid:

$$\mathbf{CH_3COOH \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}}$$

As it turns out, there are very few strong acids, which are given in the table below. If an acid is not listed here, it is a weak acid[4].

Acids	Bases
HCl	LiOH
HBr	NaOH
HI	KOH
HNO_3	RbOH
H_2SO_4	CsOH
$HClO_3$	$Mg(OH)_2$
$HClO_4$	$Ca(OH)_2$
	$Sr(OH)_2$

Table 1. Strong Acids and Bases

Strong and Weak Bases

The issue is similar with bases, a **strong base** is a base that is 100% ionized in solution. If it is less than 100% ionized in solution, it is a **weak base**. There are very few strong bases (Table 1) any base not listed is a weak base. All strong bases are OH^- compounds. So a base based on some other mechanism, such as NH_3 (which does not contain OH^- ions as part of its formula), will be a weak base.[4]

pH Definition

pH is a measure of hydrogen ion concentration, a measure of the **acidity** or **alkalinity** of a solution. The pH scale usually ranges from 0 to 14. Aqueous solutions at 25°C with a pH less than 7 are **acidic**, while those with a pH greater than 7 are **basic** or alkaline. A pH level of 7.0 at 25°C is defined as "**neutral**" because the concentration of H_3O^+ equals the concentration of OH^- in pure water. Very strong acids might have a **negative** pH, while very strong bases might have a pH **greater** than 14.[5]

The equation for calculating pH was proposed in 1909 by Danish biochemist Søren Peter Lauritz Sørensen: $\mathbf{pH = -\log[H^+]}$

pH Calculations

Before we calculate the pH for aqueous solution we must know the terms:

K_a which is the **acid dissociation constant** (equilibrium constant) for a reaction in which an acid donate a proton to the solvent**.**

K_b which is the **base dissociation constant** (equilibrium constant) for a reaction in which a base accept a proton from the solvent**.**

K_w water's dissociation constant.

$$\mathbf{K_w = [H^+][OH^-] = 1x10^{-14}} \quad \text{at } 25°C$$

$$\mathbf{[H^+] = [OH^-] = 1x10^{-7}}$$

To solve the pH problems involves a series of **steps**:[3]

1. Write all relevant equilibrium reactions and their equilibrium constant expressions.
2. Count the number of species whose concentrations appear in the equilibrium constant expressions; these are your unknowns
3. Decide how accurate your final answer needs to be. This decision will influence your evaluation of any assumptions you use to simplify the problem.
4. Combine your equations to solve for one unknown (usually the one you are most interested in knowing). Whenever possible, simplify the algebra by making appropriate assumptions.

A- One Substance In The Solution

1- Strong Acid or Strong Base**:**

When the solution contain just one substance which is strong acid or base, the equation must be written in ionic style and calculate the pH directly from the Hydrogen ion concentration (Hydronium ion).

Example1: Find the pH of a 0.03 M solution of hydrochloric acid, HCl.

Solution: there is one substance in this solution which is HCl strong acid, this acid will completely dissociation in water to form H^+ and Cl^-.

	$\mathbf{HCl \rightarrow}$	$\mathbf{H^+_{(aq)}}$	$\mathbf{+\ Cl^-_{(aq)}}$
Initial state	0.03	0	0
Equilibrium	0	0.03	0.03

$[H^+] = 0.03$ M

pH = -log[H⁺] = 1.5

Example2: Find the pH of a 0.03 M solution of NaOH.

Solution: there is one substance in this solution which is NaOH strong Base, this base will completely dissociation in water to form $\mathbf{OH^-}$ and Na^+

	$NaOH \rightarrow$	$Na^+_{(aq)}$	$+\ OH^-_{(aq)}$
Initial state	0.03	0	0
Equilibrium	0	0.03	0.03

$[\mathbf{OH^-}] = 0.03$ M

$pOH = -\log[\mathbf{OH^-}] = \mathbf{1.5}$

$pH = 14 - pOH = 12.5$

Example3: Find the pH of a 1×10^{-7} M solution of hydrochloric acid, HCl.

