CHAPTER II. *Acids - Bases*

1. Definitions of acids and bases

1.1. Acids and bases according to Arrhenius

August Arrhenius first introduced the concept of acids and bases in the 1890s, According to Arrhenius.

An acid is a substance that, when dissolved in water, increases the concentration of hydrogen ions (H^+) into the solution. This can be represented by the general equation:

$$AH \rightarrow H^+ + A^-$$

Example

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

$CH_3COOH \rightarrow H^+ + CH_3COO^-$

A **base** is a substance that, when dissolved in water, increases the concentration of hydroxide ions (**OH^-**).

$$BOH \rightarrow B^+ + OH^-$$

Example

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

$KOH \rightarrow K^+ + OH^-$

1.2. Acids and bases according to Bronsted-Lowry

A more general definition of acids and bases was introduced by Johannes Bronsted and Thomas Lowry in the 1920s.

According to Bronsted-Lowry:

An acid is a chemical species that can donate a proton (H^+), as represented by the following equation.

$$AH \rightarrow H^+ + A^-$$

Example

$$NH_4^+ \rightarrow H^+ + NH_3$$

A Base is a chemical species capable of capturing a proton (H^+), as represented by the following equation:

$$B + H^+ \rightarrow BH^+$$

$$AH \rightarrow H^+ + A^-$$

Example

$$CH_3COO^- + H^+ \rightarrow CH_3COOH$$

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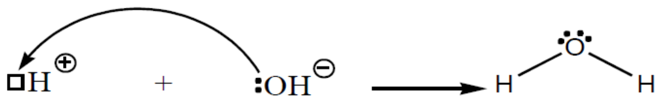
$$NH_3 + H^+ \rightarrow NH_4^+$$

1.3. Acids and Bases according to Lewis

An even broader (plus large) definition of acids and bases was proposed by Lewis in the 1920s, and his definitions are as follows :

- An acid is a compound that has a vacancy "Vacant cell": Electron acceptor.
- A base is a compound that has a free electron pair: Electron donor.



Lewis Acid Lewis base

Electron Acceptor Electron Donor

Example

$$H_2O: + H^+_{(acid)} \rightarrow H_3O^+$$

$$:NH_{3\ (base)} + H^+ \rightarrow NH_4^+$$

2. Acid/Base couple in water

Every acid in solution has a corresponding conjugate base, and vice versa:

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

Where: AH. Acid

A^- . Conjugate base

Example

Hydrofluoric acid HF:

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

The corresponding pair: (Acid/conjugate base) = (HF/F^-)

Ammonia NH_3 (A base)**:**

$$NH_3 + H^+ \leftrightarrow NH_4^+$$

The corresponding pair: (Acid/conjugate base) = (NH_4^+/NH_3)

3. Acid-base reactions

Protons (H^+) do not exist in the free state. For an acid **AH** to be able to give up protons **H^+**, it must have a base **B** capable of fixing them.

<u>First half reaction :</u>

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$$AH \leftrightarrow H^+ + A^- \quad Couple\ (AH/A^-)$$

Second half reaction:

$B + H^+ \leftrightarrow BH^+\ Couple\ (BH^+/B)$

Acid-base reaction:

$$AH + B \leftrightarrow BH^+ + A^-$$

Example

First half reaction :

$$HCOOH_{(l)} \leftrightarrow H^+_{(aq)} + HCOO^-_{(aq)}\ Couple\ (HCOOH/\ HCOO^-$$

Second half reaction:

$$NH_{3\,(g)} + H^+_{(aq)} \leftrightarrow NH^+_{4\,(aq)}\ Couple\ (NH_4^+\ /NH_3\ )$$

Acid -base reaction:

$$HCOOH_{(l)} + NH_{3\,(g)} \leftrightarrow NH^+_{4\,(aq)} + HCOO^-_{(aq)}$$

4. Autodissociation of water

The autodissociation of water is the process by which two water molecules react with each other to produce a hydronium ion (H_3O^+) and a hydroxide ion (OH^-). This reaction is represented by the following equation :

$$2H_2O \leftrightarrow H_3O^+ + OH^- \quad \textbf{or} \quad H_2O \leftrightarrow H^+ + OH^-$$

A chemical equilibrium is then established between the water molecules, the hydronium ions and the hydroxide ions, called the water autoprotolysis equilibrium.

The equilibrium constant for this reaction is:

$$K = K_e = [H_3O^+] \times [OH^-]$$

Since no other ions can be present in pure water at 25 °C, the solution's electrical neutrality requires that:

$$[H_3O^+] = [OH^-] = 10^{-7} M$$

So,

$$K_e = [H_3O^+] \times [OH^-] = 10^{-14}$$

Where: Ke is the ionic product of water or autoprotolysis constant of water.

5. The Acid-Base role of water

Water can act as an acid or a base, so it has an ampholytic character (two roles).

