ACIDS AND BASES

A. CHARACTERISTICS OF ACIDS AND BASES

1. Acids and bases are both **ionic** compounds that are dissolved in water. Since acids and bases both form ionic solutions, their **solutions conduct electricity (ELECTROLYTES).**

HCl(g) = hydrogen chloride
HCl(aq) = hydrochloric acid
$HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$

2. **Arrhenius** theory of acids and bases states:

ARRHENIUS THEORY

an **ACID** is any compound that produces hydrogen ions, **$H^+(aq)$** , in water

a **BASE** is any compound that produces hydroxide ions, **$OH^-(aq)$** , in water

e.g. $HCl(g) \rightarrow H^+(aq) + Cl^-(aq)$ **ACID**
$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$ **BASE**

To simplify things,

a) **ACIDS** are ionic compounds that **begin with "H".**

e.g. $HCl(aq)$, $H_2SO_4(aq)$, $HNO_3(aq)$

b) **BASES** are ionic compounds that **end in "OH".**

e.g. $NaOH$, $Ca(OH)_2$, $LiOH$

c) **SALTS** are all other ionic compounds, **other than acids and bases.**

e.g. KCl, Na_2SO_4, $Fe(NO_3)_3$

Note: **Organic acids** have formulas that end in **"COOH"**, do not confuse these compounds as bases.

3. When an acid and a base are mixed, a neutralization reaction occurs.

ACID + BASE → SALT + WATER

- A neutralization reaction is simply a special case of a **double–replacement reaction in which water is always one of the products.**

EXAMPLE 4.1 WRITING NEUTRALIZATION REACTIONS

Write the neutralization reaction between H_3PO_4 and $Ca(OH)_2$

First, write the formulas of the acid and base on the reactant side.

$$H_3PO_4 + Ca(OH)_2 \rightarrow _____$$

Next, determine the charges of the ions present in the mixture (use table in data booklet if unsure).

$$H^+,\ PO_4^{3-},\ Ca^{2+},\ OH^-$$

Predict the products by exchanging the two positive ions (remember water is always one of the products).

$$H_3PO_4 + Ca(OH)_2 \rightarrow Ca^{2+}\ PO_4^{3-} + H^+\ OH^-$$

Write correct formulas for the products by canceling the ionic charges.

$$H_3PO_4 + Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 + H_2O$$

Balance the equation.

$$2\ H_3PO_4 + 3\ Ca(OH)_2 \rightarrow 1\ Ca_3(PO_4)_2 + 6\ H_2O$$

4. All acids have certain properties in common as do all bases.

a) The presence of **H^+** accounts for the following properties of **ACIDS**:
- taste **SOUR**
- **conduct an electric current**
- turn litmus paper **RED**
- produce **hydrogen when reacted with certain metals such as magnesium**
- **neutralized by bases**

b) The presence of **OH^-** accounts for the following properties of **BASES**:
- taste **BITTER**
- **conduct an electric current**
- turn litmus paper **BLUE**
- feel slippery
- **neutralized by acids**

5. When an acid such as HCl is dissolved in water, it produces a **hydrogen ion or proton, $H^+(aq)$.**

- Protons do not exist on their own in water but rather readily attach themselves to water molecules to produce **hydronium ions** or **hyrdated protons, $H_3O^+(aq)$.**

H^+ is called a **PROTON**
H_3O^+ is called the **HYDRONIUM ION**

- To show that hydronium ions are actually produced when an acid ionizes, the ionization equation

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

can be re–written as

$$HCl(g) + \mathbf{H_2O(l)} \rightarrow \mathbf{H_3O^+(aq)} + Cl^-(aq)$$

- The second equation results from adding H_2O on both sides of the first equation, but on the product side, the added H_2O combines with H^+ to form H_3O^+.

B. BRØNSTED–LOWRY THEORY OF ACIDS AND BASES

1. The **Brønsted–Lowry theory was needed to explain the existence of EQUILIBRIUM** reactions between acids and bases that were not considered in the Arrhenius theory.

BRØNSTED–LOWRY THEORY

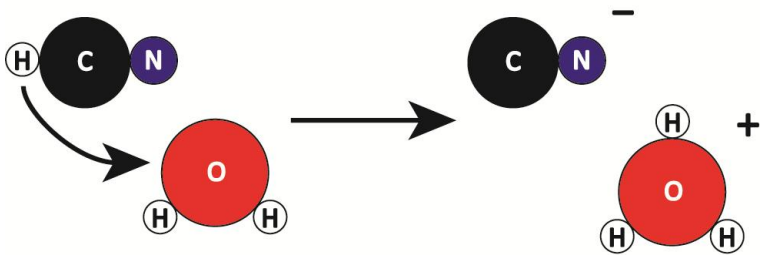
ACID is any substance that can **DONATE** a proton to another substance

BASE is any substance that can **ACCEPT** a proton from another substance

Simply stated, an acid is a proton donor and a base is a proton acceptor

2. Consider the following Brønsted–Lowry acid–base equation:

$$HCN(g) + H_2O(l) \rightleftarrows H_3O^+(aq) + CN^-(aq)$$



In the forward reaction:

- HCN acts as an **acid it loses an "H" and a "+1" charge to become CN^-.**
- H_2O acts as a **base it gains an "H" and a "+1" charge to become H_3O^+.**

In the reverse reaction:

- H_3O^+ is acting as the **acid** and CN^- is acting as the **base.**

$$\underset{\text{acid}}{HCN(g)} + \underset{\text{base}}{H_2O(l)} \rightleftarrows \underset{\text{acid}}{H_3O^+(aq)} + \underset{\text{base}}{CN^-(aq)}$$

Notice that in a Brønsted–Lowry equilibrium that there is an **acid and base in the forward reaction and in the reverse reaction.**

3. In the equation:

$$HCN(g) + H_2O(l) \rightleftarrows H_3O^+(aq) + CN^-(aq)$$

- **HCN and CN^-** only differ from each other by one proton, H^+.
- **H_2O and H_3O^+** also only differ from one another by one proton, H^+.
- Two substances that differ from each other by only **one** proton are referred to as **CONJUGATE ACID–BASE PAIRS.**
- In any Brønsted–Lowry equation there are two conjugate pairs.

$$\mathbf{HCN(g) + H_2O(l) \rightleftarrows H_3O^+(aq) + CN^-(aq)}$$

CONJUGATE ACID–BASE PAIRS = **pairs of chemical that differ by only ONE PROTON**

CONJUGATE ACID has an extra proton

CONJUGATE BASE lacks a proton

SAMPLE 4.1 CONJUGATE ACID–BASE PAIRS

1. What is the conjugate base of nitric acid, HNO_3 and HSO_4^-?
2. What is the formula for the conjugate acid of OH^- and PO_4^{3-}?
3. Identify the two Brønsted acids and two bases in the reaction:

$$HSO_4^- + PO_4^{3-} \rightleftarrows SO_4^{2-} + HPO_4^{2-}$$

4. Consider the following two Brønsted–Lowry equilibria:

$$HCN(g) + H_2O(l) \rightleftarrows H_3O^+(aq) + CN^-(aq)$$
$$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

- In the first equation, H_2O gains a proton to become H_3O^+ so it is acting as a **BASE**
- In the second equation, H_2O loses a proton to become OH^- hence it is acting as an **ACID.**

> **AMPHIPROTIC** = **substances that can act as either an acid or a base** depending on the kind of substances they react with.

5. Acids that can only donate one proton are called monoprotic acids while acids that can donate more than one proton are polyprotic.

MONOPROTIC acid $\rightarrow$ **ONE** proton

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

DIPROTIC acid $\rightarrow$ **TWO** protons

$$H_2SO_4 \rightarrow H^+ + HSO_4^- \rightarrow H^+ + SO_4^{2-}$$

TRIPROTIC acid $\rightarrow$ **THREE** protons

$$H_3PO_4 \rightarrow H^+ + H_2PO_4^- \rightarrow H^+ + HPO_4^{2-} \rightarrow H^+ + PO_4^{3-}$$

- Notice that the chemical species HSO_4^-, $H_2PO_4^-$, HPO_4^{2-} are also amphiprotic.

