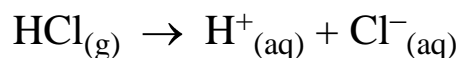


Acids And Bases

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**).

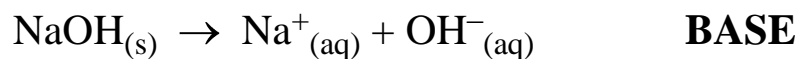
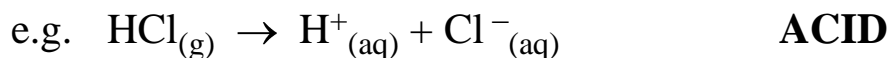


2. **Arrhenius** theory of acids and bases states:

ARRHENIUS THEORY

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

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



To simplify things,

- i) **ACIDS** are ionic compounds that begin with “H”.



ii) **BASES** are ionic compounds that end in “OH”.

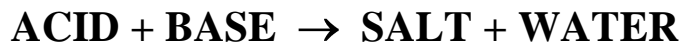
e.g. NaOH , Ca(OH)₂ , LiOH

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

e.g. KCl, Na₂SO₄, Fe(NO₃)₃

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.

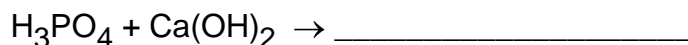


Recall that a neutralization reaction is simply a special case of a double-replacement reaction in which water is always one of the products.

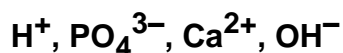
EXAMPLE 4.1 WRITING NEUTRALIZATION REACTIONS

Write the neutralization reaction between H_3PO_4 and $\text{Ca}(\text{OH})_2$

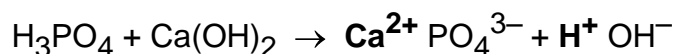
First, write the formulas of the acid and base on the reactant side.



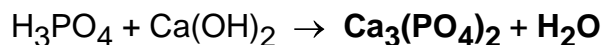
Next, determine the charges of the ions present in the mixture (use table in data booklet if unsure).



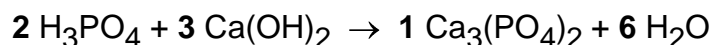
Predict the products by exchanging the two positive ions (remember water is always one of the products).



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



Balance the equation.



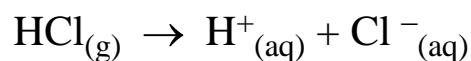
4. All acids have certain properties in common as do all bases. The presence of $\mathbf{H^+}$ accounts for the following properties of **ACIDS**:
- taste **SOUR**
 - conduct an electric current
 - turn litmus paper **RED**
 - produce hydrogen when reacted with certain metals such as magnesium
 - neutralized by bases

The presence of OH^- accounts for the following properties of **BASES**:

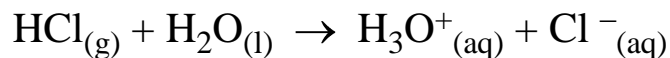
- a) taste **BITTER**
 - b) conduct an electric current
 - c) turn litmus paper **BLUE**
 - d) feel slippery
 - e) neutralized by acids
5. When an acid such as HCl is dissolved in water, it produces a hydrogen ion or **proton**, $\text{H}^+_{(\text{aq})}$. Protons do not exist on their own in water but rather readily attach themselves to water molecules to produce **hydronium ions** or **hydrated protons**, $\text{H}_3\text{O}^+_{(\text{aq})}$.

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

To show that hydronium ions are actually produced when an acid dissociates, the dissociation equation



can be re-written as



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 is a more general theory of acids and bases than the Arrhenius theory. 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.

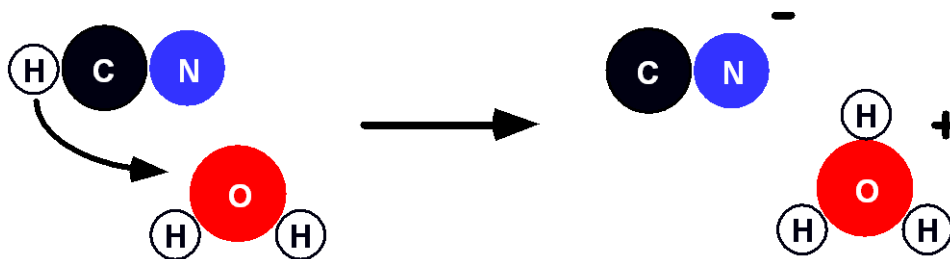
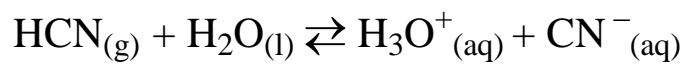
BRØNSTED–LOWRY THEORY

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

A **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:

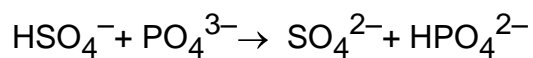


CONJUGATE ACID is the member of the conjugate pair that **HAS** the extra proton

CONJUGATE BASE is the member of the conjugate pair that **LACKS** the extra proton

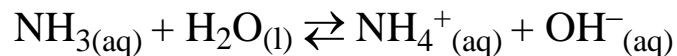
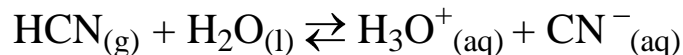
SAMPLE 4.1 CONJUGATE ACID–BASE PAIRS

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:



1. _____
2. _____
3. _____

4. Consider the following two Brønsted–Lowry equilibria:



In the first equation, H_2O gains a proton to become H_3O^+ so it is acting as a **BASE** and 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 → **ONE** proton



DIPROTIC acid → **TWO** protons



TRIPROTIC acid → **THREE** protons



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***

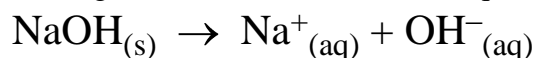
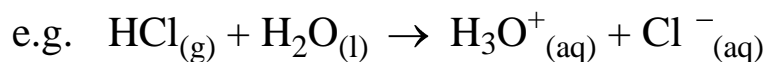
then the substance will be **AMPHIPROTIC**

*Apart from hydrogens attached to carbon, assume that all hydrogens on a negatively charged ion are “easily removable”.