5.1. As an acid

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With a base B, water plays the role of an acid (Water can donate a proton (H^+) to a base, forming a hydroxide ion (OH^-).

$$H_2O \leftrightarrow H^+ + OH^- \quad Couple\ (H_2O/\ OH^-)$$

$$B + H^+ \leftrightarrow BH^+ \quad Couple\ (BH^+/\ B)$$

$$B + H_2O \leftrightarrow BH^+ + OH^- \quad Acid\ base\ reaction$$

5.2. As a base

With an acid AH, water plays the role of a base (Water can also accept a proton (H^+) from an acid, forming a hydronium ion (H_3O^+).

$$AH \leftrightarrow H^+ + A^- \quad Couple\ (AH/\ A^-)$$

$$H_2O + H^+ \leftrightarrow H_3O^+ \quad Couple\ (H_3O^+/\ H_2O)$$

$$AH + H_2O \leftrightarrow H_3O^+ + A^- \quad Acid\ base\ reaction$$

6. Strength of acids and bases

6.1. Acid strength

Consider the dissociation reaction of an acid, AH, in water:

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

$$K_e = \frac{[H_3O^+] \times [A^-]}{[AH]} = K_a$$

With: K_a is the acidity constant of the couple (AH/A^-)

Since the values of K_a are typically small (often negative powers of 10), it is preferred to use the base 10 logarithm of K_a, with the sign changed, a quantity known as pK_a :

$$pK_a = -log_{10}K_a$$

Note

An acid is considered stronger when its acidity constant K_a is higher (indicating a lower pK_a). Conversely, an acid is weaker when its acidity constant K_a, is lower (indicating a higher pK_a).

Example

Consider the twoaid/base pairs:

$pK_{a1}(CH_3COOH/\ CH_3COO^-) = 4.8$

$pK_{a2}(HCN/\ CN^-) = 9.2$

The corresponding base constants are:

$pK_{b1} 14 - 4.8 = 9.2$

$pK_{b2} 14 - 9.2 = 4.8$

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Since: $pK_{a1} < pK_{a2}$, (CH_3COOH) is a stronger acid than hydrogen cyanide (HCN).

Since: $pK_{b2} < pK_{b1}$, (CN^-) is a stronger base than (CH_3COO^-) .

Key take aways:

$K_a \uparrow \rightarrow pK_a \downarrow \rightarrow acid\ strength \uparrow$

$K_b \uparrow \rightarrow pK_b \downarrow \rightarrow base\ strength \uparrow$

A strong acid has a weak conjugate base, while a weak acid has a strong conjugate base.

In an acid–base reaction, the stronger acid donates a proton to the base.

Therefore, acetic acid donates its proton to CN⁻:

$$CH_3COOH + CN^- \rightarrow CH_3COO^- + HCN$$

So, the reaction proceeds to the right, forming the weaker acid (HCN) and the weaker base (CH_3COO^-), which is thermodynamically favored.

6.2. Base strength

Consider the protonation reaction of a base B in the presence of water

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

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

With: K_b is the basicity constant of the couple (BH^+/B)

$$pK_b = -log_{10}K_b$$

Note: A base is considered stronger when its basicity constant K_b is higher (indicating a lower pK_b). Conversely, a base is weaker when its basicity constant K_b is lower (indicating a higher pK_b).

6.3. Relationship between K_a and K_b

Consider the pair (AH/A^-):

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

$$K_a = \frac{[H_3O^+] \times [A^-]}{[AH]} \qquad (1)$$

$A^- + H_2O \leftrightarrow AH + OH^-$

$$K_b = \frac{[OH^-] \times [AH]}{[A^-]} \qquad (2)$$

By multiplying equations (1) and (2), we obtain:

$$K_a \times K_b = [H_3O^+][OH^-] = K_e = 10^{-14}$$

$$\rightarrow pK_a + pK_b = pK_e = 14$$

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6.4. The pK_a of water pairs

Water can act as both an acid and a base, and it has two relevant pKa values depending on which proton transfer equilibrium is considered.

1. Water acting as an acid: When water donates a proton, it dissociates to form hydroxide ions (OH^-):

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

The equilibrium constant for this dissociation is:

$$K_e = [H^+][OH^-] = 10^{-14} \rightarrow pK_a \approx 14$$

2. Water acting as a base: When water accepts a proton, it forms the hydronium ion (H_3O^+):

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

For this protonation, the pKa of the hydronium ion is approximately:

$$pK_a \approx -1.7$$

6.5. Ostwald's Dilution Law

Ostwald's dilution law is a fundamental principle in chemistry that deals with the dissociation of weak acids and bases in solution. It describes how the dilution of a solution affects the degree of dissociation of a weak acid or base.

As the concentration of a weak acid (or weak base) decreases, its tendency to dissociate increases, leading to a higher dissociation coefficient α.

Weak acid

Consider the equilibrium of a weak acid HA

	AH	+	H_2O	⇌	A^-	+	H_3O^+
T=0	C		ex		0		0
T=eq	C- αC		ex		αC_0		αC_0

$$K_a = \frac{[A^-][H_3O^+]}{[AH]} = \frac{\propto C \times \propto C}{C(1-\propto)} = \frac{\propto^2}{(1-\propto)} \rightarrow \frac{K_a}{C} = \frac{\propto^2}{(1-\propto)}$$

Case 1: If C increase => (Ka/C) decrease => (α^2 / (1-α) decrease => α decrease

Case 2: If C decrease => Ka/ C increases => (α^2 / (1-α) increases => α increase.