> **RECOGNIZING AMPHIPROTIC SUBSTANCES**
>
> If a substance:
> a) possesses a **NEGATIVE CHARGE** and
> b) still has an easily removable **HYDROGEN***
>
> then the substance will be **AMPHIPROTIC**
>
> *Apart from hydrogens attached to carbon, assume that all hydrogens on a negatively charged ion are "easily removable".

C. STRENGTHS OF ACIDS AND BASES

1. The relative strength of an acid or a base depends on **how well it ionizes in water to produce ions.**

- **STRONG** acids and bases ionize completely**, 100% IONIZED**

e.g. $HCl(g) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$
$NaOH(s) \rightarrow Na^+(aq) + OH^-(aq)$

- **WEAK** acids and bases do not ionize completely, **LESS THAN 100% IONIZED.**
- **Weak acids are better represented by an equilibrium system** where the conjugate acid and base pairs both exist.

e.g. $HF(aq) + H_2O(l) \rightleftarrows F^-(aq) + H_3O^+(aq)$
$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$

> The terms strong or weak refer to the degree of ionization of the acid or base **NOT** molar concentration.
>
> 0.0010 M **HCl** is a **STRONG** acid
> 6.0 M **HF** is a **WEAK** acid

2. Refer to the Data Booklet, **"Relative Strengths of Acids and Bases"** table.

a) **STRONG ACIDS**

- The strong acids are the **top six acids** on the left side of the table:

HBr , HCl , HI , HNO_3 , $HClO_4$, H_2SO_4

- All six reaction have **ONE–WAY reaction** arrows, pointing to the right. This means that aqueous molecules of the acid do not exist and the **conjugate bases cannot accept a proton from water.**

$HCl(aq) + H_2O(l) \rightarrow H_3O^+(aq) + Cl^-(aq)$

b) **STRONG BASES**

- The strong bases are the **bottom two bases** listed on the right side of the table:

O^{2-} and NH_2^-

- Once again, these two reactions have **ONE–WAY reaction** arrows, pointing to the left. This means that aqueous molecules of the base do not exist and the **conjugate acids cannot donate a proton to water.**

$$NH_3(aq) + OH^-(aq) \leftarrow NH_2^-(aq) + H_2O(l)$$

$$NH_2^-(aq) + H_2O(l) \rightarrow NH_3(aq) + OH^-(aq)$$

- In addition to these two strong bases, **soluble metal hydroxides are also strong bases.**
  e.g. NaOH, KOH, $Mg(OH)_2$, $Ca(OH)_2$, $Fe(OH)_3$, $Zn(OH)_2$

c) **WEAK ACIDS**

- The weak acids are the species on the **left side of the table** from **HIO_3** down to **H_2O.**
- Aqueous molecules of the conjugate acid and base coexist in solution.

$$\mathbf{HIO_3} \rightleftarrows H^+ + IO_3^-$$
$$\downarrow$$
$$\mathbf{H_2O} \rightleftarrows H^+ + OH^-$$

- The last two species on the left, **O^{2-} and NH_2^-**, cannot act as acids in aqueous solutions.

d) **WEAK BASES**

- The weak bases are the species on the **right side of the table** from **H_2O** down to **PO_4^{3-}**.
- Aqueous molecules of the conjugate base and acid coexist in solution.

$$H_3O^+ \rightleftarrows H^+ + \mathbf{H_2O}$$
$$\downarrow$$
$$HPO_4^{2-} \rightleftarrows H^+ + \mathbf{PO_4^{3-}}$$

- The top six species on the right, **HSO_4^-, NO_3^-, Cl^-, Br^-, I^-, ClO_4^-**, cannot act as bases in aqueous solutions.

LEVELLING EFFECT = All strong acids have **IDENTICAL STRENGTHS** in water because they are **all 100% ionized in aqueous solutions.**

Note: Although all of the reactions are written as ionization equations, they are all occurring in aqueous solutions. When a substance acts as an acid, water accepts the proton to become H_3O^+, so all acid solutions will produce H_3O^+. Likewise, when a substance acts as a base, water donates the proton to become OH^-, so all base solutions will produce OH^-.

Note: Since strong acid and bases ionize completely, they will have a higher electrical conductivity than weak acids and bases. This property can be used to distinguish between strong and weak acids and bases.

Note: The six strong acids, $HClO_4$, HI, HBr, HCl, HNO_3, and H_2SO_4, cannot exist as molecules in aqueous solutions because they ionize completely to produce H_3O^+ and an anion. Hence H_3O^+ is the strongest acid that can exist in aqueous solution.

In the same way, O^{2-} and NH_2^-, cannot exist in aqueous solution because they produce OH^-. Hence, OH^- is the strongest base that can exist in aqueous solution.

D. EQUILIBRIUM CONSTANT FOR THE IONIZATION OF WATER

1. A solution can be classified as acidic, basic, or neutral based on the relative concentrations of H_3O^+ and OH^-.

ACIDIC	**$[H_3O^+] > [OH^-]$**
NEUTRAL	**$[H_3O^+] = [OH^-]$**
BASIC	**$[H_3O^+] < [OH^-]$**

2. Even in the absence of acids or bases, **pure water contains a very small amounts of H_3O^+ and OH^- as a result of collisions between water molecules.**

- The **SELF–IONIZATION** of water can be represented as:

$$\text{energy} + H_2O + H_2O \rightleftarrows H_3O^+ + OH^-$$

An equilibrium constant for this reaction can be written as:

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

- Since water is a pure liquid, the $[H_2O]$ is constant at a particular temperature, we can incorporate it into the constant, $K_{eq} \times [H_2O]^2$, and define a new constant called the **EQUILIBRIUM CONSTANT OF WATER, K_w.**

$$\mathbf{K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14} \quad (at\ 25\ °C)}$$

- The **value of K_w only varies with temperature.**
- When K_w or the temperature is not stated, it can be assumed that $K_w = 1.00 \times 10^{-14}$.

EXAMPLE 4.2 USING K_W TO DETERMINE $[OH^-]$

What is the $[OH^-]$ in 0.025 M HCl?

Assume that the temperature is 25 °C, so $K_w = 1.00 \times 10^{-14}$

$$K_w = [H_3O^+][OH^-]$$

HCl is a strong acid, so $[H_3O^+] = [HCl] = 0.025\ M$

$$1.00 \times 10^{-14} = (0.025)\,[OH^-]$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{0.025\ M}$$

$$[OH^-] = \mathbf{4.0 \times 10^{-13}\ M}$$

E. PH AND POH

1. When working with dilute solutions of strong acids or weak acids and likewise with bases, the $[H_3O^+]$ or $[OH^-]$ is very small, often around 10^{-6} or smaller. With such small quantities, it is difficult to compare concentrations; hence the **pH and pOH scales** were developed.

   - The **pH** of a solution is the **negative logarithm of the molar concentration of hydronium ion** and **pOH** is the negative logarithm of the molar concentration of hydroxide ion.

$$\mathbf{pH = -\log[H_3O^+]}$$

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

Note: The logarithm of a number is the exponent to which 10 must be raised to represent a certain number.

For example: What is the logarithm of 1000?

1000 can be represented as 10^3, so the log of (1000) = 3

The reverse procedure of log is called antilog.