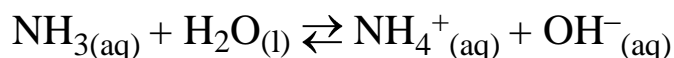
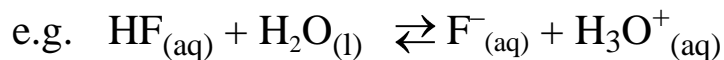
C. Strengths of Acids and Bases

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

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



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



The **strength** of an acid or base (i.e. strong or weak) refers to the degree of ionization of the acid or base **NOT** its molar concentration.

0.0010 M HCl is still a **STRONG** acid

6.0 M HF is still a **WEAK** acid

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

STRONG ACIDS

The strong acids are the **top six acids** on the left side of the table, in particular:



Notice that all six reaction have **ONE-WAY** reaction arrows, pointing to the product side. This means that the **REVERSE REACTIONS DO NOT OCCUR AT ALL.**

STRONG BASES

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



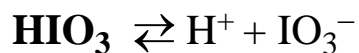
Once again, these two reactions have **ONE-WAY** reaction arrows, pointing to the reactant side. This means that the **FORWARD REACTIONS DO NOT OCCUR AT ALL.**

In addition to these two strong bases, soluble metal hydroxides are also strong bases.

e.g. NaOH , KOH , $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$

WEAK ACIDS

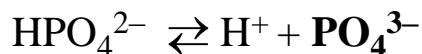
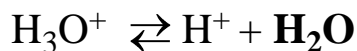
The weak acids are the species on the left side of the table from **HIO₃** down to **H₂O**.



The last two species on the left, **O²⁻** and **NH₂⁻**, never act as acids in aqueous solutions.

WEAK BASES

The weak bases are the species on the right side of the table from **H₂O** down to **PO₄³⁻**.



The top six species on the right, **HSO₄⁻**, **NO₃⁻**, **Cl⁻**, **Br⁻**, **I⁻**, **ClO₄⁻**, never act as bases in aqueous solutions.

LEVELLING EFFECT

All strong acids have **IDENTICAL STRENGTHS** in water because they are all 100% dissociated in aqueous solutions.

Note: Although all of the reactions are written as dissociation 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 dissociate 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.

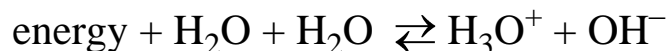
Note: The six strong acids, HClO_4 , HI , HBr , HCl , HNO_3 , and H_2SO_4 , cannot exist as molecules in aqueous solutions because they dissociate completely to produce H_3O^+ and an anion. Hence H_3O^+ is the strongest acid that can exist in aqueous solution. In the same way, O^{2-} and NH_2^- , cannot 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	$[\text{H}_3\text{O}^+] > [\text{OH}^-]$
NEUTRAL	$[\text{H}_3\text{O}^+] = [\text{OH}^-]$
BASIC	$[\text{H}_3\text{O}^+] < [\text{OH}^-]$

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



An equilibrium constant for this reaction can be written as:

$$K_{\text{eq}} = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

and since water is a pure liquid, the $[\text{H}_2\text{O}]$ is constant at a particular temperature, we can incorporate it into the constant, $K_{\text{eq}} \times [\text{H}_2\text{O}]^2$, and define a new constant called the **EQUILIBRIUM CONSTANT OF WATER, K_w** .

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14} \quad (\text{at } 25 \text{ }^\circ\text{C})$$

As with any other equilibrium constant, 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 $[\text{OH}^-]$

What is the $[\text{OH}^-]$ in 0.025 M HCl?

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

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

HCl is a strong acid, so $[\text{H}_3\text{O}^+] = [\text{HCl}] = 0.025 \text{ M}$

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

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

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

E. PH and POH

1. When working with dilute solutions of strong acids or weak acids and likewise with bases, the $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ 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.
2. 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.

$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$
$$\text{pOH} = -\log [\text{OH}^-]$$

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 10 to 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 $[\text{H}_3\text{O}^+]$ AND $[\text{OH}^-]$ TO pH AND pOH

a) If the $[\text{H}_3\text{O}^+] = 4.67 \times 10^{-5}$ M, what is the pH?

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

a) $\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (4.67 \times 10^{-5}) = -(-4.331) = \mathbf{4.331}^*$

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

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

3. Consider the following:

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

If we want to rearrange this equation to solve for $[\text{H}_3\text{O}^+]$ first remove the negative sign by multiplying both sides of the equation by negative 1 to give:

$$-\text{pH} = \log [\text{H}_3\text{O}^+]$$

Since the reverse of taking the log of a number is taking the antilog, the $[\text{H}_3\text{O}^+]$ can be determined by taking the antilog of both sides of the equation:

$$\mathbf{\text{antilog} (-\text{pH}) = \text{antilog} (\log [\text{H}_3\text{O}^+]) = [\text{H}_3\text{O}^+]}$$

$$\text{antilog} (-\text{pH}) = [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

Similarly, $[\text{OH}^-]$ can be determined from the pOH.

$$[\text{H}_3\text{O}^+] = \text{antilog} (-\text{pH}) = 10^{-\text{pH}}$$

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

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) $[H_3O^+] = \text{antilog}(-\text{pH}) = \text{antilog}(-3.17) = 10^{-3.17} = 6.8 \times 10^{-4} \text{ M}$

b) $[OH^-] = \text{antilog}(-\text{pOH}) = \text{antilog}(-5.32) = 10^{-5.32} = 4.8 \times 10^{-6} \text{ M}$

4. 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:

$$\begin{aligned} \log([H_3O^+][OH^-]) &= \log K_w \\ \log [H_3O^+] + \log [OH^-] &= \log K_w \end{aligned}$$

Multiply by negative one

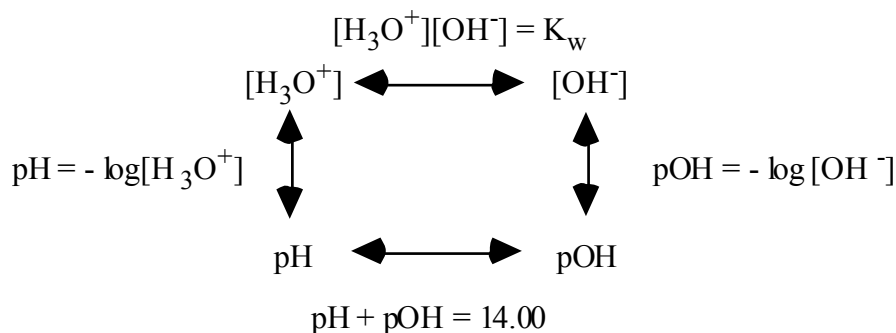
$$\begin{aligned} (-\log [H_3O^+]) + (-\log [OH^-]) &= (-\log K_w) \\ \text{pH} + \text{pOH} &= \text{p}K_w \end{aligned}$$

At 25 °C $K_w = 1.0 \times 10^{-14}$

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

$$\text{pH} + \text{pOH} = 14.00$$

5. Using the following relationships, you can work back and forth from the any of $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH, and pOH.



