

# Acids and Bases

Acids and Bases are Electrolytes, as are salts. An electrolyte is a substance that produces ions when dissolved to form an aqueous solution

The properties of acids and bases have been well known for many hundreds of years and many industrial and agricultural processes depend on them.

## Properties of Acids and Bases (Operational Definition)

### Acids

- (1) They react with active metals such as Zinc or Magnesium to liberate HYDROGEN gas. e.g.  $2\text{HCl}_{(aq)} + \text{Zn}_{(s)} \longrightarrow \text{ZnCl}_{2(aq)} + \text{H}_{2(g)}$
  - (2) They have a SOUR Taste, a property that should be accepted as a fact – no tasting!! (The man who discovered that sulfuric acid tasted sour was posthumously awarded the Nobel Prize for Idiocy in 1923.)
  - (3) Acids conduct electricity (electrolytes).
  - (4) They turn the indicator Litmus, a red colour.
  - (5) they react with metal carbonates to release carbon dioxide gas. (Test for  $\text{CO}_2$  ??)
- Most acids are corrosive to metals and organic matter and quickly destroy tissue (skin, bone, etc.). They should be handled with extreme caution. ACIDS ARE DANGEROUS CHEMICALS.

### Bases

- (The term base replaced the term alkali as meaning the opposite of an acid)
- (1) Bases have a BITTER taste. (Again, accept this as a fact)
  - (2) Bases feel slippery. (They are forming a soap by dissolving the fats in the skin of your fingers.)
  - (3) Being electrolytes, bases conduct electricity in solution.
  - (4) Bases such as Sodium Hydroxides, NaOH, (LYE or Caustic Soda) are used as industrial cleaners and cause severe burns and inflammation to skin. They should be handles with care.
  - (5) Bases turn the indicator Litmus, a Blue colour.
- Bases react with acidic solutions to destroy or neutralize the acidic properties.  
Conversely, Acids can be used to neutralize bases.

### Nomenclature of Acids

The name of a binary acid is related to the parent anion (the anion that combines with  $\text{H}^{1+}$  to form the acid). Binary acids have the prefix **hydro-** and the suffix **-ic acid**

$\text{F}^{-1}$	fluoride	HF	hydrofluoric acid
$\text{Br}^{-1}$	bromide	HBr	hydrobromic acid

Acids formed from oxyanions are called **oxyacids**. If the anion ends in **-ate**, (i.e one more oxygen than the **-ite**), then the corresponding acid will have the suffix **-ic acid**. If the anion ends in **-ite** (less oxygen, then the acid will be **-ous acid**, (one less oxygen in the formula than the **-ic acid**).

Two less oxygen in the formula than the **-ic acid**  $\longrightarrow$  **hypo ~ -ous acid**  
(Hypo ~ -ite ion)

One more oxygen in the formula than the **-ic acid**  $\longrightarrow$  **per ~ -ic acid**  
(Per ~ -ate ion)

Prefixes in the names of the anions are retained. Some examples are:

Some examples are: Chloric acid	$\text{HClO}_3$	Chlorate ion	$\text{ClO}_3^{-1}$
Chlorous acid	$\text{HClO}_2$	Chorite ion	$\text{ClO}_2^{-1}$
Hypochlorous acid	HClO	hypochlorous ion	$\text{ClO}^{-1}$
Perchloric acid	$\text{HClO}_4$	perchlorate ion	$\text{ClO}_4^{-1}$

## Three Definitions of Acids and Bases (Conceptual Definitions)

### I: Arrhenius Theory (1885)

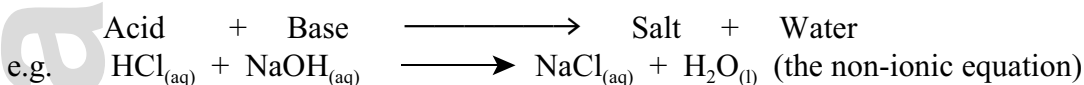
In 1887, the Swede Svante Arrhenius, presented the idea of electrolytic dissociation in his Ph.D. thesis (which earned him a minimal passing grade). In 1903, the Royal Swedish Academy of Sciences awarded the Nobel Chemistry prize for that same work.