Antilog is the equivalent of raising 10to the power of a certain exponent.

$$\text{antilog}(x) = 10^x$$

For example: What is the antilog of 2?

$$\text{antilog}(2) = 10^2 = 100$$

EXAMPLE 4.3 CONVERTING FROM $[H_3O^+]$ AND $[OH^-]$ TO PH AND POH

a) If the $[H_3O^+] = 4.67 \times 10^{-5}$ M, what is the pH?

b) If the $[OH^-] = 2.83 \times 10^{-6}$ M, what is the pOH?

a) $pH = -\log [H_3O^+] = -\log (4.67 \times 10^{-5}) = -(-4.331) =$ ***4.331****

b) $pOH = -\log [OH^-] = -\log (2.83 \times 10^{-6}) = -(-5.548) =$ ***5.548***

**Note: In pH and pOH, only the numbers after the decimal are significant.*

2. Consider the following:

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

- If we want to rearrange this equation to solve for $[H_3O^+]$ first remove the negative sign by multiplying both sides of the equation by negative 1 to give:

$$\mathbf{-pH} = \log [H_3O^+]$$

- Since the reverse of taking the log of a number is taking the antilog, the $[H_3O^+]$ can be determined by taking the antilog of both sides of the equation:

$$\textbf{antilog}\ (-pH) = \textbf{antilog}\ (\log [H_3O^+]) = [H_3O^+]$$

$$\text{antilog}\ (-pH) = [H_3O^+]$$

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

- Similarly, $[OH^-]$ can be determined from the pOH.

$$\mathbf{[H_3O^+]} = \textbf{antilog}\ (-pH) = 10^{-\mathbf{pH}}$$

$$\mathbf{[OH^-]} = \textbf{antilog}\ (-pOH) = 10^{-\mathbf{pOH}}$$

EXAMPLE 4.4 CONVERTING FROM PH AND POH TO $[H_3O^+]$ AND $[OH^-]$

a) If the pH is 3.17, what is the $[H_3O^+]$?

b) If the pOH = 5.32, what is the $[OH^-]$?

a) $[H_3O^+]$ = antilog (– pH) = antilog (–3.17) = $10^{-3.17}$ = ***6.8×10^{-4} M***

b) $[OH^-]$ = antilog (– pOH) = antilog (–5.32) = $10^{-5.32}$ = ***4.8×10^{-6} M***

3. There is a very simple but important relationship between pH, pOH, and K_w.

- Starting with the K_w expression:

$$[H_3O^+][OH^-] = K_w$$

- Taking the logarithm of both sides of the equation:

$$\log ([H_3O^+][OH^-]) = \log K_w$$

$$\log [H_3O^+] + \log [OH^-] = \log K_w$$

- Multiply by negative one

$$(– \log [H_3O^+]) + (– \log [OH^-]) = (– \log K_w)$$

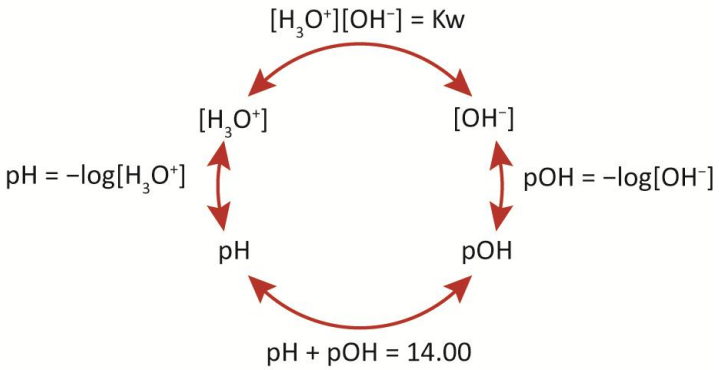
$$pH + pOH = pK_w$$

- At 25 °C $K_w = 1.0 \times 10^{-14}$

$$pH + pOH = – \log (1.0 \times 10^{-14}) = 14.00$$

pH + pOH = 14.00

4. Using the following relationships, you can work back and forth from the any of $[H_3O^+]$, $[OH^-]$, pH, and pOH.



5. Since the pH and pOH scales are **logarithmic scales**, a difference in one pH or pOH unit is equivalent to a ten–fold (10 ×) difference in concentration.

- pH and pOH are the negative of the exponent, **low pH and pOH values** mean relatively **high values of $[H_3O^+]$ and $[OH^-]$**, and high values of pH and pOH mean relatively low $[H_3O^+]$ and $[OH^-]$.

- At 25 °C

pH < 7.00	acidic solution
pH > 7.00	basic solution
pH = 7.00	neutral solution

- **Negative pH values** are possible for **concentrated** strong acids

2.00 M HCl has a $[H_3O^+]$ = 2.00 mol/L

pH = – log (2.00) = – 0.30

F. MIXING STRONG ACIDS AND BASES

1. When a strong acid and base are mixed, a neutralization reaction occurs and the resulting solution may be **acidic basic or neutral depending on the relative amounts of acids and base that were reacted.**

EXAMPLE 4.5 CALCULATING PH WHEN STRONG ACIDS AND BASES ARE MIXED

What is the pH that results when 25.0 mL of 0.250 M HCl is mixed with 35.0 mL of 0.200 M NaOH?

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

$$\text{moles HCl} = (0.0250\ L)(0.250\ mol/L) = 0.00625\ mol\ HCl$$

$$\text{moles NaOH} = (0.0350\ L)(0.200\ mol/L) = 0.00700\ mol\ NaOH$$

$$\text{moles NaOH remaining} = 0.00700 - 0.00625 = 0.00075\ mol\ NaOH$$

$$[NaOH] = [OH^-] = \frac{0.00075\ mol}{(0.025\ L) + (0.035\ L)} = 0.013\ M$$

$$pOH = -\log [OH^-] = -\log (0.013) = 1.89$$

$$pH = 14.00 - pOH = 14.00 - 1.89 = \mathbf{12.11}$$

Alternatively, we can work with concentrations:

$$[HCl] = \frac{(0.250\ M)(25.0\ mL)}{60.0\ mL} = 0.104\ M$$

$$[NaOH] = \frac{(0.200\ M)(35.0\ mL)}{60.0\ mL} = 0.117\ M$$

$$[NaOH]\ \text{remaining} = 0.117\ M - 0.104\ M = 0.013\ M$$

$$pOH = -\log [OH^-] = -\log (0.013) = 1.89$$

$$pH = 14.00 - pOH = 14.00 - 1.89 = \mathbf{12.11}$$

EXAMPLE 4.6 CALCULATING MOLES OF ACID NEEDED TO REACH DESIRED PH

How many moles of HCl(g) must be added to 40.0 mL of 0.180 M NaOH to produce a solution that has a pH = 12.500? Assume that there is no change in volume when the HCl is added.

Need to convert pH to $[OH^-]$ since this is a basic solution:

$$pOH = 14.000 - pH = 14.000 - 12.500 = 1.500$$

$$[OH^-]_{after\ mixing} = \text{antilog}\ (-pOH) = \text{antilog}\ (-1.500) = 0.03162\ M$$

$$\Delta[OH^-] = 0.180\ M - 0.03162\ M = 0.148\ M$$

$$\text{moles } OH^- = \text{moles HCl added} = (0.148\ \text{mol/L})\ (0.0400\ L) = \mathbf{0.00594\ moles}$$

G. ACID AND BASE EQUILIBRIUM CONSTANTS

1. Weak acids and weak bases can be represented as **equilibrium** systems because they do not completely ionize.

   - The **ACID IONIZATION** reaction of a **WEAK** acid such as CH_3COOH with water is shown by:

   $$CH_3COOH(aq) + H_2O(l) \rightleftarrows CH_3COO^-(aq) + H_3O^+(aq)$$

   - An equilibrium expression can be written for the ionization as:

   $$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = 1.76 \times 10^{-5}$$

   - The **value** of K_a is called the **ACID IONIZATION CONSTANT.**
   - The **greater the value of K_a , the stronger the acid.**
   - Large K_a value indicates that the equilibrium favours the products, hence these acids are stronger because they have greater ionization.
   - The **K_a values for a STRONG acids are not listed** in the table of **Strengths of Acids** since these acids are 100% ionized and the concentration of the unionized acid in the denominator of the K_a expression is zero.