6. Since the pH and pOH scales are logarithmic scales, a difference in one pH or pOH unit is equivalent to a ten-fold difference in concentration.

In addition, since pH and pOH are the negative of the exponent, low pH and pOH values mean relatively high values of $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$, and high values of pH and pOH mean relatively low $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$.

At 25 °C

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

It is possible to have **negative pH values**, this would only occur in concentrated strong acids. The pH scale was developed as a means of expressing and comparing **small** $[\text{H}_3\text{O}^+]$ hence negative pH values are of little use.

2.00 M HCl has a $[\text{H}_3\text{O}^+] = 2.00 \text{ mol/L}$

$\text{pH} = -\log(2.00) = -0.30$

F. Mixing Strong Acids and Bases

1. When a strong acid and base are mixed, a neutralization reaction occurs. 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?

First calculate the diluted concentrations of H_3O^+ and OH^-

$$[\text{H}_3\text{O}^+] = [\text{HCl}] = \frac{(25.0 \text{ mL})(0.250 \text{ M})}{(60.0 \text{ mL})} = 0.104 \text{ M}$$

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

Since the neutralization reaction, $\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$, involves a 1:1 ratio between H_3O^+ and OH^- , OH^- is in excess.

$$[\text{OH}^-] = 0.117 \text{ M} - 0.104 \text{ M} = 0.013 \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (0.013) = 1.90$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 1.90 = \mathbf{12.10}$$

EXAMPLE 4.6 CALCULATING MOLES OF ACID NEEDED TO REACH DESIRED pH

How many moles of $\text{HCl}_{(g)}$ 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.

The pH given is for a basic solution:

$$\text{pOH} = 14.000 - \text{pH} = 14.000 - 12.500 = 1.500$$

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

$$\text{moles OH}^- = (0.03162 \text{ mol/L}) (0.0400 \text{ L}) = 0.00126 \text{ mol}$$

The change in $[\text{OH}^-]$ is the amount that was neutralized by the acid and since H_3O^+ and OH^- react in a 1:1 ratio, the moles of OH^- = moles of H_3O^+ .

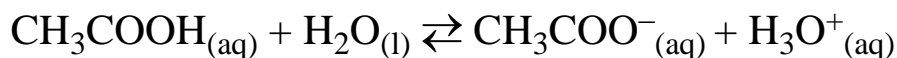
$$\Delta[\text{OH}^-] = 0.180 \text{ M} - 0.03162 \text{ M} = 0.148 \text{ M}$$

$$\text{mol OH}^- = \text{mol H}_3\text{O}^+ = \text{mol HCl} = 0.148 \text{ M} \times 0.0400 \text{ L} = \mathbf{0.00594 \text{ moles}}$$

G. Acid and Base Equilibrium Constants

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

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

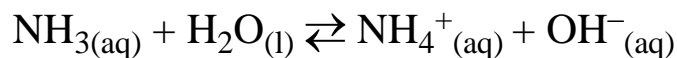


An equilibrium expression can be written for the ionization as:

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.76 \times 10^{-5}$$

The **value** of K_a is called the **ACID IONIZATION CONSTANT**. The greater the value of K_a , the stronger the acid. A 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:



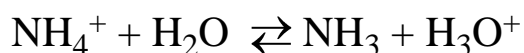
The equilibrium expression for the ionization is:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.79 \times 10^{-5}$$

The value of K_b is called the **BASE IONIZATION CONSTANT**.

Similar to K_a , the greater the K_b value for a base, the stronger the base. The table of Strengths of Acids does not list K_b values but these values can be calculated using K_a values in the table.

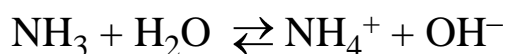
3. There is an important relationship that exists between K_a and K_b for conjugate acid–base pairs. Consider the following: the acid NH_4^+ , has the **ACID IONIZATION** equation:



and the acid ionization expression:

$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

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



and the base ionization expression:

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

When K_a and K_b are multiplied together we get

$$K_a \times K_b = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} \times \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = [\text{H}_3\text{O}^+][\text{OH}^-]$$

and since $[\text{H}_3\text{O}^+][\text{OH}^-] = K_w$

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

EXAMPLE 4.7 CALCULATING K_b FROM K_a

Calculate the K_b for $\text{C}_2\text{O}_4^{2-}$.

To calculate K_b we need the value of K_a for the conjugate acid of $\text{C}_2\text{O}_4^{2-}$.

Since $\text{C}_2\text{O}_4^{2-}$ is a base we look up $\text{C}_2\text{O}_4^{2-}$ on the **right** side of the table and use the K_a corresponding to its conjugate acid HC_2O_4^- .

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

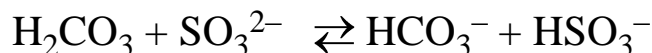
Note: Because of the reciprocal nature of K_a and K_b

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

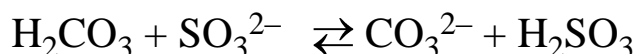
the conjugate base of a weak acid is a strong base and the conjugate acid of a strong base is a weak acid.

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-} can only act as a base since it has no protons to donate.

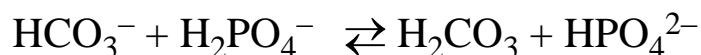


Note: All Brønsted–Lowry reactions studied in Chemistry 12 will only involve the transfer of a single proton. There will **NOT** be two–proton transfers such as

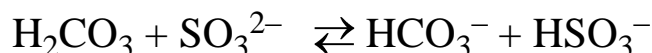


If solutions containing amphiprotic ions such as HCO_3^- and H_2PO_4^- are mixed, the stronger of the two acids will donate a proton while the other ion accepts a proton.

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^- .