Electrolytic dissociation explained why dissolving substances make their solutions strong or weak conductors, or remain nonconductors like the solvent. Substances which dissolve to make strongly conducting solutions are **strong electrolytes**; substances which dissolve to make weak conducting solutions are **weak electrolytes**. **Acids and bases are electrolytes**. The Arrhenius theory of acids and bases can be stated as follows:

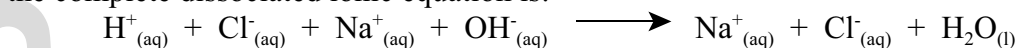
- Arrhenius defined an acid as a substance that produces hydrogen ions,  $H^+$ , (a.k.a *proton*, why?), when dissolved in water.
- He defined a base as a substance that produces hydroxide ions,  $OH^-$ , when dissolved in water

\*These definitions would imply that all acids must have hydrogen in their formulas and all bases must have hydroxides in their formulas. This is partly true, but most hydrogen-containing compounds are NOT acids and some bases do not have hydroxide in their formulas.

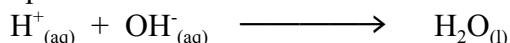
According to the Arrhenius definitions, when equal molar quantities of acid and base are mixed in water, the resulting solution is neither acidic nor basic, but neutral. Such reactions are called **neutralization** reactions.



the complete dissociated ionic equation is:



the net - ionic equation is:



By Arrhenius' definition, in addition to acids and bases, salts are **electrolytes**.

Hydrochloric acid is clearly an Arrhenius acid. However, when dissolved in toluene (a non-polar) solvent, the solution does not conduct electricity, nor does the solution produce hydrogen gas when magnesium is added. Arrhenius did not explain this clear importance of the role of the solvent.

Sodium phosphate, and sodium carbonate react with the acid base indicator litmus to produce blue (the colour produced by a base), and ammonium chloride and aluminum nitrate cause litmus to turn red (the colour produced by an acid). Other salts are neutral. That none of these compounds directly produce hydrogen ions or hydroxide ions, and that the solvent plays a key role in acid – base character, showed a great hole in the Arrhenius definitions of acids and bases.

Arrhenius definition is limited to reactions in water, it does not allow for non-aqueous solvents and for gas phase reactions. This model explains the constant heat of neutralisation, (see later notes on Thermodynamics), of strong acids and strong bases, and the Arrhenius definition also explains the fact that acids catalyse certain reactions and the catalytic effect of acids increases as the number of hydrogen ions increases in the solution

## II: The Bronsted-Lowry definition of acids and Bases (1925)

*This concept allows for non-aqueous solvents and for gas phase reactions.*

In 1923 the Dane Johannes Bronsted and Englishman Thomas Lowry independently developed a new theory of acids and bases:

- Acid is defined as a proton donor ( $H^+$  is a proton)
- Base is defined as a proton acceptor.

*\* Bronsted-Lowry is the preferred definition*

Thus, a:

Bronsted – Lowry **acid** is said to be a **hydrogen ion donor**, and a  
Bronsted – Lowry **base** a **hydrogen ion acceptor**.

Hence,  $NH_3$  and  $Cl^-$  are both Bronsted -Lowry bases because they accept protons. However, they can not be called Arrhenius bases since in aqueous solution they do not dissociate to form  $OH^-$ . The advantage of the Bronsted-Lowry concept of acids and bases is that it is not limited to aqueous solutions.

The relationship is:  $Acid \rightleftharpoons Base + H^+$

All acids, HA, have a base associated with them, B $^-$ :  $HB \rightleftharpoons H^+ + B^-$

The acid and base which are related in this way, by the exchange of a proton, are called a **conjugate acid - base pair**. Since,

and  $Acid_1 \rightleftharpoons Conjugate\ base_1 + H^+$   
 $Base_2 + H^+ \rightleftharpoons Conjugate\ acid_2$

a reaction between an acid and a base is



$Acid_1$  is transformed into its conjugate base, and  $Base_2$  is transformed into its conjugate acid. No substance can act as an acid in solution unless a base is present to accept a proton: the reactions of acids are reactions between acids and bases. Similarly, all reactions of bases in solution are acid-base reactions.

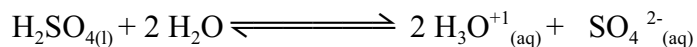
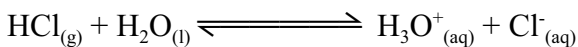
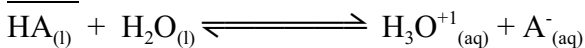
[John L. Park, notes that Bronsted – Lowry acids “donate” hydrogen ions the way a pickpocket’s victim donates their wallet; the proton is pulled away by the base (-- the proton acceptor).]

According to the Bronsted – Lowry definition of an acid, in water, the acid molecule donates a proton to water, thus forming, the “hydronium ion,”  $H_3O^+$  ( by means of a covalent bond known as a co-ordinate or a dative bond, -- write the equation for this reaction please).