2. The **BASE IONIZATION** reaction of a **WEAK** base such as NH_3 with water is shown by:

   $$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$$

   - The equilibrium expression for the ionization is:

   $$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.79 \times 10^{-5}$$

   - The **value** of K_b is called the **BASE IONIZATION CONSTANT.**
   - The **greater the K_b value for a base, the stronger the base.**
   - **K_b values must be calculated** using the K_a values of the **conjugate acids.**

3. There is an important relationship that exists between K_a and K_b for conjugate acid–base pairs. Consider the following:

- The acid NH_4^+, has the **ACID IONIZATION** equation:

$$NH_4^+ + H_2O \rightleftarrows NH_3 + H_3O^+$$

- The acid ionization expression:

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

- The conjugate base NH_3, has the **BASE IONIZATION** equation:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$$

and the base ionization expression:

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

- When K_a and K_b are multiplied together we get

$$K_a \times K_b = \frac{[NH_3][H_3O^+]}{[NH_4^+]} \times \frac{[NH_4^+][OH^-]}{[NH_3]} = [H_3O^+][OH^-]$$

and since $[H_3O^+][OH^-] = K_w$

$K_a \times K_b = K_w$ (at 25 °C, $K_w = 1.00 \times 10^{-14}$)

EXAMPLE 4.7 CALCULATING K_B FROM K_A

Calculate the K_b for $C_2O_4^{2-}$.

*To calculate K_b we need the value of K_a for the conjugate acid of $C_2O_4^{2-}$. Since $C_2O_4^{2-}$ is a base we look up $C_2O_4^{2-}$ on the **right** side of the table and use the K_a corresponding to its conjugate acid $HC_2O_4^-$.*

$$K_b = \frac{K_w}{K_a} = \frac{(1.0 \times 10^{-14})}{(6.4 \times 10^{-5})} = \mathbf{1.6 \times 10^{-10}}$$

There is a reciprocal nature between K_a and K_b

$$K_a \propto \frac{1}{K_b}$$

So the **conjugate base of a weak acid is a strong base**

and the **conjugate base of a strong acid is a weak base**

H. THE RELATIVE STRENGTHS OF ACIDS AND BASES

1. If solutions containing H_2CO_3 and SO_3^{2-} are mixed, the SO_3^{2-} acts as a base since it has no protons to donate.

$$H_2CO_3 + SO_3^{2-} \rightleftarrows HCO_3^- + HSO_3^-$$

> All Brønsted–Lowry reactions studied in Chemistry 12 will only involve the **transfer of a single proton**. There will **NOT** be two–proton transfers such as
>
> $$H_2CO_3 + SO_3^{2-} \rightleftarrows CO_3^{2-} + H_2SO_3$$

- If solutions containing **amphiprotic ions** such as HCO_3^- and $H_2PO_4^-$ are mixed, the **stronger of the two acids will donate a proton** to the other ion.
- HCO_3^- ($K_a = 5.6 \times 10^{-11}$) and $H_2PO_4^-$ ($K_a = 6.2 \times 10^{-8}$), since $H_2PO_4^-$ has a larger K_a it will donate a proton to HCO_3^-.

$$HCO_3^- + H_2PO_4^- \rightleftarrows H_2CO_3 + HPO_4^{2-}$$

2. The position of a equilibrium depends of the strengths of the acids. Consider the equilibrium:

$$H_2CO_3 + SO_3^{2-} \rightleftarrows HCO_3^- + HSO_3^-$$

- There are two conjugate acid–base pairs and there is a sort of **"proton competition"** set up in the solution.
- The two acids **H_2CO_3** and **HSO_3^-** compete to donate their protons.
- H_2CO_3 ($K_a = 4.3 \times 10^{-7}$) is a **stronger** acid than HSO_3^- ($K_a = 1.0 \times 10^{-7}$)
- H_2CO_3 has a greater tendency to donate protons than HSO_3^-. There will be more products than reactants **("products are favoured").**

$$\mathbf{H_2CO_3} + SO_3^{2-} \rightleftarrows HCO_3^- + \mathbf{HSO_3^-}$$

> Stronger acids and bases will react to produce their weaker conjugates.
>
> **Weaker acids and bases are favoured in an equilibrium.**

EXAMPLE 4.8 USING K_A TO PREDICT THE POSITION OF AN EQUILIBRIUM

Predict whether K_{eq} for the equilibrium:

$$HCO_3^- + HF \rightleftarrows H_2CO_3 + F^-$$

will be large or small.

Identify the acids and look up their K_a values.
K_a (HF) = 6.7×10^{-4} and K_a (H_2CO_3) = 4.4×10^{-7}

HF is a stronger acid than H_2CO_3; the equilibrium will favour the products.

Since the equilibrium favours the products, K_{eq} for the equilibrium will be large.

I. SALT HYDROLYSIS

1. Many salts contain a cation (+) or an anion (–) that can react with water.

> **HYDROLYSIS** = **reaction between water and the cation or anion (or both) contained in the salt** to produce an acidic or basic solution.

- **SPECTATOR IONS** are ions that do not participate in the reaction being considered. When considering the hydrolysis of ions, the following ions are spectators and do **NOT** hydrolyze:

> **SPECTATOR CATIONS (+)**
> **alkali metals (group 1) and alkaline earth metals (group 2)**
>
> **SPECTATOR ANIONS (–)**
> first five ions found at the top right of the table of Relative Strengths of Acids
> **(conjugate bases of strong acids): ClO_4^-, I^-, Br^-, Cl^- and NO_3^-**
>
> **(HSO_4^- is not a spectator ion since it is a weak acid)**

2. When an ion hydrolyzes, it is merely acting as a Brønsted acid or base with water.

a) ANIONIC (–) HYDROLYSIS

- If the **ANION (–)** of the salt hydrolyzes, it acts as a **BASE** with water to accept a proton and produce $OH^-(aq)$.

$$B^-(aq) + H_2O(l) \rightleftarrows HB(aq) + OH^-(aq)$$

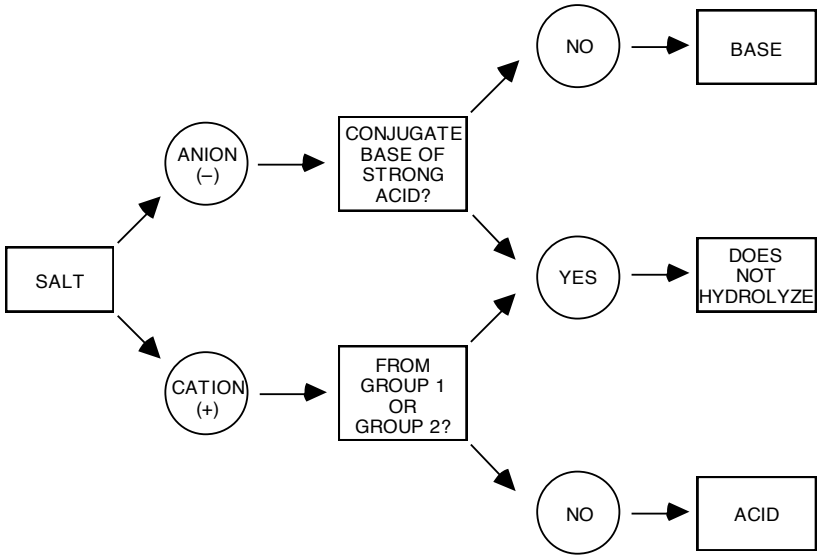
b) CATIONIC (+) HYDROLYSIS

- If the **CATION (+)** of the salt hydrolyzes, it acts as an **ACID** with water and donates a proton to produce $H_3O^+(aq)$.

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

> **ANIONS (–) hydrolyze to give basic solutions**
>
> **CATIONS (+) hydrolyze to give acidic solutions**

3. Procedure for determining the behaviour of a salt in water.
   - Determine the ions produced when the salt dissociates.
   - Omit spectator ions.
   - Remaining ions will behave as acids (anions) or bases (cations).