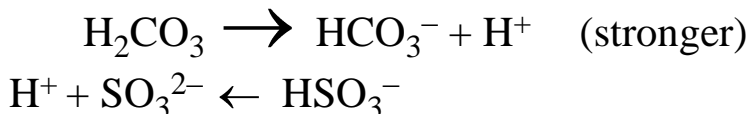


2. In the equilibrium:



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.

From the table of Relative Strengths of Acids, we can see that H_2CO_3 ($K_a = 4.3 \times 10^{-7}$) is a stronger acid than HSO_3^- ($K_a = 1.0 \times 10^{-7}$)

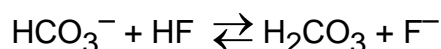


As a result, H_2CO_3 has a greater tendency to donate protons that does HSO_3^- . Therefore there will be more products than reactants (“products are favoured”).

In an equilibrium between Brønsted acids and bases, the position of the resulting equilibrium can be predicted based on the strengths of the **conjugate acids**. As a general rule **Stronger acids and bases will react to produce their weaker conjugates.**

EXAMPLE 4.8 USING K_a TO PREDICT THE POSITION OF AN EQUILIBRIUM

Predict whether K_{eq} for the equilibrium:



will be large or small.

Identify the acids and look up their K_a values.

$$K_a(\text{HF}) = 6.7 \times 10^{-4} \text{ and } K_a(\text{H}_2\text{CO}_3) = 4.4 \times 10^{-7}$$

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

- Many salts contain a cation (+) or an anion (–) that can react with water. The **HYDROLYSIS** of a salt is the reaction between water and the cation or anion (or both) contained in the salt so as to produce an acidic or basic solution.

Note: All salts are considered to be 100% ionized in water.
Hence, the ions making up the salt are of concern, not the salt itself.

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

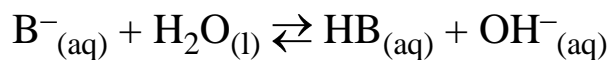
SPECTATOR CATIONS (+) are the ions of the alkali metals (group 1) and alkaline earth metals (group 2)

SPECTATOR ANIONS (–) are the first five ions found at the top right of the table of Relative Strengths of Acids (i.e. the conjugate bases of strong acids): **ClO₄[–], I[–], Br[–], Cl[–] and NO₃[–]** (HSO₄[–] is not a spectator ion since it is a weak acid)

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

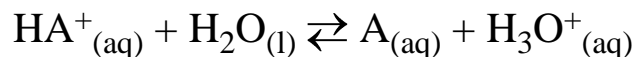
ANIONIC (–) HYDROLYSIS

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



CATIONIC (+) HYDROLYSIS

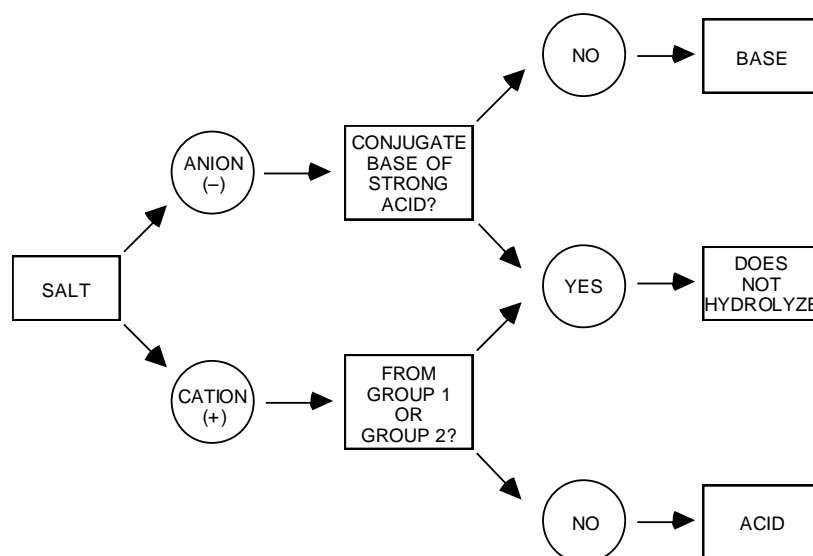
If the **CATION (+)** of the salt hydrolyzes, it acts as an **ACID** with water and donates a proton to produce $\text{H}_3\text{O}^+_{(\text{aq})}$.



ANIONS (-) hydrolyze to give **basic** solutions while **CATIONS (+)** hydrolyze to give **acidic** solutions.

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).



EXAMPLE 4.9 PREDICTING SALT HYDROLYSIS

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

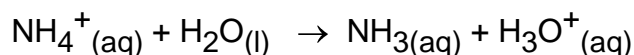
- a) NaCl b) NH₄Cl c) KF d) NH₄NO₂ e) NaHCO₃

a) NaCl → Na⁺(aq) + Cl⁻(aq) ; **Na⁺ and Cl⁻ are both spectator ions**

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

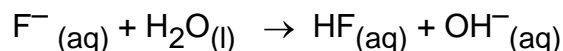
b) NH₄Cl → NH₄⁺(aq) + Cl⁻(aq) ; **Cl⁻ is a spectator**

NH₄⁺ undergoes **cationic** hydrolysis to give a **BASIC** solution:



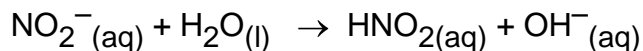
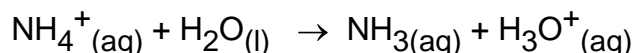
c) KF → K⁺(aq) + F⁻(aq) ; **K⁺ is a spectator**

F⁻ undergoes **anionic** hydrolysis to give an **ACIDIC** solution:



d) NH₄NO₂ → NH₄⁺(aq) + NO₂⁻(aq) ; **Both ions hydrolyze**

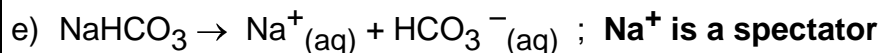
NH₄⁺ undergoes **cationic** hydrolysis and NO₂⁻ undergoes **anionic** hydrolysis:



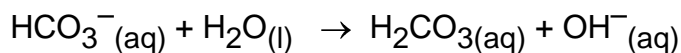
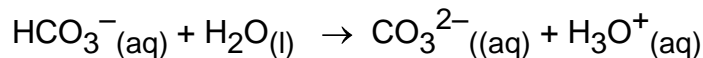
Since one ion is producing H₃O⁺ and the other ion OH⁻, we need to compare the K_a and K_b values to find out whether more H₃O⁺ or OH⁻ is being produced.

$$K_a(\text{NH}_4^+) = 5.6 \times 10^{-10} \quad \text{and} \quad K_b(\text{NO}_2^-) = \frac{K_w}{K_a(\text{HNO}_2)} = \frac{1.0 \times 10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{-11}$$

Since K_a(NH₄⁺) > K_b(NO₂⁻), the solution will be **ACIDIC**.