Solution: there is one substance in this solution which is HCl strong acid, this acid will completely dissociation in water to form H^+ and Cl^-**,**

$$\mathbf{HCl \rightarrow H^+_{(aq)} + Cl^-_{(aq)}}$$

Initial state	1×10^{-7}	0	0
Equilibrium	0	1×10^{-7}	1×10^{-7}

The concentration of the Hydrogen ion is very small and the pH (for the Hydrogen ion from the HCl) will be 7 and this refer to neutral solution but we have an acid in the solution so we must combine the Hydrogen ion from the acid and water (common ion) to find the right concentration of H^+ (we use common ion just if we have very small concentration of the acid or base)

$$\mathbf{H_2O \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}}$$

$K_w = [H^+][OH^-] = 1x10^{-14}$

The $[H^+]$ for the solution equal

$[H^+] = [H^+]_{acid} + [H^+]_{water}$

$([H^+]_{acid} + [H^+]_{water}) [OH^-] = 1x10^{-14}$

$(X + 1x10^{-7}) (X) = 1x10^{-14}$

$X^2 + 1x10^{-7} X - 1x10^{-14} = 0$

To solve this we need to use quadratic equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$X = 6.2x10^{-8}$

$[H^+] = [H^+]_{acid} + [H^+]_{water}$

$[H^+] = 1x10^{-7} + 6.2x10^{-8} = 1.62x10^{-7}$ M

pH= 6.8

2- Weak Acid or Weak base

If the solution contain one substance which is weak acid or base, we can calculate the pH value by using K (dissociation constant).

Example4: Find the pH of a 0.01 M solution of acetic acid, CH_3COOH.
The $K_a = 1.75x10^{-5}$.

Solution : The solution has one substance which is weak acid will partially ionized in water to form very small concentration of **$CH3COO^-$ H^+** .

$$CH3COOH \rightleftharpoons CH3COO^-_{(aq)} + H^+_{(aq)}$$

Initial state	0.01	0	0
Equilibrium	0.01 – x	x	x

$$K_a = \frac{[CH3COO-]\ [H+]}{[CH3COOH]}$$

$$K_a = \frac{[X]2}{0.01-x}$$

The value (x) will very small for we can approximate the value to

[CH3COOH] $\simeq$ 0.01M (x value neglected for all the substances with K equals or lower than 10^{-5}, or dissociation percentage < 5%)

$$K_a = \frac{[X]2}{0.01}$$

$X = [H^+] = \sqrt{Ka * 0.01}$

$[H^+] = 0.316x10^{-3}$

pH= 3.5

3- Salts

If the solution containing the salt alone we must recognize the type of this salt, there are four major types:

- **Neutral Salts**
  Salts of **strong** acid and base (NaCl) this type has neutral acidity (pH = 7)
- **Basic Salts**
  Salts of **weak** acid and **strong** base (CH_3COONa) this type of salt has pH > 7.

$$[H^+] = \sqrt{\frac{KwKa}{[salt]}}$$

$$pH = \frac{1}{2}\ (pK_w + pK_a + \log [salt]\ )$$

- **Acidic Salts**

  Salts of **strong** acid and **weak** base (NH_4Cl) this type of salt has pH < 7.

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

$$pH = \frac{1}{2}\ (pK_w - pK_b - \log [salt]\ )$$

We can manipulate the equations above by using:

$$\mathbf{K_w = K_a \times K_b}$$

Example5: Calculate the pH value for 0.2 M ammonium chloride,(Ka 0.55×10^{-9}).