STRONG ACID – STRONG BASE salts → NEUTRAL
STRONG ACID – weak base salts → ACIDIC
weak acid – STRONG BASE salt → BASIC

EXAMPLE 4.9 PREDICTING SALT HYDROLYSIS

Predict whether each of the following salts hydrolyzes in water and write the hydrolysis equation for the reactions.

a) NaCl b) NH_4Cl c) KF d) NH_4NO_2 e) $NaHCO_3$

a) $NaCl \rightarrow Na^+(aq) + Cl^-(aq)$

Na^+ and Cl^- are both spectator ions

Since neither ion reacts with water, the solution of NaCl is ***NEUTRAL.***

b) $NH_4Cl \rightarrow NH_4^+(aq) + Cl^-(aq)$

Cl^- is a spectator

NH_4^+ undergoes ***cationic*** *hydrolysis to give a* ***BASIC*** *solution:*

$NH_4^+(aq) + H_2O(l) \rightleftarrows NH_3(aq) + H_3O^+(aq)$

c) $KF \rightarrow K^+(aq) + F^-(aq)$

K^+ is a spectator

F^- undergoes ***anionic*** *hydrolysis to give an* ***ACIDIC*** *solution:*

$F^-(aq) + H_2O(l) \rightleftarrows HF(aq) + OH^-(aq)$

d) $NH_4NO_2 \rightarrow NH_4^+(aq) + NO_2^-(aq)$

Both ions hydrolyze

NH_4^+ undergoes ***cationic*** *hydrolysis and NO_2^- undergoes* ***anionic*** *hydrolysis:*

$NH_4^+(aq) + H_2O(l) \rightleftarrows NH_3(aq) + H_3O^+(aq)$

$NO_2^-(aq) + H_2O(l) \rightleftarrows HNO_2(aq) + OH^-(aq)$

Compare the K_a and K_b values to find out whether more H_3O^+ or OH^- is being produced.

$$K_a\,(NH_4^+) = \mathbf{5.6 \times 10^{-10}}$$

$$K_b\,(NO_2^-) = \frac{K_w}{K_a(HNO_2)} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = \mathbf{2.2 \times 10^{-11}}$$

Since $K_a\,(NH_4^+) > K_b\,(NO_2^-)$, the solution will be ***ACIDIC.***

e) $NaHCO_3 \rightarrow Na^+(aq) + HCO_3^-(aq)$

Na^+ is a spectator

$HCO_3^-(aq)$ is an amphiprotic ion (can act as an acid or a base):

$HCO_3^-(aq) + H_2O(l) \rightleftarrows CO_3^{2-}(aq) + H_3O^+(aq)$

$HCO_3^-(aq) + H_2O(l) \rightleftarrows H_2CO_3(aq) + OH^-(aq)$

Compare $K_a(HCO_3^-)$ and $K_b(HCO_3^-)$ to determine predominant reaction for $HCO_3^-(aq)$.

$$K_a\,(HCO_3^-) = \mathbf{5.6 \times 10^{-11}}$$

$$K_b\,(HCO_3^-) = \frac{K_w}{K_a(H_2CO_3)} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = \mathbf{2.3 \times 10^{-8}}$$

*Since $K_b\,(HCO_3^-) > K_a\,(HCO_3^-)$, the solution will be **BASIC.***

4. Some **metal ions**, those with 3+ or 2+ and very small ionic radii such as **Fe^{3+}, Cr^{3+}, and Al^{3+}**, will react with water to form acidic solutions.

- The hydrolysis reactions for these ions can be found in the table of Relative Strengths of Acids.

$$Al(H_2O)_6^{3+}(aq) + H_2O \rightleftarrows [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+$$

- Metal ions from Group 1 or 2 (except Be^{2+}) do not hydrolyze.

5. Along with salt that hydrolyze there are also certain **oxygen–containing compounds, OXIDES,** that also react with water to produce acidic or basic solutions.

a) **METAL OXIDES**

- When a metal oxide is added to water, there is an initial dissociation of ions:

$$Na_2O(s) \rightarrow 2Na^+(aq) + O^{2-}(aq)$$

$$CaO(s) \rightarrow Ca^{2+}(aq) + O^{2-}(aq)$$

- The metal ions are spectator ions and the oxide ion, O^{2-}, is a strong base. The hydrolysis of the oxide ion is given by:

$$O^{2-}(aq) + H_2O(l) \rightarrow 2OH^-(aq)$$

- Since both $Na^+(aq)$ and $OH^-(aq)$ ions are present in solution, we can write the hydrolysis of $Na_2O(s)$ and $CaO(s)$ as:

$$Na_2O(s) + H_2O \rightarrow 2NaOH(aq)$$

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(aq)$$

b) **NONMETAL OXIDES**

- When a nonmetal oxide reacts with water, the water bonds to the existing oxide molecule to produce an **ACIDIC** solution.
- Referred to as **acid anhydrides.**

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

$$N_2O_5(g) + H_2O(l) \rightarrow 2HNO_3(aq)$$

$$CO_2(g) + H_2O(l) \rightarrow H_2CO_3(aq)$$
$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$
$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$$

c) **METALLOID OXIDES**

- Many metals and most metalloids for oxides or hydroxides that can react as either acids or bases.
- Common elements that form **amphoteric** oxides: Zn, Al, Pb, Be, Fe, Co, Sn.

$$\text{In Acids: } ZnO + 2H^+ \rightarrow Zn^{2+} + H_2O$$

$$\text{In Bases: } ZnO + H_2O + 2OH^- \rightarrow [Zn(OH)_4]^{2-}$$

AMPHOTERIC = **substances that react as acids or bases**

METAL OXIDES produce **BASIC** solutions when dissolved in water

NONMETAL OXIDES produce **ACIDIC** solutions when dissolved in water

METALLOID OXIDES are **AMPHOTERIC**

J CALCULATIONS INVOLVING K_A

1. When a weak acid, HA, is put into water, some of the acid ionizes. As a result of the ionization, there will be a certain amount of H_3O^+ produced; the smaller the value of K_a for the acid, the less H_3O^+ is formed. Many of the problems that you will encounter will require the use of an **I**nitial – **C**hange – **E**quilibrium **(ICE)** table.

EXAMPLE 4.10 USING INITIAL CONCENTRATION OF ACID AND K_A TO DETERMINE $[H_3O^+]$ OR PH

Calculate the pH of a 0.75 M acetic acid solution.

Write the equilibrium equation and K_a expression:

$$HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^-$$

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = 1.8 \times 10^{-5}$$

Setup an ICE table as follows:

$$HC_2H_3O_2 + H_2O \rightleftarrows H_3O^+ + C_2H_3O_2^-$$

I	0.75 M	–	0.00 M	0.00 M
C	$-x$	–	$+x$	$+x$
E	$0.75 - x$ $\approx 0.75^*$	–	x	x

* it is assumed that × is negligible with respect to 0.75 and so it will be nearly equal to 0.75 — this assumption should be stated. This assumption can only be made if the initial concentration is more than 1000 times greater than K.

Substitute into the K_a expression:

$$K_a = \frac{[H_3O^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)\,(x)}{0.75} = 1.8 \times 10^{-5}$$

$$x = [H_3O^+] = 3.7 \times 10^{-3}$$

$$pH = -\log (3.7 \times 10^{-3}) = \mathbf{2.43}$$

EXAMPLE 4.11 CALCULATING K_A FROM $[H_3O^+]$ OR PH

If the pH of 0.100 M $HCHO_2$ is 2.38 at 25°C, calculate K_a.