$\text{HCO}_3^-_{(\text{aq})}$ is an amphiprotic ion (can act as an acid or a base):



Need to compare $K_a(\text{HCO}_3^-)$ and $K_b(\text{HCO}_3^-)$ to determine predominant reaction for $\text{HCO}_3^-_{(\text{aq})}$.

$$K_a(\text{HCO}_3^-) = 5.6 \times 10^{-11}$$

$$K_b(\text{HCO}_3^-) = \frac{K_w}{K_a(\text{H}_2\text{CO}_3)} = \frac{1.0 \times 10^{-14}}{4.3 \times 10^{-7}} = 2.3 \times 10^{-8}$$

Since $K_b(\text{HCO}_3^-) > K_a(\text{HCO}_3^-)$, the solution will be **BASIC**.

3. 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.

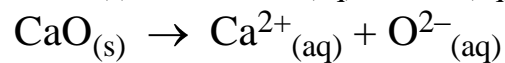
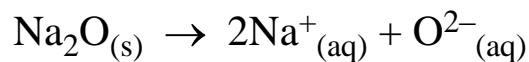


Metal ions from Group 1 or 2 (except Be^{2+}) do not hydrolyze. Other **metal** ions may hydrolyze to produce **acidic** solutions.

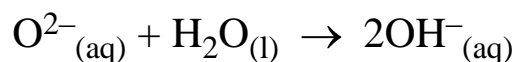
4. Along with salt that hydrolyze there are also certain oxygen-containing compounds, **OXIDES**, that also react with water to produce acidic or basic solutions.

METAL OXIDES

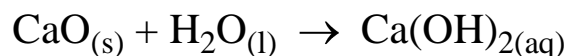
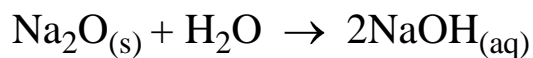
When a metal oxide is added to water, there is an initial dissociation of ions:



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:

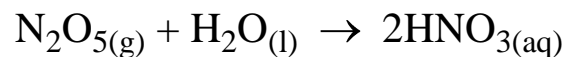
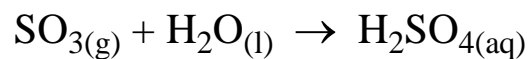


Since both $\text{Na}^+_{(aq)}$ and $\text{OH}^-_{(aq)}$ ions are present in solution, we can write the hydrolysis of $\text{Na}_2\text{O}_{(s)}$ and $\text{CaO}_{(s)}$ as:

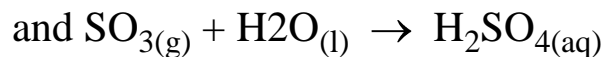
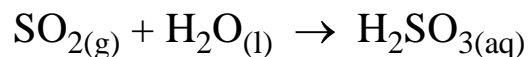
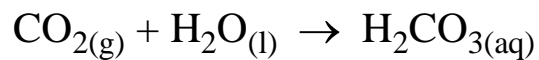


NONMETAL OXIDES

When a nonmetal oxide reacts with water, the water bonds to the existing oxide molecule to produce an **ACIDIC** solution.



Note: the only reactions between **NONMETAL OXIDES** and water that you should know are:



METAL OXIDES produce **BASIC** solutions when dissolved in water and **NONMETAL OXIDES** produce **ACIDIC** solutions when dissolved in water.

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 **Initial – Change – Equilibrium (ICE)** table.

The following information is important for solving K_a problems:

- [HA], the initial concentration of the weak acid
- K_a for the acid
- [H_3O^+] or pH of the acid solution

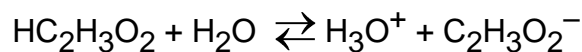
There are three types of K_a problems to be solved:

- given [HA] and K_a , find [H_3O^+] (or pH)
- given [HA] and [H_3O^+] (or pH), find K_a
- given [H_3O^+] (or pH) and K_a , find [HA]

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.



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

Setup an ICE table as follows:

	$HC_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$			
I	0.75 M	–	0.00 M	0.00 M
C	– x	–	+ x	+ x
E	0.75 – x $\approx 0.75^x$	–	x	x

* it is assumed that x 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

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

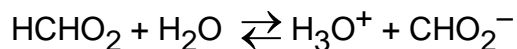
$$x = [H_3O^+] = 3.7 \times 10^{-3}$$

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

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 .



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

Setup an ICE table as follows:

	$HCHO_2 + H_2O \rightleftharpoons H_3O^+ + CHO_2^-$			
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.

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

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

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

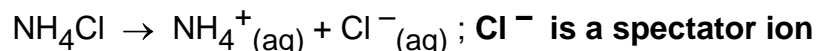
Substitute into the K_a expression:

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

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:



Since K_a for NH_4^+ is in the Table and pH is given, then $[\text{NH}_4^+]$ must be found. The $[\text{NH}_4^+]$ and the volume of the solution is then used to find moles and mass of NH_4Cl .

Set up and ICE table

	$\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3$			
I	y	–	0.00 M	0.00 M
C	– x	–	+ x	+ x
E	y – x	–	x	x

Use pH to find $[\text{H}_3\text{O}^+]_{\text{eq}}$

$$[\text{H}_3\text{O}^+]_{\text{eq}} = \text{antilog}(-4.75) = 1.78 \times 10^{-5} \text{ M} = x$$

At equilibrium:

$$\text{Assume } [\text{NH}_4^+]_{\text{eq}} = y - (1.78 \times 10^{-5}) \approx y$$

$$[\text{H}_3\text{O}^+]_{\text{eq}} = x = 1.78 \times 10^{-5}$$

$$[\text{NH}_3]_{\text{eq}} = x = 1.78 \times 10^{-5}$$

Substituting into the K_a expression:

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{(1.78 \times 10^{-5})^2}{y} = 5.6 \times 10^{-10}$$

$$y = [\text{NH}_4^+] = [\text{NH}_4\text{Cl}] = \frac{(1.78 \times 10^{-5})^2}{5.6 \times 10^{-10}} = 0.565 \text{ M}$$

Finally,

$$\text{mass of NH}_4\text{Cl} = 0.565 \frac{\text{mol}}{\text{L}} \times 1.50 \text{ L} \times \frac{53.5 \text{ g}}{\text{mol}} = \mathbf{45 \text{ g}}$$

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:

- the K_b value must be calculated; cannot be taken directly from Table
- the resulting solution will be basic, not acidic, which means using the $[\text{OH}^-]$ rather than $[\text{H}_3\text{O}^+]$

EXAMPLE 4.13 USING INITIAL CONCENTRATION OF BASE AND K_b TO DETERMINE pH

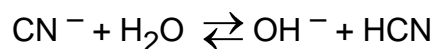
Calculate the pH of a 0.10 M NaCN.