Solution: in this example the solution has one substance which is Ammonium chloride (NH_4Cl) we use the equation directly to find pH.

$$pH = \frac{1}{2}\ (pK_w - pK_b - \log [salt]\ )$$

$$K_b = \frac{Kw}{Ka} = 1.8\times10^{-5}\ ,\ pK_b = 4.74$$

$$pH = \frac{1}{2}(14 - 4.74 - \log (0.2)$$

$$pH = 4.98$$

B- Two Substances In The Solution

1- Basic Salt & Weak Acid

When the solution has basic salt (**CH_3COONa**) and it's weak acid (**CH_3COOH**), and this is called the **buffer solution**.

To find pH we can use these equation:

$$[H^+] = K_a \times \frac{[acid]}{[salt]}$$

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

Example6: Calculate the pH value for solution contain 0.2 M $\mathbf{CH_3COONa}$ and 0.1 $\mathbf{CH_3COOH}$ (Ka 1.75×10^{-5}).

Solution**:** we have two substance in the solution the weak acid and the basic salt, we can use the above equation to calculate the pH directly without any derivatives

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

$$pH = 4.75 + \log 2 = 5.05$$

2- Acidic Salt & Weak Base

When the solution has acidic salt ($\mathbf{NH_4Cl}$) and it's weak base ($\mathbf{NH_3}$), this is also known as **buffer solution.**

To find pH we can use these equation:

$$[OH^-] = K_b \times \frac{[base]}{[salt]}$$

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

Example7: Calculate the concentration of $\mathbf{NH_4Cl}$ in solution contain 0.1 M NH_3 (K_b 1.75×10^{-5}) to make the pH = 9.
Solution**:** in this example we have two substance $\mathbf{NH_4Cl}$, $\mathbf{NH_3}$ weak base and the acidic salt, we can use the equation directly:

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

$$pOH = 14 - pH = 5$$

$$5 = 4.75 + \log \frac{[salt]}{[0.1]}$$

$$[salt] = 0.182 \text{ M}$$

C- Three Substances In The Solution

1- Basic salt & Weak Acid + Strong (Acid or Base)

When we add a strong acid or base to the buffer solution the pH value will change in very small amount because of the buffering effect, the new pH calculate by the equations :

$$pH = pK_a + \log \frac{[salt] - [Strong\ Acid]}{[acid] + [Strong\ Acid]}$$

$$pH = pK_a + \log \frac{[salt] + [Strong\ base]}{[acid] - [Strong\ base]}$$

Example8: Calculate the pH value after adding 1ml of 10M HCl to letter of buffer solution contain 0.1 M CH_3COOH (K_a 1.75x10^{-5}) and 0.1 M CH_3COONa**.**

Solution: at first we must calculate the HCl concentration after adding 1 ml of 10M to 1 letter

C_1 x V_1 = C_2 x V_2

10 M x 1 ml = C_2 x 1000 ml

C_2 = 0.01 M of HCl added to the solution

Now we use the equation above to find the pH value

$$pH = pK_a + \log \frac{[salt] - [Strong\ Acid]}{[acid] + [Strong\ Acid]}$$

$$pH = 4.75 + \log \frac{[0.1] - [0.01]}{[0.1] + [0.01]}$$

pH = 4.66

2- Acidic salt & Weak Base + Strong (Acid or Base)

We can use the following equations to solve this type of problems:

$$pOH = pK_b + \log \frac{[salt] + [Strong\ Acid]}{[base] - [Strong\ Acid]}$$

$$pOH = pK_b + \log \frac{[salt] - [Strong\ base]}{[base] + [Strong\ base]}$$

Problems And Solutions

A- Common Ion

Example 9: What happen to the H^+ concentration when adding 0.1 mole of CH3COONa to letter of 0.1 M CH3COOH (1.75×10^{-5})?