Write the equilibrium equation and K_a.

$$HCHO_2 + H_2O \rightleftarrows H_3O^+ + CHO_2^-$$

$$K_a = \frac{[H_3O^+][CHO_2^-]}{[HCHO_2]}$$

Setup an ICE table as follows:

$$HCHO_2 + H_2O \rightleftarrows H_3O^+ + CHO_2^-$$

I	*0.100 M*	–	*0.00 M*	*0.00 M*
C	*– x*	–	*+ x*	*+ x*
E	*0.100 – x*	–	*x*	*x*

Use pH to calculate the $[H_3O^+]$ at equilibrium.

$$[H_3O^+]_{eq} = \text{antilog}\,(-2.38) = 0.0042 = x$$

$$[CHO_2^-]_{eq} = 0.0042$$

$$[HCHO_2]_{eq} = 0.100 - 0.0042 = 0.0958$$

Substitute into the K_a expression:

$$K_a = \frac{(4.2 \times 10^{-3})\,(4.2 \times 10^{-3})}{0.0958} = \mathbf{1.8 \times 10^{-4}}$$

EXAMPLE 4.12 FINDING THE INITIAL CONCENTRATION OF A WEAK ACID

What mass of NH_4Cl will produce 1.50 L of a solution having a pH of 4.75?

First dissociate the salt:

$$NH_4Cl \rightarrow NH_4^+(aq) + Cl^-(aq)\ ;\ \mathbf{Cl^-\ is\ a\ spectator\ ion}$$

Since K_a for NH_4^+ is in the Table and pH is given, then $[NH_4^+]$ must be found. The $[NH_4^+]$ and the volume of the solution is then used to find moles and mass of NH_4Cl.

Set up and ICE table:

$$NH_4^+ + H_2O \rightleftarrows H_3O^+ + NH_3$$

I	*y*	–	*0.00 M*	*0.00 M*
C	*– x*	–	*+ x*	*+ x*
E	*y – x*	–	*x*	*x*

Use pH to find $[H_3O^+]_{eq}$

$$[H_3O^+]_{eq} = \text{antilog}\,(-4.75) = 1.78 \times 10^{-5}\ M = x$$

At equilibrium:

$$[NH_4^+]_{eq} = y - (1.78 \times 10^{-5})$$
$$[H_3O^+]_{eq} = x = 1.78 \times 10^{-5}$$
$$[NH_3]_{eq} = x = 1.78 \times 10^{-5}$$

Substituting into the K_a expression:

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]} = \frac{(1.78 \times 10^{-5})^2}{y - 1.78 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$y = [NH_4^+] = [NH_4Cl] = \frac{(1.78 \times 10^{-5})^2}{5.6 \times 10^{-10}} + 1.78 \times 10^{-5} = 0.565\ M$$

$$\text{mass of } NH_4Cl = 0.565\ \frac{mol}{L} \times 1.50\ L \times \frac{53.5\ g}{mol} = \mathbf{45\ g}$$

K. CALCULATIONS INVOLVING K_B

1. There are two types of calculations involving K_b, calculating K_b from pH and calculating equilibrium concentrations from K_b and initial concentrations.

   - Calculations involving weak bases are similar to the calculations involving weak acids with two important differences:

     i. the **K_b value must be calculated**; cannot be taken directly from Table
     ii. the resulting solution will be basic, not acidic, which means **using the $[OH^-]$ rather than $[H_3O^+]$**

EXAMPLE 4.13 USING INITIAL CONCENTRATION OF BASE AND K_B TO DETERMINE PH

Calculate the pH of a 0.10 M NaCN.

First dissociate the salt: $NaCN \rightarrow Na^+ + CN^-$

Na^+ is a spectator ion and CN^- acts as a weak base.

Write the equilibrium equation and K_a expression.

$$CN^- + H_2O \rightleftarrows OH^- + HCN$$

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} = K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5}$$

Setup an ICE table as follows:

$$CN^- + H_2O \rightleftarrows OH^- + HCN$$

I	*0.10 M*	–	*0.00 M*	*0.00 M*
C	*– x*	–	*+ x*	*+ x*
E	*0.10 – x* ≈ *0.10*	–	*x*	*x*

Substitute into the K_b expression:

$$K_b = \frac{[OH^-][HCN]}{[CN^-]} = \frac{x^2}{0.10} = 2.04 \times 10^{-5}$$

$$x = [OH^-] = 1.43 \times 10^{-3}\ M$$

$$pOH = -\log(1.43 \times 10^{-3}) = 2.845$$

$$pH = 14.00 - pOH = \mathbf{11.15}$$

EXAMPLE 4.14 CALCULATING K_B FROM POH OR PH

The pH of a 0.50 M solution of the weak base NaB is 10.64. What is K_a for the conjugate acid HB?

In this question, calculate K_b for the weak base first and then find K_a since $K_a = \frac{K_w}{K_b}$

First, write the equilibrium equation and K_a expression:

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

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

Setup an ICE table

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

I	*0.50 M*	–	*0.00 M*	*0.00 M*
C	*– x*	–	*+ x*	*+ x*
E	*0.50 – x*	–	*x*	*x*

Convert pH to $[OH^-]$

$$pOH = 14.00 - pH = 14.00 - 10.64 = 3.36$$

$$[OH^-] = \text{antilog}(-3.36) = 4.37 \times 10^{-4}\ M = x$$

$$[HB] = x = 4.37 \times 10^{-4}\ M$$

$$[B^-] = 0.50 - (4.37 \times 10^{-4}) = 0.4996 \approx 0.50$$

Substitute into the K_a expression:

$$K_b = \frac{[HB][OH^-]}{[B^-]} = \frac{(4.37 \times 10^{-4})^2}{0.50} = 3.81 \times 10^{-7}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{3.81 \times 10^{-7}} = \mathbf{2.6 \times 10^{-8}}$$

L. ACID AND BASE TITRATIONS

1. **Titrations** are used to determine the concentration of a solution by adding titrant until the equivalence point is reached.

> **TITRATION** = **quantitative chemical analysis used to determine the unknown concentration of a known reactant.**

> **EQUIVALENCE POINT** = mole ratio in the reaction exactly equals the mole ratio required by the stoichiometry of the reaction **(stoichiometric equivalent amounts of reactants).**
>
> $$\mathbf{a}A + \mathbf{b}B \rightarrow \mathbf{c}C + \mathbf{d}D$$
>
> $$\frac{\text{moles A}}{\text{moles B}} = \frac{\mathbf{a}}{\mathbf{b}}$$

2. All titration problems involve at least **FIVE PARAMETERS:**

concentration of acid **concentration of base** **acid/base mole ratio**
volume of acid **volume of base**

- When the reaction equation is given, the acid/base ratio is read directly from the balanced equation so that one of the concentrations or volumes must be known.
- These problems involve three parts to the calculation:
  i. use M = n/V to calculate moles of the first substance
  ii. use acid/base ratio to calculate moles of the second substance
  iii. use M = n/V to calculate either the concentration or volume of the second substance

> Often when titrations are done, several trials are necessary to check the accuracy. Ideally volumes **should agree within ± 0.02 mL.**
>
> Only volumes within ± 0.02 mL are used to determine the average volume of the titrant. **Volumes that exceed this tolerance are discarded.**

EXAMPLE 4.15 CALCULATING CONCENTRATION FROM TITRATION

In the reaction

$$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$$

23.10 mL of 0.2055 M NaOH is needed to titrate a 25.00 mL sample of H_2SO_4 to its equivalence point. What is the $[H_2SO_4]$?

First, calculate moles of first substance

$$moles\ NaOH = M \times V = 0.2055\ \frac{mol}{L} \times 0.02310\ L = 0.004747\ mol$$

Next, use mole ratio

$$moles\ of\ H_2SO_4 = 0.004747\ moles\ NaOH \times \frac{1\ H_2SO_4}{2\ NaOH} = 0.002374\ mol$$

Finally, calculate concentration

$$M = \frac{n}{V} = \frac{0.002374\ mol}{0.02500\ L} = \mathbf{0.09494\ M}$$

3. Titrations are often used to calculate the percentage purity of a solid acid or base.

- Actual concentration can be calculated from titration data.
- The expected concentration is calculated from the impure compound.

$$\textbf{Percentage purity} = \frac{\textbf{Actual concentration}}{\textbf{Expected concentration}}\ \textbf{x 100\%}$$

EXAMPLE 4.16 CALCULATING PERCENTAGE PURITY

A 3.4786 g sample of impure $NaHSO_4$ is diluted to 250.0 mL. A 25.00 mL sample of the solution is titrated with 26.77 mL of 0.09974 M NaOH. What is the percentage purity of the $NaHSO_4$?