Weak base

Consider the equilibrium of a weak base

$$B \quad + \quad H_2O \quad \rightleftharpoons \quad BH^+ \quad + \quad OH^-$$

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Give the dissociation coefficient (α) expressed in terms of K_b ?

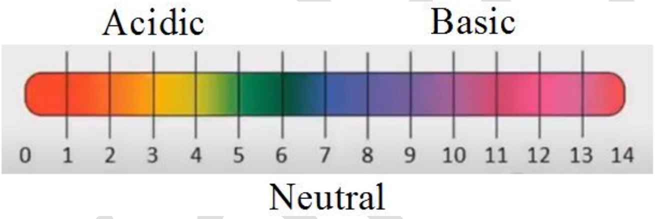
7. pH of Aqueous Solutions

The pH of an aqueous solution is a measure of its acidity or basicity, indicating the concentration of hydrogen ions (H+) present in the solution.

$$pH = -log_{10}[H_3O^+]$$

The pH scale ranges from 0 to 14, with:

- **pH < 7** : Acidic solutions ($[H_3O^+] > [OH^-]$).
- **pH = 7** : Neutral solutions ($[H_3O^+] = [OH^-]$).
- **pH > 7** : Basic (or alkaline) solutions ($[H_3O^+] < [OH^-]$).



7.1. Case of a strong acid

If the acid AH is strong, it means it dissociates completely in water, and the equilibrium is fully shifted toward the products.

The reaction can be written as:

	AH	+	H_2O	→	A^-	+	H_3O^+
T=0	C		ex		0		0
T=eq	0		ex		C		C

If [AH] =C → $[AH] = [H_3O^+] = C$

By definition → **$pH = -log_{10} [H_3O^+]$**

$$\rightarrow pH = -log_{10}C$$

Example

Calculate the pH of a 0.1 M solution of HCl.

$HCl_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$

0.1 M 0.1 M

$[H_3O^+]$ = C = The original concentration of the strong acid [HCl] = 0.1 M

$pH = -\log [H_3O^+] = -\log (0.1) = 1$

7.2. Case of a strong base

	B	+	H_2O	→	BH^+	+	OH^-
T=0	C		ex		0		0
T=eq	0		ex		C		C

Since B is a strong base, it dissociates completely in water:

if $[B] = C \rightarrow [B] = [OH^-] = C$

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

And since: $pH + pOH = 14 \rightarrow pH = 14 - pOH$

We have:

$$\rightarrow \boldsymbol{pH = 14 + log_{10}[H_3O^+]}$$

Example

Let's take a solution of NaOH, a strong base, with a concentration of (C = 0.01 mol/L).

Since NaOH is a strong base, it dissociates completely in water:

So: $[NaOH] = [OH^-] = C = 0.01$ mol/L

$pH = 14 + \log_{10} [H_3O^+]$

$pH = 14 + \log_{10} (0.01) = 12$

7.3. Case of a weak acid

A weak acid AH with concentration C in water, partially dissociates according to the following reaction:

$$AH + H_2O \rightleftharpoons A^- + H_3O^+$$

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

1. according to the law of conservation of mass

$C = [AH] + [A^-]$ and $[AH] >> [A^-]$, $[AH] + [A^-] \approx [AH] \rightarrow C = [AH]$

2. according to the electroneutrality law

$\sum$positive charges = $\sum$negative charges $\rightarrow [H_3O^+] = [A^-] + [OH^-]$

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The medium is acidic $[H_3O^+] >> [OH^-] \rightarrow [H_3O^+] >> [A^-] \rightarrow K_a = \frac{[A^-][H_3O^+]}{[AH]}$

$\rightarrow K_a.C = [H_3O^+]^2 \rightarrow [H_3O^+] = (K_a.C)^{1/2} \rightarrow -\log_{10} [H_3O^+] = -\log_{10} (K_a.C)^{1/2}$

$= ½ (-\log_{10} K_a - \log C) = ½ (pK_a - \log C)$

$$\rightarrow \boldsymbol{pH = \frac{1}{2} (pK_a - log_{10} C)}$$

Example

Calculate the pOH and pH of the following strong base solutions:

a) 0.05 M NaOH,

b) 0.05 M $La(OH)_3$.

Solution

a) $NaOH \rightarrow Na^+ + OH^-$

0.05 M 0.05 M

$pOH = - \log [OH^-] = - \log (5 \times 10^{-2}) = 1.3$

As $pH + pOH = 14 \rightarrow pH = 14 – 1.3 = 12.7$

b) $La(OH)_3 \rightarrow La^{3+} + 3OH^-$ (1:3)

$pOH = 0.82 \rightarrow pH = 13.18$

7.4. Case of a weak base

A weak base B with concentration C, in water, partially dissociates according to the following reaction:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

The base dissociation constant K_b is given by :

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

1. according to the law of conservation of mass

$C = [B] + [BH^+]$ and $[B] >> [BH^+]$, $[B] + [BH^+] \approx [B] \rightarrow C = [B]$

2. according to the electroneutrality law

$\sum$positive charges = $\sum$negative charges $\rightarrow [OH^-] = [BH^+] + [H_3O^+]$

The medium is basic $[OH^-] >> [H_3O^+] \rightarrow [H_3O^+] = [BH^+] \rightarrow K_b = \frac{[BH^+][OH^-]}{[B]}$