First dissociate the salt:



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

Write the equilibrium equation and K_a expression.



$$K_b = \frac{[\text{OH}^-][\text{HCN}]}{[\text{CN}^-]}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5}$$

Setup an ICE table as follows:

	$\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HCN}$			
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

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

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

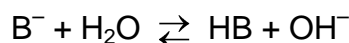
$$\text{pOH} = -\log(1.43 \times 10^{-3}) = 2.845 \quad \text{and} \quad \text{pH} = 14.00 - \text{pOH} = \mathbf{11.15}$$

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



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

Setup an ICE table

	$B^- + H_2O \rightleftharpoons HB + OH^-$			
I	0.50 M	–	0.00 M	0.00 M
C	– x	–	+ x	+ x
E	0.50 – x	–	x	x

Convert pH to $[OH^-]$

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

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

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

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

Substitute into the K_a expression

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

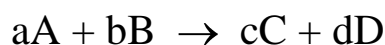
$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{3.81 \times 10^{-7}} = 2.6 \times 10^{-8}$$

L. Acid and Base Titrations

1. A **TITRATION** is a process in which a measured amount of a solution is reacted with a known volume of another solution (one of the solutions has an unknown concentration) until a desired **EQUIVALENCE POINT** (or “**STOICHIOMETRIC POINT**”) is reached.

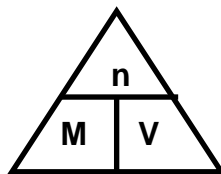
The purpose of titration is to determine the concentration of a particular solution.

The Equivalence point of a reaction occurs when the mole ratio in the reaction exactly equals the mole ratio required by the stoichiometry of the reaction.



$$\frac{\text{moles A}}{\text{moles B}} = \frac{a}{b}$$

2. Recall that **Molarity** = $\frac{\text{mole}}{\text{volume}}$



n = moles in solution

M = molar concentration (molarity)

V = volume in litres

All titration problems involve at least **FIVE PARAMETERS**
concentration of acid **concentration of base** **acid/base mole ratio**
volume of acid **volume of base**

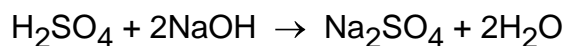
When the reaction equation is given, the acid/base ratio is read directly from the balanced equation so that one of the concentrations or volumes must be known. These problems involve three parts to the calculation:

- use $M = n/V$ to calculate moles of the first substance
- use acid/base ratio to calculate moles of the second substance
- use $M = n/V$ to calculate either the concentration or volume of the second substance

Note: Often when titrations are done, several trials are necessary to check the accuracy. Ideally the volumes added from the burette should agree within $\pm 0.02 \text{ mL}$. As a result, when several volumes are determined for a titration, only the volumes that are within $\pm 0.02 \text{ mL}$ are used to determine the average volume of the titrant. Any volumes that exceed this tolerance are discarded.

EXAMPLE 4.15 CALCULATING CONCENTRATION FROM TITRATION

In the reaction



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 $[\text{H}_2\text{SO}_4]$?

First, calculate moles of first substance

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

Next, use mole ratio

$$\text{moles of H}_2\text{SO}_4 = 0.004747 \text{ moles NaOH} \times \frac{1 \text{ H}_2\text{SO}_4}{2 \text{ NaOH}} = 0.002374 \text{ mol}$$

Finally, calculate concentration

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

3. Titrations are often used to calculate the percentage purity of a solid acid or base. The following steps can be used to calculate percentage purity:

- calculate the concentration of the acid or base using the titration data (**ACTUAL CONCENTRATION**)
- use the mass of the impure solid acid or base to calculate the **EXPECTED CONCENTRATION**
- calculate the percentage purity from the equation:

$$\text{Percentage purity} = \frac{\text{Actual concentration}}{\text{Expected concentration}} \times 100\%$$

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

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

NaHSO_4 is monoprotic, so

$$\text{moles of NaHSO}_4 \text{ used} = \text{moles of NaOH used} = 0.002670 \text{ mol}$$

Next, calculate the $[\text{NaHSO}_4]$ in the 25.00 mL sample

$$[\text{NaHSO}_4] = \frac{n}{V} = \frac{0.002670 \text{ mol}}{0.02500 \text{ L}} = 0.1068 \text{ M (Actual)}$$

Now, calculate the expected $[\text{NaHSO}_4]$

$$[\text{NaHSO}_4] = \frac{3.4786 \text{ g}}{0.2500 \text{ L}} \times \frac{1 \text{ mol}}{120.1 \text{ g}} = 0.1159 \text{ M (Expected)}$$

Finally, calculate percentage purity

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

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. By using titration data it is possible to calculate the moles of the acid or base. The 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

$$\text{moles of acid} = \text{moles of KOH} = 0.002046 \text{ mol}$$

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

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

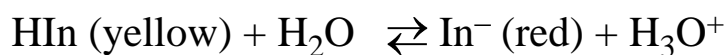
Finally, calculate the molar mass

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

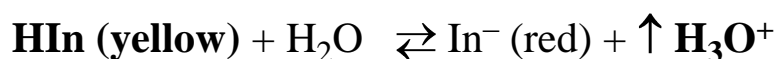
M. Indicators

1. An **INDICATOR** is a 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:

**IN ACID**

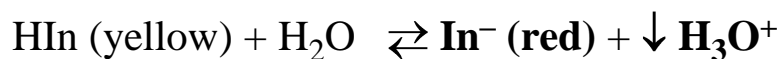
When an indicator is placed into an acid solution, the excess H_3O^+ causes a shift in the indicators equilibrium



An indicator is in its **CONJUGATE ACID (HIn)** form when in **HIGHLY ACIDIC** solutions.