First, calculate moles of NaOH

$$\text{moles NaOH} = M \times V = 0.09974 \frac{mol}{L} \times 0.02677\ L = 0.002670\ mol$$

*Na**H**SO_4 is monoprotic, so*

moles of $NaHSO_4$ used = moles of NaOH used = 0.002670 mol

Next, calculate the [$NaHSO_4$] in the 25.00 mL sample

$$[NaHSO_4] = \frac{n}{V} = \frac{0.002670\ mol}{0.02500\ L} = 0.1068\ M$$ ***(Actual)***

Now, calculate the expected [$NaHSO_4$]

$$[NaHSO_4] = \frac{3.4786 g}{0.2500\ L} \times \frac{1\ mol}{120.1\ g} = 0.1159\ M$$ ***(Expected)***

Finally, calculate percentage purity

$$\%\ \text{purity} = \frac{0.1068\ M}{0.1159\ M} \times 100\% =$$ ***92.1%***

4. Titration can also be used to calculate the molar mass of an unknown solid acid or base, if it is known whether the acid or base is monoprotic, diprotic, etc.

- Titration data allows us to calculate the moles of the acid or base.
- Molar mass is given by dividing the mass of the acid or base used to prepare the solution by the moles.

EXAMPLE 4.17 CALCULATING MOLAR MASS

A 3.2357 g sample of unknown monoprotic acid is diluted to 250.0 mL. A 25.00 mL sample of the acid solution is titrated with 16.94 mL of 0.1208 M KOH. What is the molar mass of the acid?

First, calculate moles of KOH

$$\text{moles KOH} = M \times V = 0.1208 \frac{\text{mol}}{\text{L}} \times 0.01694 \text{ L} = 0.002046 \text{ mol}$$

Since the acid is monoprotic, then

moles of acid = moles of KOH = 0.002046 mol

Next, calculate concentration of the acid

$$M = \frac{n}{V} = \frac{0.002046 \text{ mol}}{0.02500 \text{ L}} = 0.08185 \text{ M}$$

Now, calculate the moles of acid in the original 250.0 mL volume

$$\text{moles of acid} = 0.08185 \frac{\text{mol}}{\text{L}} \times 0.2500 \text{ L} = 0.02046 \text{ mol}$$

Finally, calculate the molar mass

$$\text{molar mass} = \frac{3.2357 \text{ g}}{0.02046 \text{ mol}} = \mathbf{158.1 \text{ g/mol}}$$

M. INDICATORS

1. Indicators are used to determine the pH of a solution.

INDICATOR = **weak organic acid or base that has different colours for their conjugate acid and base forms.**

- Indicators are often indicated by the symbol **HIn (acid form)** and **In^- (base form).** Since an indicator is a weak acid or base, the following equilibrium equation can be written:

$$HIn\ (yellow) + H_2O \rightleftarrows In^-\ (red) + H_3O^+$$

- When an indicator is placed into an acid solution, the excess H_3O^+ causes a shift in the indicators equilibrium

$$\textbf{HIn (yellow)} + H_2O \rightleftarrows In^-\ (red) + \uparrow \textbf{H}_3\textbf{O}^+$$

An indicator will be in its **CONJUGATE ACID (HIn)** form in **HIGHLY ACIDIC solutions.**

- When an indicator is placed into a base solution, the OH^- reacts to decrease the $[H_3O^+]$ and causes a shift in the indicators equilibrium

$$HIn\ (yellow) + H_2O \rightleftarrows \textbf{In}^-\ \textbf{(red)} + \downarrow \textbf{H}_3\textbf{O}^+$$

An indicator will be in its **CONJUGATE BASE (In^-)** form in **HIGHLY BASIC solutions.**

2. The colour of an indicator depends on the relative concentrations of the conjugate acid and base forms of the indicator.

TRANSITION POINT = **indicator is mid–way through its colour change and [HIn] = [In^-]**

- Consider the following indicator equilibrium:

$$HIn + H_2O \rightleftarrows In^- + H_3O^+$$

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]}$$

- At the transition point [HIn] = [In^-], so

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]} = [H_3O^+]$$

- In addition,

$$-\log K_{In} = -\log [H_3O^+]$$
$$pK_{In} = pH$$

At the transition point of any indicator, the following relationships exist:

[HIn] = [In^-] **$K_{In} = [H_3O^+]$** **$pK_{In} = pH$**

3. The K_a of an indicator, **K_{In}, can be calculated using the pH range over which the indicator changes colour.**

EXAMPLE 4.18 USING INDICATOR TABLES TO CALCULATE THE K_{IN} OF AN INDICATOR

What is the K_{In} for phenolphthalein.

Look up pH range of phenolphthalein from data booklet. pH range is 8.2 – 10.0.
$[HIn] = [In^-]$ midway through the pH range.

$$[HIn] = [In^-] \text{ at } pH = \frac{8.2 + 10.0}{2} = 9.1$$

since $[HIn] = [In^-]$

$$K_{In} = \frac{[H_3O^+][In^-]}{[HIn]} = [H_3O^+]$$

$$[H_3O^+] = 10^{-9.1}$$

$$[H_3O^+] = K_{In} = \mathbf{7.9 \times 10^{-10}}$$

EXAMPLE 4.19 USING INDICATORS TO DETERMINE PH OF A SOLUTION

What is the approximate pH range of a solution that changes methyl red $\rightarrow$ yellow and neutral red $\rightarrow$ red?

Look up pH range for each indicator in the data booklet.

*pH range of methyl red is 4.8 (red) – **6.0 (yellow)***

*pH range of neutral red is **6.8 (red)** – 8.0 (orange)*

pH of solution must be greater than 6.0 but less than 6.8

EXAMPLE 4.20 PREDICTING THE COLOUR OF INDICATORS AT VARIOUS PH

A mixture of the indicators methyl orange, phenol red and thymol blue is added to a pH 5.0 and pH 8.0 solution? What is the colour of the mixture at pH 3.0 and 8.0?

Look up pH range of each indicator in data booklet.

methyl orange	*phenol red*	*thymol blue*
red – yellow	*yellow – red*	*yellow – blue*
(3.2 — 4.4)	*(6.6 — 8.0)*	*(8.0 — 9.6)*

	Methyl Orange	***Phenol Red***	***Thymol Blue***	***Mixture***
pH 5.0	*yellow*	*yellow*	*yellow*	*yellow*
pH 8.0	*yellow*	*red*	*yellow*	*orange*

N. TITRATION CURVES

1. In order to perform a titration, you must start with a solution with a standardized solution.

> **STANDARD SOLUTION** or **STANDARDIZED SOLUTION** = **solution with precisely known concentration.**

- Standard solutions can be prepared by:

  a) Using a substance which can be obtained in a pure and stable form (does not absorb water or carbon dioxide from the air) and which has a known molar mass so that it can be used to prepare a solution of known concentration **(PRIMARY STANDARD).**

  e.g. Potassium hydrogen phthalate $KHC_8H_4O_4$
  Oxalic acid dihydrate $H_2C_2O_4 \bullet 2H_2O$

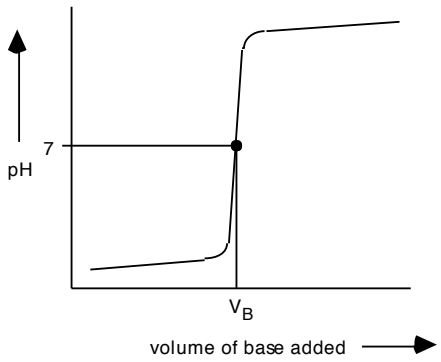
  b) Titrating a base with an acidic primary standard.