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→ $K_b. C = [OH^-]^2 \rightarrow [OH^-] = (K_b. C)^{1/2} \rightarrow -\log_{10} [OH^-] = -\log_{10} (K_b. C)^{1/2}$

$= \frac{1}{2} (-\log_{10} K_b -\log_{10} C) = \frac{1}{2} (pK_b - \log_{10} C)$

$$\rightarrow \boldsymbol{pOH = \frac{1}{2}\,(pK_b - log_{10}C)}$$

In an aqueous solution at 25°C, we have:

$pH + pOH = 14$ **and** $pK_a + pK_b = 14$

From the equation:

$14 - pH = 1/2(14 - pK_a - \log_{10}C) = 7 - 1/2(pK_a + \log_{10}C) \rightarrow pH = 14 - 7 + 1/2(pK_a + \log_{10}C)$

We find:

$$\rightarrow \boldsymbol{pH = 7 + \frac{1}{2}\,(pK_a + log_{10}C)}$$

8. pH of mixed solutions

8.1. Case of a mixture of two strong acids (AH_1 and AH_2)

When two strong acids are mixed, each one dissociates completely in water according to the reaction:

$$AH_{\,1} + H_2O \rightarrow H_3O^+ + A_1^-$$

$$AH_{\,2} + H_2O \rightarrow H_3O^+ + A_2^-$$

As both acids release hydronium ions (H_3O^+)) into the solution, the total concentration of $[H_3O^+]$ in the final mixture is the sum of the contributions from both acids.

If: C_{H1}: molar concentration of the first strong acid

C_{H2}: molar concentration of the second strong acid

Because both acids are completely dissociated

$$[H_3O^+] = C_{AH1} + C_{AH2}$$

By definition:

$$\rightarrow \boldsymbol{pH = -log_{10}[H_3O^+] = -log_{10}(C_{AH1} + C_{AH2})}$$

Example

If we mix two strong acids: HCl at 0.01 M and HNO_3 at 0.02 M, the pH of the final solution

$[H_3O^+] = C_{AH1} + C_{AH2} = 0.01 + 0.02 = 0.03$

So: $pH = -log_{10}[H_3O^+] = -log_{10}(0.03) \approx 1.52$

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8.2. Case of a mixture of a strong acid (AH_1) and a weak acid (AH_2).

Strong acid (AH_1) : completely dissociates

$$AH_1 + H_2O \rightarrow H_3O^+ + A_1^-$$

Weak acid (AH_2):partially dissociates

$$AH_2 + H_2O \leftrightarrow H_3O^+ + A_2^-$$

With equilibrium constant:

$$K_a = \frac{[H_3O^+][A_2^-]}{[AH_2]}$$

Because the strong acid (AH_1) dissociates completely, it produce a large concentration of H_3O^+, this shifts the equilibrium of the weak acid to the left (Le Châtelier's principle), suppressing its dissociation even more.

As a result, the contribution of (AH_2) to ($[H_3O^+]$) is negligible compared to that of (AH_1). So the total hydronium concentration

$$[H_3O^+] = [H_3O^+]\,(from\ AH_1) + [H_3O^+]\,(from\ AH_2)$$

Since: $[H_3O^+]\,(from\ AH_2)$ is very small

So: $[H_3O^+] = [H_3O^+]\,(from\ AH_1) = C_{AH_1}$

By definition:

$$\rightarrow \boldsymbol{pH = -log_{10}[H_3O^+] = -log_{10}(C_{AH1})}$$

8.3. Case of a mixture of two weak acids (AH_1) and (AH_2).

Weak acid (AH_1) : partially dissociates

$$AH_1 + H_2O \leftrightarrow H_3O^+ + A_1^-$$

Weak acid (AH_2): partially dissociates

$$AH_2 + H_2O \leftrightarrow H_3O^+ + A_2^-$$

Their acid dissociation constant are:

$$K_{a,AH_1} = \frac{[H_3O^+][A_1^-]}{[AH_1]}$$

$$K_{a,AH_2} = \frac{[H_3O^+][A_2^-]}{[AH_2]}$$

Since both acids are weak

$$x = [H_3O^+]$$

Since both acids are weak ($x \ll [H_3O^+]$), we can approximate:

$$[AH_1] \approx C_{AH1}\,, [AH_2] \approx C_{AH2}$$

From the equilibrium constants

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$$K_{a,AH_1} = \frac{[H_3O^+][A_1^-]}{[AH_1]} \rightarrow [A_1^-] = \frac{K_{a,AH_1} \times C_{AH_1}}{x}$$

$$K_{a,AH_2} = \frac{[H_3O^+][A_1^-]}{[AH_2]} \rightarrow [A_2^-] = \frac{K_{a,AH_2} \times C_{AH_2}}{x}$$

$$x = \frac{K_{a,AH_1} \times C_{AH_1}}{x} + \frac{K_{a,AH_2} \times C_{AH_2}}{x}$$

$$x^2 = K_{a,AH_1} \times C_{AH_1} + K_{a,AH_2} \times C_{AH_2}$$

$$[H_3O^+] = \sqrt{K_{a,AH_1} \times C_{AH_1} + K_{a,AH_2} \times C_{AH_2}}$$

By definition

$$pH = -log_{10}[H_3O^+]$$

$$\rightarrow \boldsymbol{pH = -\frac{1}{2}\, log(K_{a(AH1)}.C_{AH1} + K_{a(AH2)}.C_{AH2})}$$

8.4. Case of a mixture of two strong bases

Each strong base dissociates completely in water

$$B_1 + H_2O \rightarrow BH_1^+ + OH^-$$

$$B_2 + H_2O \rightarrow BH_2^+ + OH^-$$

Since both bases are strong, they fully dissociate, releasing hydroxide (OH^-) ions into the solution.