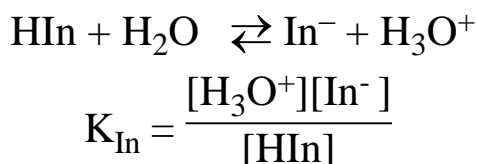
IN BASE

When an indicator is placed into a base solution, the OH^- reacts to decrease the $[\text{H}_3\text{O}^+]$ and causes a shift in the indicators equilibrium



An indicator is in its **CONJUGATE BASE (In⁻)** form when in **HIGHLY BASIC** solutions.

2. When a base is added to an acidic solution then at some point $[\text{HIn}] = [\text{In}^-]$. At this point, the indicator is half way through its colour change because there equal numbers of molecules in the acid and base form. This point is called the **END POINT** or **TRANSITION POINT** for the indicator.



At the transition point $[\text{HIn}] = [\text{In}^-]$, so

$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} = [\text{H}_3\text{O}^+]$$

In addition,

$$-\log K_{\text{In}} = -\log [\text{H}_3\text{O}^+]$$

$$\text{p}K_{\text{In}} = \text{pH}$$

At the transition point of any indicator, the following are true:

$$[\text{HIn}] = [\text{In}^-]$$

$$K_{\text{In}} = [\text{H}_3\text{O}^+]$$

$$\text{p}K_{\text{In}} = \text{pH}$$

3. Usually tables don't list specific values for K_{In} but instead, list ranges over which colour change occurs. The transition point of an indicator will occur at the mid-point of the indicators pH range.

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.

Assume that $[HIn] = [In^-]$ midway through the pH range.

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

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

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

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

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

EXAMPLE 4.19 USING INDICATORS TO DETERMINE pH OF A SOLUTION

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

What colour will each of the following indicators be in a pH 3.5 solution? Methyl violet, methyl orange, phenol red, and thymol blue.

Look up pH range of each indicator in data booklet.

methyl violet → blue
yellow – blue
(0.0 — **1.6**)

methyl orange → red
red – yellow
(**3.2** — 4.4)

phenol red → yellow
yellow – red
(**6.6** — 8.0)

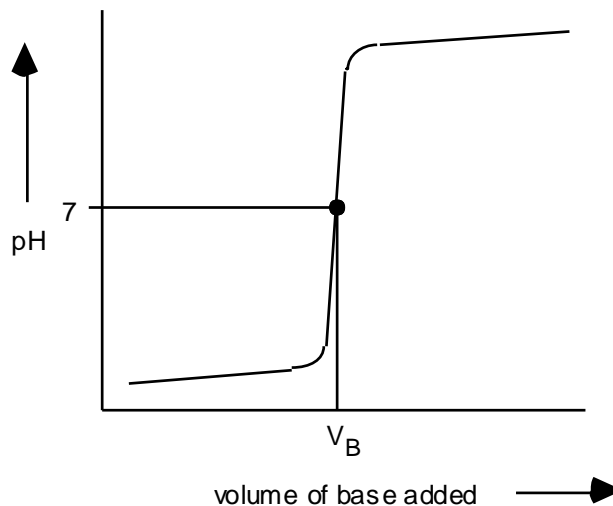
thymol blue → yellow
yellow – blue
(**8.0** — 9.6)

N. Titration Curves

1. In order to carry out a titration, you must start with a solution with an accurately known concentration. Such a solution is called a **STANDARD SOLUTION** or a **STANDARDIZED SOLUTION**. A standard solution is used to titrate other solutions and determine their concentrations. 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. Such a substance is called a **PRIMARY STANDARD**.
e.g. Potassium hydrogen phthalate $\text{KHC}_8\text{H}_4\text{O}_4$
Oxalic acid dihydrate $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
 - b) Titrating a base with an acidic primary standard.
2. As part of Chemistry 12, you will need to be able to look at the details of the shapes of titration curves and establish some “rules of thumb” which allow you to predict the approximate pKa values of the indicators needed to find the equivalence point of titrations.

Titration of a **STRONG ACID** with a **STRONG BASE**

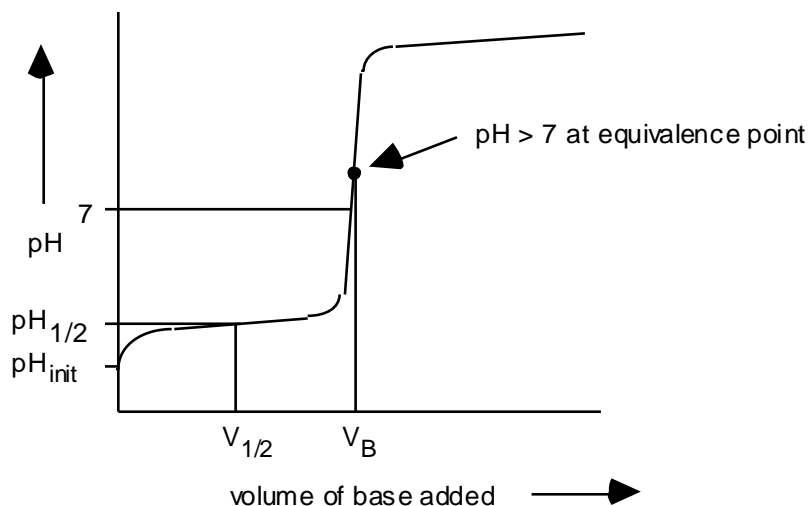
- The following titration curve is typical of when a **strong acid** is titrated with a **strong base**.



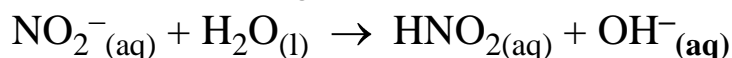
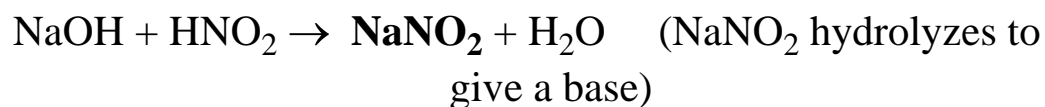
- V_B is the volume of the base required to reach the equivalence point.
 - The pH rises almost vertically around the value of V_B .
 - The salt that is formed when a **STRONG ACID** is titrated with a **STRONG BASE** titration is **NEUTRAL** in solution. As such, V_B can be found by determining the volume required to reach $\text{pH} = 7$.
- $\text{NaOH} + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O}$ (NaCl does not hydrolyze)
- The titration requires an **indicator which changes colour around $\text{pH} = 7$** ; that is, has a $\text{pK}_a = 7$

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**.