2. A titration curve is produced by plotting the pH change that occurs during a titration.

a) Titration of a STRONG ACID with a STRONG BASE

- The following titration curve is typical of when a strong acid is titrated with a strong base.

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

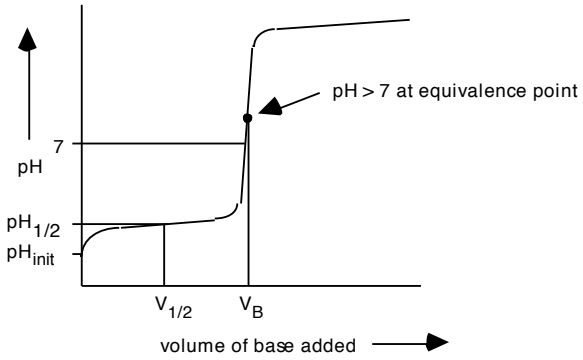


- The pH rises almost vertically around the value of V_B.
- V_B is the volume of the base required to reach the equivalence point.
- **STRONG ACID–STRONG BASE** titration produce a **NEUTRAL** salt solution so **pH = 7 at the equivalence point.**
- Choose indicator which changes colour around pH = 7 (pK_{In} = 7), such as phenol red or neutral red.

b) Titration of a WEAK ACID with a STRONG BASE

- The following titration curve is typical of when a **weak acid** is titrated with a **STRONG BASE**.

$$NaOH + HNO_2 \rightarrow \mathbf{NaNO_2(aq)} + H_2O$$



- Initial upswing in the pH at the start of the titration **(BUFFERING ZONE).**
- **weak acid–STRONG BASE** titration produces a **BASIC** salt solution. As such, the **pH > 7 at the equivalence point.**

($NaNO_2$ hydrolyzes to give a base)

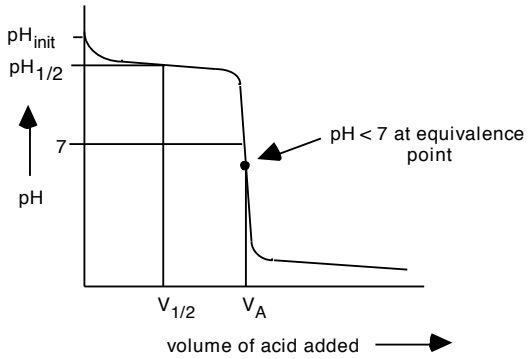
$$NO_2^-(aq) + H_2O(l) \rightarrow HNO_2(aq) + \mathbf{OH^-(aq)}$$

- Titration requires an **indicator that changes colour at pH > 7** (pK_a > 7) such as phenolphthalein.

c) Titration of a WEAK BASE with a STRONG ACID

- The following titration curve is typical of when a **weak base** is titrated with a **STRONG ACID**.

$$NH_4OH(aq) + HCl(aq) \rightarrow \mathbf{NH_4Cl(aq)} + H_2O(l)$$



- Similar to weak acid and strong base, except that the curve is flipped upside down.
- Graph gives pH values not pOH, therefore pH's need to be converted to pOH.
- **weak base–STRONG ACID** titration produces an **ACIDIC** salt solution. As such, the **pH<7 at the equivalence point.**

(NH_4Cl hydrolyzes to give acid)

$$NH_4^+(aq) + H_2O(l) \rightarrow NH_3(aq) + H_3O^+(aq)$$

- The titration requires an **indicator which changes colour at pH < 7** ($pK_a < 7$) such as methyl red.

STRONG ACID + STRONG BASE → **neutral (pH = 7)**
weak acid + **STRONG BASE** → **basic (pH > 7)**
STRONG ACID + weak base → **acidic (pH < 7)**

Note: **Phenolphthalein** (pH 8.2 – 10.0) is used for weak acid – strong base titrations but it is also often used for strong acid – strong base titrations even though pH = 7 at the equivalence point. This occurs because there is a dramatic colourless to magenta colour change.

O. BUFFERS

1. **BUFFERS** resist large changes in pH resulting from the addition of acids or bases.

- Consist of a **weak acid and its conjugate weak base** (usually close to equal concentrations of acid and base).
- Often added as **soluble salts**

e.g. CH_3COOH and $NaCH_3COO$
NH_4NO_3 and NH_3
NaH_2PO_4 and Na_2HPO_4

BUFFER = **solution where the solutes protect it against large changes in pH even when strong acids or bases are added.**

2. Buffers are Bronsted–Lowry equilibria that work by shifting to reduce the effects of adding H_3O^+ or OH^-.

- Consider the equation of a buffer:

$$CH_3COOH(aq) + H_2O(l) \rightleftarrows CH_3COO^-(aq) + H_3O^+(aq)$$

- If H_3O^+ is added the **$[H_3O^+]$ increases and the equilibrium shifts left:**

$$CH_3COOH(aq) + H_2O(l) \rightleftarrows \mathbf{CH_3COO^-(aq)} + \uparrow \mathbf{H_3O^+(aq)}$$

- If OH^- is added it combines with H_3O^+ to form water and **$[H_3O^+]$ decreases and the equilibrium shift right:**

$$\mathbf{CH_3COOH(aq)} + H_2O(l) \rightleftarrows CH_3COO^-(aq) + \downarrow \mathbf{H_3O^+(aq)}$$

- Bronsted–Lowry acids and bases **do not act effectively as buffers on their own.** Both conjugate acid and bases must be present in approximately equal amounts to allow shifting in both directions.

$$\mathbf{CH_3COOH(aq)} + H_2O(l) \rightleftarrows \mathbf{CH_3COO^-(aq)} + H_3O^+(aq)$$

3. The pH of a buffer depends on the ratio of conjugate acid and base. The **HENDERSON–HASSELBALCH** equation allows us to calculate the pH of a buffer solution.

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

- Buffers are most effective when the pH ≈ pK_a for the acid.

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

Since $[CH_3COOH] = [CH_3COO^-]$

$K_a = [H_3O^+]$

$pK_a = pH$

- The **CAPACITY** of a buffer refers to the amount, moles, of acid or base a buffer can react with until a large change in pH will occur.
- The actual **number of moles of acid and base** that are used to prepare the buffer that determine its capacity.
- When selecting an acid for a buffer, it is best to choose an acid that **$pK_a = pH \pm 1$.**

EXAMPLE 4.21 CALCULATING THE PH OF A BUFFER

A buffer is made by adding 0.11 M $NaC_2H_3O_2$ to 0.090 M $HC_2H_3O_2$. What is the pH of this buffer? K_a for acetic acid is 1.8×10^{-5}.

Using the Henderson–Hasselbach equation, substitute in the concentrations and K_a value.

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

$$pH = 4.74 + \log \frac{(0.11)}{(0.090)} = \mathbf{4.82}$$

EXAMPLE 4.22 CALCULATING THE RATIO OF ACID TO BASE NEEDED FOR A BUFFER

A solution buffered at pH 5.00 is needed in a chemistry experiment. Can acetic acid and sodium acetate be used to make it? If so, what ratio of acetate to acetic acid is needed?

Check pK_a to see if it falls within desired range, should be 5.00 ± 1.

$$K_a = 1.8 \times 10^{-5}$$

$$pK_a = 4.74$$

Ratio of solutes can be determined using

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

$$5.00 = 4.74 + \log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

$$\log \frac{[\text{conjugate base}]}{[\text{conjugate acid}]} = 5.00 - 4.74 = 0.26$$

$$\frac{[\text{anion}]}{[\text{acid}]} = 10^{0.26} = \mathbf{1.8}$$

A ratio of 1.8 moles of acetate ions to 1.0 mole of acetic acid is needed.

Note: **Diluting a buffer has no effect on the pH** because both conjugate acid and base are diluted equally.

Buffers DO NOT maintain a CONSTANT pH, they simply resist large changes.