Let: C_{B1}: molar concentration of the first strong base

C_{B2}: molar concentration of the second strong base

Because dissociation is complete:

$[OH^-]_{B1} = C_{B1}$, $[OH^-]_{B2} = C_{B2} \rightarrow [OH^-]_{TOT} = C_{B1} + C_{B2}$

$pOH = -log_{10}[OH^-]$

$pOH = -log_{10}(C_{B1} + C_{B2})$

At 25°C, the relation is

$pH + pOH = 14$

Therefore:

$pH = 14 - pOH$

Substitute $pOH = -log_{10}(C_{B1} + C_{B2})$

$pH = 14 - (-log_{10}(C_{B1} + C_{B2}))$

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$$\rightarrow \boldsymbol{pH = 14 + \log(C_{B1} + C_{B2})}$$

8.5. Case of a mixture of strong base on the weak base

Since B_1 is a strong base, it dissociates completely in water:

$$B_1 + H_2O \rightarrow BH_1^+ + OH^-$$

Thus: $[OH^-]_{B1} = C_{B1}$

Since B_2 is a weak base, it dissociates partially according to

$$B_2 + H_2O \rightleftharpoons BH_2^+ + OH^-$$

With:

$$K_b = \frac{[BH_2^+] \times [OH^-]}{[B_2]}$$

Since the strong base completely dissociates, it produces a large concentration of hydroxide ions (OH^-), this increases the $[OH^-]$ in the solution and therefore suppresses the dissociation of the weak base (Châtelier's principle).

Hence, the contribution of the weak base B_2 to OH^- is negligible compared to that of the strong base B_1.

Total hydroxide concentration

$$[OH^-]_{TOT} = [OH^-]_{B1} + [OH^-]_{B2} \approx [OH^-]_{B1}$$

Thus : $[OH^-] = C_{B1}$

$$pOH = -\log_{10}[OH^-] = -\log_{10}(C_{B1})$$

And using the relation

$pH + pOH = 14$

We obtain:

$pH = 14 - pOH = 14 - (-\log_{10}(C_{B1}))$

$$\rightarrow \boldsymbol{pH = 14 + \log(C_{B_1})}$$

8.5. Case of a mixture of two weak bases (B_1) and (B_2)

For a single weak base B:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

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

At typical dilute conditions $[B] \approx C_B$ and $[OH^-] \ll C_B$ giving $[OH^-] \approx \sqrt{K_b . C_B}$

For the two weak bases in the same solution, their hydroxide contributions add:

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$$[OH^-] \approx \sqrt{K_{b1}.C_{B1} + K_{b2}.C_{B2}}$$

$$K_{b1}.K_{B2} = K_W$$

We have at 25°C:

$pOH = -log_{10}[OH^-]$ and $pH + pOH = 14$

So: $pH = 14 - \left(-\frac{1}{2}log_{10}(K_{b1}.C_{B1} + K_{b2}.C_{B2})\right) = 14 + \frac{1}{2}log_{10}(K_{b1}.C_{B1} + K_{b2}.C_{B2})$

Because $K_{b1}.K_{B2} = K_W$ and $K_W = 10^{-14}$ $at\ 25°C\ we\ have\ K_b = \frac{K_w}{K_a}$

Substitute: $K_{b1}.C_{B1} + K_{b2}.C_{B2} = K_w\left(\frac{C_{B1}}{K_{a,B1}} + \frac{C_{B2}}{K_{a,B2}}\right)$

Then: $pH = 14 + \frac{1}{2}log\ K_w + \frac{1}{2}log\left(\frac{C_{B1}}{K_{a,B1}} + \frac{C_{B2}}{K_{a,B2}}\right)$

Since: $\log K_w = log\ 10^{-14} = -14$

$$\rightarrow \boldsymbol{pH = 7 + \frac{1}{2}\ log(\frac{C_{B_1}}{K_{a,B_1}} + \frac{C_{B_2}}{K_{a,B_2}})}$$

8.5. Case of an amphoteric solution

An amphoteric (amphiprotic) substance can act both as an acid or a base; it can donate or accept a proton; leading to two equilibria:

$$AH_2^+ \rightleftharpoons AH + H^+ \qquad (K_{a1})$$

$$AH \rightleftharpoons A^- + H^+ \qquad (K_{a2})$$

At equilibrium, for the amphoteric species AH, we have two acid dissociation constante:

$$K_{a1} = \frac{[H^+][AH]}{[AH_2^+]}$$

$$K_{a2} = \frac{[H^+][A^-]}{[AH]}$$

At the isoelectric point (where the species mainly exists as AH), the concentration of $[AH_2^+]$ and $[A^-]$ are approximately equal: $[AH_2^+] = [A^-]$

So by multiplying both equations:

$K_{a1}.K_{a1} = \frac{[H^+][AH]}{[AH_2^+]}.\frac{[H^+][A^-]}{[AH]} = [H^+]^2\frac{[A^-]}{[AH_2^+]}$

But since $[AH_2^+] = [A^-]$

So $K_{a1}.K_{a2} = [H^+]^2$

$$[H]^+ = \sqrt{K_{a1}.K_{a2}}$$

$$pH = -log_{10}[H^+] = -\frac{1}{2}\ log(K_{a1}.K_{a2})$$

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$$\rightarrow pH = \frac{1}{2}\, log(pK_{a_1} + pK_{a_2})$$

8.6. Case of salts solution

When a salt dissolves in water, it dissociates into its ions.