Solution: To solve this type of problems we need to write the dissociation equations of the two substances in the solution:

	CH_3COOH	$\rightleftharpoons$	$\boxed{CH_3COO^-_{(aq)}}$	$+ H^+_{(aq)}$
Initial C.	0.1		0	0
Equilibrium	0.1-x		x	x
	CH_3COONa	$\rightleftharpoons$	$CH_3COO^-_{(aq)}$	$+ Na^+_{(aq)}$
Initial C.	0.1		0	0
Equilibrium	0		0.1	0.1

Common ion

- $[H^+]$ Before adding the salt

$$K_a = \frac{[CH3COO-]\ [H+]}{[CH3COOH]}$$

$$1.75 \times 10^{-5} = \frac{X*X}{[0.1-X]} \qquad 0.1 - X \simeq 0.1 \quad \text{(small value of X)}$$

$$X = [H^+] = 1.3 \times 10^{-3}\ M$$

- $[H^+]$ After adding the salt

$$[CH_3COO^-] = x + 0.1$$

$$K_a = \frac{[CH3COO-]\ [H+]}{[CH3COOH]}$$

$K_a = \frac{[0.1+X]\ [X]}{[0.1]}$ $0.1 + X \simeq 0.1$ (small value of X)

$1.75x10^{-5} = \frac{0.1X}{0.1}$

$X = [H^+] = 1.8x10^{-5}$ M

B – Titration problems

Example10 : Find the pH after adding 10 ml of 0.2 M of NaOH to solution contain 20 ml of 0.1 M CH_3COOH. ($K_a = 1.75x10^{-5}$).

Solution: we must find the moles of the remaining substances to predict the equation to use in the solution.

	NaOH +	CH_3COOH ⇌	CH_3COONa + H2O
	(0.2*10)	(0.1*20)	
n. of milimoles	2 mmole	2 mmole	0
At Eq.	-2 mmole	-2 mmol	+2 mmole
The remaining moles	0	0	2 mmole

The solution has one substance at equilibrium state this substance is a basic salt we can use one these equations :

$$[H^+] = \sqrt{\frac{KwKa}{[salt]}}$$

$$pH = \frac{1}{2}\ (pK_w + pK_a + \log [salt]\ )$$

$$pH = \frac{1}{2}\ (14 + 4.75 + \log (\frac{2mmole}{30\ ml})$$

we use mmole/ml to calculate the concentration of the salt (30ml the solution volume)

pH = 8.78

Example11 : Find the pH after adding 10 ml of 0.2 M of NaOH to solution contain 20 ml of 0.3 M CH_3COOH. ($K_a = 1.75x10^{-5}$).

Solution: we must find the moles of the remaining substances to predict the equation to use in the solution.

	NaOH	**+ CH_3COOH**	**⇌ CH_3COONa**	**+ H2O**
	(0.2*10)	(0.3*20)		
n. of milimoles	2 mmole	6 mmole	0	
At Eq.	-2 mmole	-2 mmol	+2 mmole	
The remaining moles	0	4 mmole	2 mmole	

The solution has two substances at equilibrium these substances are a basic salt & weak acid we can use buffer equations to solve this problem :

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

$$pH = 4.75 + \log \frac{\frac{[2 mmole]}{30\ ml}}{\frac{[4\ mmole]}{30\ ml}}$$

pH = 4.44

Example12 : Find the pH after adding 20 ml of 0.2 M of NaOH to solution contain 20 ml of 0.1 M CH_3COOH. ($K_a = 1.75x10^{-5}$).

Solution: we must find the moles of the remaining substances to predict the equation to use in the solution.

	NaOH	**+ CH_3COOH**	**⇌ CH_3COONa**	**+ H2O**
	(0.2*20)	(0.1*20)		
n. of milimoles	4 mmole	2 mmole	0	
At Eq.	-2 mmole	-2 mmol	+2 mmole	
The remaining moles	2 mmole	0	2 mmole	

The solution has two substances at equilibrium these substances are a basic salt & strong base the effect of the basic salt will be very weak on the pH value so we can neglected the concentration in the solution and use strong base equation :

	$NaOH$	$\rightarrow$	Na^+	$+ OH^-$
Initial C.	2/40ml (0.05M)		0	0
Eq.	0		0.05	0.05

pOH =-log $[OH^-]$ = 1.3

pH = 14 – 1.3 = 12.7

References

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