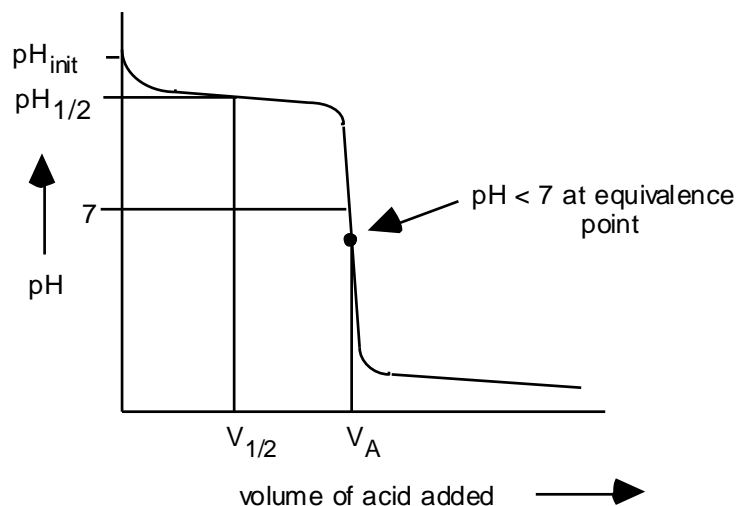
- There is an initial upswing in the pH at the start of the titration.
- The salt that is formed when a **WEAK ACID** is titrated with a **STRONG BASE** titration is **BASIC** in solution. As such, the **pH at the equivalence point is greater than 7**.



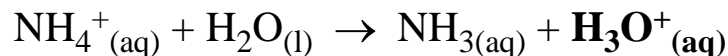
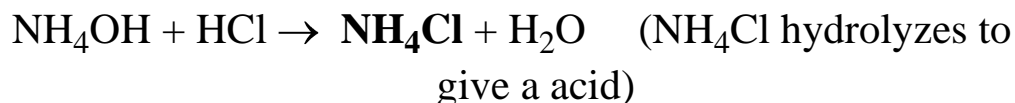
- The titration requires an **indicator which changes colour at pH > 7**; that is, has a $pK_a > 7$ ($pK_a = 8 - 10$).

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**.



- 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.
- The salt that is formed when a **WEAK BASE** is titrated with a **STRONG ACID** titration is **ACIDIC** in solution. As such, the **pH at the equivalence point is less than 7**.



- The titration requires an **indicator which changes colour at pH < 7**; that is, has a $\text{pK}_a < 7$ ($\text{pK}_a = 4 - 6$).

STRONG ACID + STRONG BASE → neutral (pH = 7)

weak acid + STRONG BASE → basic (pH > 7)

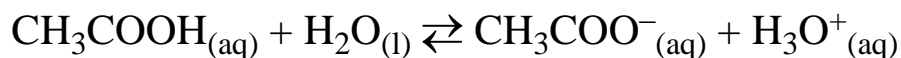
STRONG ACID + weak base → acidic (pH < 7)

Note: When choosing an indicator for a titration, you need to choose an indicator that changes colour near the pH of the equivalence point.

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 for phenolphthalein.

O. Buffers

1. A **BUFFER** is a solution containing appreciable amounts of a weak acid and its conjugate weak base (usually close to equal concentrations of acid and base).



When a solution is buffered, its solutes protect it against large changes in pH even when strong acids or bases are added.

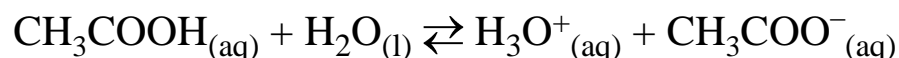
$$K_a = \frac{[\text{CH}_3\text{COO}^{-}][\text{H}_3\text{O}^{+}]}{[\text{CH}_3\text{COOH}]}$$

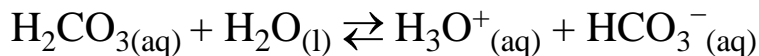
Since $[\text{CH}_3\text{COOH}] = [\text{CH}_3\text{COO}^{-}]$

$$K_a = [\text{H}_3\text{O}^{+}]$$

$$\text{p}K_a = \text{pH}$$

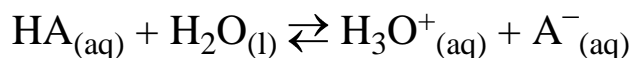
2. Buffers usually consist of two solutes
 - a weak Brønsted acid, HA,
 - its conjugate base, A^{-} , soluble salt of the acid, such as NaA.



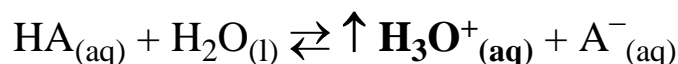


3. Buffers are equilibriums that work by shifting to reduce the effects of adding acid or base.

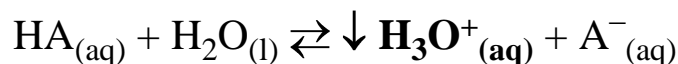
Consider



If H_3O^+ is added the $[\text{H}_3\text{O}^+]$ increases and the equilibrium shifts left:



If OH^- is added it combines with H_3O^+ to form water and $[\text{H}_3\text{O}^+]$ decreases and the equilibrium shift right:



Note: The equation that describes a buffer is simply a Brønsted–Lowry equilibrium equation. However, a solution of CH_3COOH or H_2CO_3 by itself does not make a buffer because there must also be large amounts the conjugate base present in order for the buffer to protect against addition of H_3O^+ .

4. 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.

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

EXAMPLE 4.21 CALCULATING THE pH OF A BUFFER

A buffer is made by adding 0.11 M $\text{NaC}_2\text{H}_3\text{O}_2$ to 0.090 M $\text{HC}_2\text{H}_3\text{O}_2$. 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.

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

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

5. 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 **$\text{pK}_a = \text{pH} \pm 1$** .

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 moles of acetic acid is needed.

Note: Buffers are solutions that contain solutes that prevent large changes in pH even when strong acid or strong base is added.

Buffers contain a weak acid (or base) and the salt of its conjugate base (or acid).

A buffer works best when its pK_a is close to the desired pH.

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

Acidic buffers are made from weak acids while basic buffers are made from weak bases.