Depending on whether those ions come from strong or weak acids/bases, they may or may not react (hydrolyze) with water, which affects the pH.

a. Salt of a strong acid and a strong base

Example

NaCl (from NaOH and HCl):

$$NaOH + HCl \rightarrow H_2O + NaCl$$

The resulting salt (NaCl) dissociates completely into (Na+) and (Cl-) ions, which are neutral and do not react with water.

$$NaCl \rightarrow Na^+ + Cl^-$$

Since there is no excess acid or base, and the ions from the salt do not affect water equilibrium:

[H3O+] = [OH-]

$$\rightarrow pH = 7$$

b. Salt of a strong acid and a weak base

Example

NH_4Cl (from NH_3 and HCl)

$$NH_3 + HCl \rightarrow NH_4Cl$$

In water, NH_4Cl dissociate completely

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

Since, the conjugate base of the strong acid is a base of zero strength, and the conjugate acid of the weak base is a weak acid, the pH of the solution is that of weak acid:

$$\rightarrow pH = \frac{1}{2}\,(pK_a - log C_{salts})$$

c. Salt of a weak acid and a strong base

Example

CH_3COONa (from CH_3COOH and NaOH)

$$CH_4COOH + NaOH \rightarrow CH_3COONa + H_2O$$

In aqueous solution, sodium acetate dissociates completely

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$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

Since, Na+ is the cation of a strong base it does not hydrolyse, while the CH3COO- the conjugate bese of the weak acid (CH3COO) undergoes hydrolysis, so the pH of the solution is:

$$\rightarrow \boldsymbol{pH = 7 + \frac{1}{2}\,(pK_a - \log C_{salts})}$$

d. Salt of a weak acid and a weak base

Example

NH_4CH_3COO (from NH_3 and CH_3COOH):

$$NH_3 + CH_3COOH \rightarrow NH_4CH_3COO$$

In water, ammonium acetate dissociates completely

$$NH_4CH_3COO \rightarrow NH_4^+ + CH_3COO^-$$

Both ions can hydrolyze in water, so, both hydrolysis reactions occur simultaneously, , so the pH of the solution is:

Both ions can hydrolyze in water; therefore, the two hydrolysis reactions occur simultaneously, and the pH of the solution depends on the relative strengths of the conjugate acid and the conjugate base.

$$\rightarrow \boldsymbol{pH = \frac{1}{2}\,(pK_a + pK_b)}$$

8.7. Case of buffer solution

A buffer solution is composed of a mixture of a weak acid AH and its conjugate base A^-. The equilibrium for this system can be represented as follows:

$AH + H_2O \leftrightharpoons H_3O^+ + A^-$

The acid dissociation constant K_a for the acid-base pair AH/A^- is defined by the equation

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

$$-\log\ K_a = -\log\left(\frac{[A^-][H_3O^+]}{[AH]}\right)$$

$$-\log\ K_a = -\log([H_3O^+]) - \log\left(\frac{[A^-]}{[AH]}\right)$$

$$-\log([H_3O^+]) = -\log\ K_a + \log\left(\frac{[A^-]}{[AH]}\right)$$

$$\rightarrow\ \boldsymbol{pH = pK_a + \log_{10}\left(\frac{[A^-]}{[AH]}\right) = pK_a + \log_{10}\left(\frac{[Base]}{[Acid]}\right)}$$

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The buffer zone $pK_a - 1 < pH < pK_a + 1$

9. Color indicators

A color indicator is typically a weak monoprotic acid with a specific pKa, where the form HA has a distinctly different color from its conjugate base form A^-.

Table 1. Some indicators and their color change range

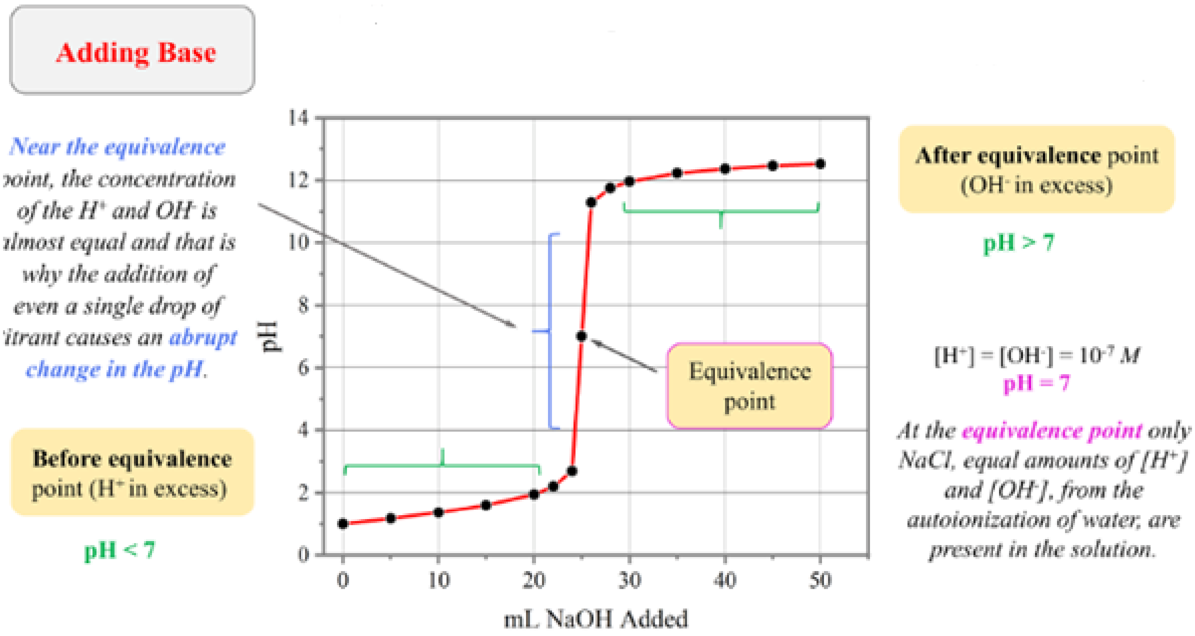
Indicator	Color change range	Color in acidic state	Color in basic state
Thymol Blue	1.2 - 2.8	Red	Yellow
Methyl Orange	3.1 - 4.4	Orange	Yellow
Phenol Red	6.6 - 8.0	Yellow	Red
Bromothymol Blue	6.0 - 7.6	Yellow	Blue
Phenolphthalein	8.3 - 10	Colorless	Pink

10. Acid-Base titrations

10.1. Titration of a strong acid by a strong base

Example

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



The strong acid and strong base dissociate completely in water.

$AH + BOH \rightarrow AB + H_2O$

The titration curve can be divided into three distinct parts:

Before the equivalence point

Before the equivalence point, Ca·Va is greater than Cb·Vb ($[H_3O^+] > [OH^-]$). The OH^- ions react with an equal number of H_3O^+ ions to form water, leaving in solution a remaining amount of H_3O^+ ions equal to Ca·Va−Cb·Vb.

$$[H_3O^+] = \frac{C_aV_a - C_bV_b}{V_a + V_b}$$

$$pH = -log_{10}\left(\frac{C_aV_a - C_bV_b}{V_a + V_b}\right)$$

At the equivalence point

This corresponds to calculating the pH of a strong acid solution that has been exactly neutralized by a strong base :

Ca·Va = Cb·Vb ($[H_3O^+] = [OH^-]$). At this point, pH=7 at 25°C.

After the equivalence point

After the equivalence point, Ca·Va is less than Cb·Vb ($[OH^-] > [H_3O^+]$). The OH− ions react with all the H3O+ ions to form water, leaving in solution an amount of OH− ions equal to Cb·Vb−Ca·Va.

$$[OH^-] = \frac{C_bV_b - C_aV_a}{V_a + V_b}$$

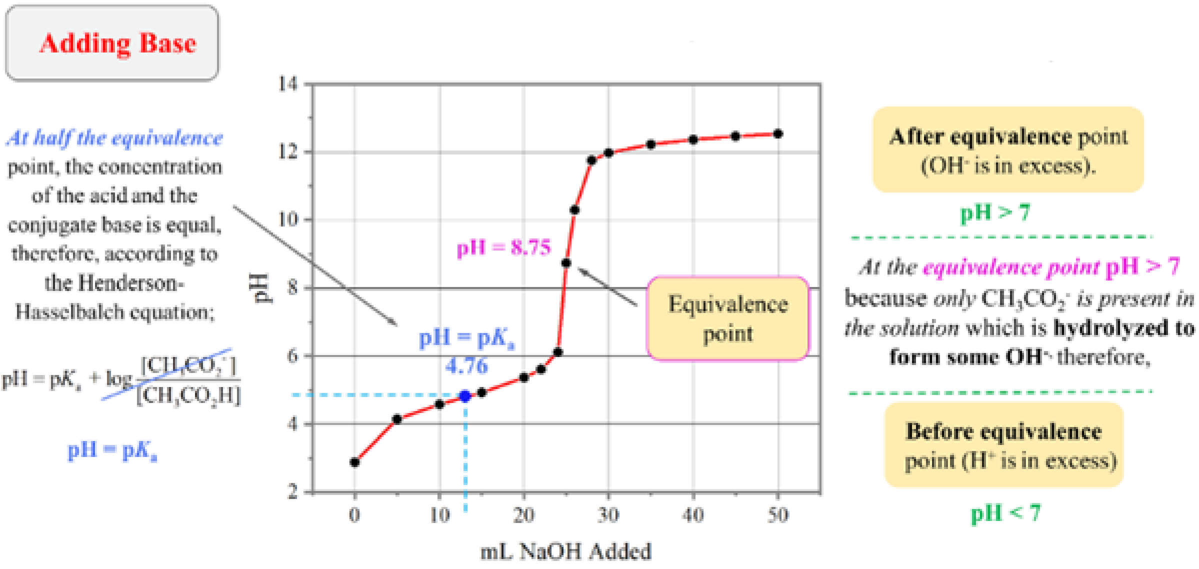
$$pOH = -log_{10}\left(\frac{C_aV_a - C_bV_b}{V_a + V_b}\right)$$

$$pH = 14 + log_{10}\left(\frac{C_aV_a - C_bV_b}{V_a + V_b}\right)$$

9.2. Titration of a weak acid by a strong base

Example

$$CH_3CO_2H(aq) + OH^-(aq) \rightarrow CH_3CO_2^-(aq) + H_2O\ (l)$$



At half the equivalence point, the concentration of the acid and the conjugate base is equal, therefore, according to the Henderson-Hasselbalch equation;

$$pH = pK_a + \log\cancel{\frac{[CH_3CO_2^-]}{[CH_3CO_2H]}}$$

$pH = pK_a$

At the *equivalence point* pH > 7 because *only* $CH_3CO_2^-$ *is present in the solution* which is **hydrolyzed to form some** OH^-, therefore,

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9.3. Titration of a strong acid with a weak base

Example

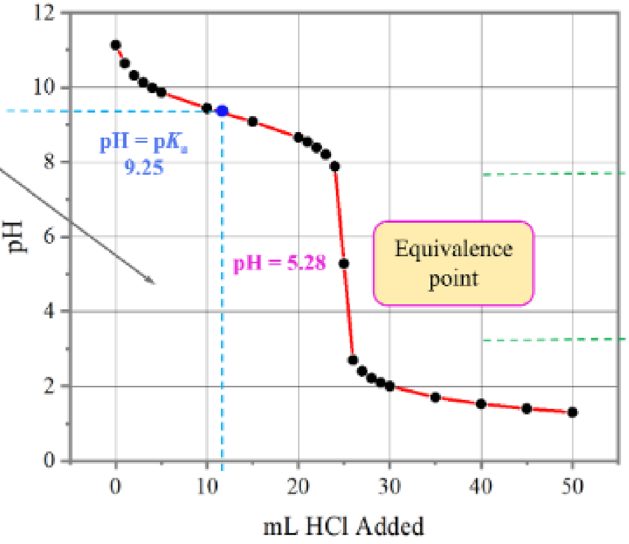
$$NH_3(aq) + HCl\,(aq) \rightarrow NH_4Cl\,(aq)$$

Adding Acid

At half the equivalence point, the concentration of the ammonia and its conjugate acid, NH_4^+ are equal, therefore, according to the Henderson-Hasselbalch equation;

$$pH = pK_a + \log \frac{\cancel{[NH_3]}}{\cancel{[NH_4^+]}}$$

$pH = pK_a(NH_4^+) = 9.25$



Before equivalence point (H^+ is in excess)

$pH > 7$

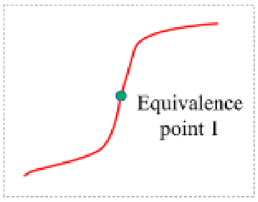
At the equivalence point $pH < 7$ because *only* NH_4^+ *is present in the solution* which is **hydrolyzed to form some H_3O^+.**

After equivalence point (OH^- is in excess).

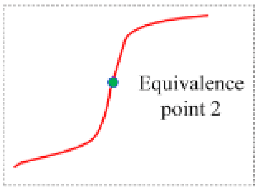
$pH < 7$

9.4. Titration of a polyacid with a strong base

Neutralization of each proton has a separate equivalence point.



$H_2SO_3(aq) + OH^-(l) \leftrightarrows HSO_3^-(aq) + H_2O\,(aq)$

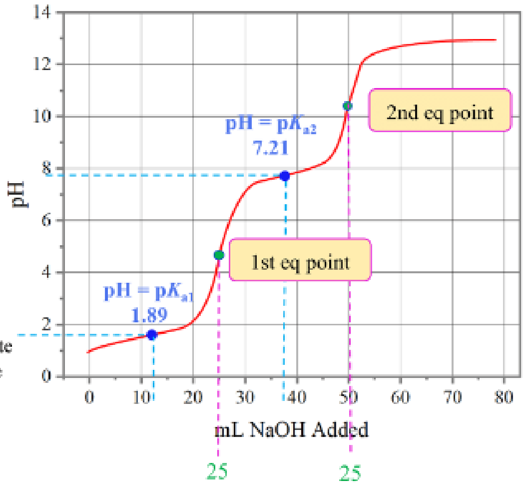


$HSO_3^-(aq) + OH^-(l) \leftrightarrows SO_3^{2-}(aq) + H_2O\,(aq)$

At half the equivalence point, the concentration of the acid and the conjugate base is equal, therefore, according to the Henderson-Hasselbalch equation;

$$pH = pK_{a1} + \log \frac{\cancel{[HSO_3^-]}}{\cancel{[H_2SO_3]}}$$

$pH = pK_a$



Both equivalence points require the same volume of titrant because HSO_3^- is produced from H_2SO_3.