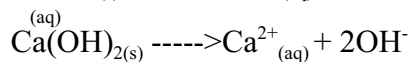
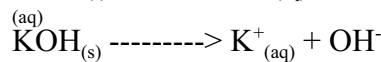
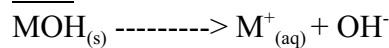
According to the Bronsted – Lowry definition of a base, hydroxide compounds dissociate to produce a free  $OH^-$  ion, which readily react with protons to form water. Ammonia has no hydroxide, however, it is a base because it does react with water to receive a proton and become  $NH_4^+$ :  $NH_{3(g)} + H_{2O(l)} \rightleftharpoons NH_{4(aq)}^+ + OH_{(aq)}^-$

## Ionization of acids and bases in water

Acid:

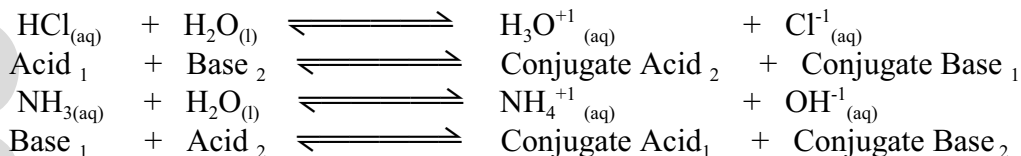


Base:



The Hydronium Ion,  $\text{H}_3\text{O}^{+}_{(aq)}$  is a water molecule with an attached proton, formed by a **co-ordinate bond**. Draw the Lewis Structure of the Hydronium Ion,  $\text{H}_3\text{O}^{+}_{(aq)}$ :

## Examples of Conjugate Acid - Base Pair



Notice several things:

1. Water can act as both a Bronsted acid or a Bronsted base. In other words it can either accept or donate a proton. This leads to the term “**Amphiprotic**”, can either be ... ?
2. There are several related pairs of molecules and ions in each equation.

**Molecules / ions that differ by only a proton are referred to as conjugate acid-base pairs.**

$\text{NH}_3 / \text{NH}_4^{+}$  are conjugate acid base pairs (which will always be the acid, which the base?)

$\text{H}_2\text{O} / \text{OH}^{-}$  are also conjugate acid / base pairs. The proton is the only difference.

**Monoprotic** acids donate or accept one proton per mole, **polyprotic** acids donate more than one proton per mole. Some substances can act as either as an acid or as a base, they are known as **amphiprotic**.

Aqueous forms of the following molecules have the following names:

### **Monoprotic Acids**

HF

$\text{HNO}_3$

$\text{CH}_3\text{COOH}$

HCl

$\text{HNO}_2$

HBr

$\text{HClO}_4$

HI

$\text{HClO}_3$

### **Diprotic Acids**

$\text{H}_2\text{CO}_3$

$\text{H}_2\text{SO}_4$

$\text{H}_2\text{SO}_3$

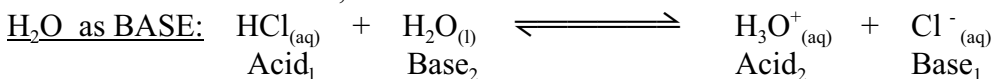
### **Triprotic Acids**

$\text{H}_3\text{PO}_4$

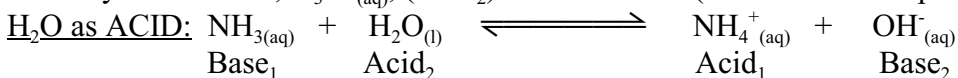
The **STRENGTH** (degree of ionization-dissociation) of an **ACID depends on the acid's CONJUGATE BASE (ANION)**.

\*Note: Since  $\text{H}^{+}$  is common to all Bronsted-Lowry acids, it cannot be a factor that determines an acid's strength.\*

Water is **AMPHIPROTIC**, it can act as an acid or a base.

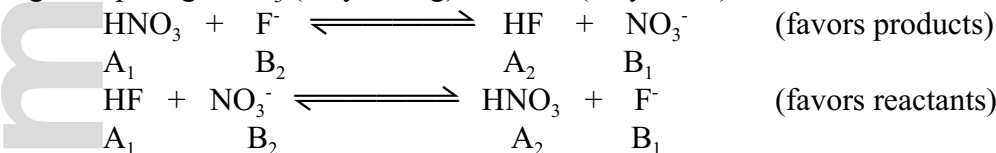


Again the reaction lies almost 100% to the right, since HCl (Acid<sub>1</sub>) is a very strong acid while hydronium ion, H<sub>3</sub>O<sup>+</sup><sub>(aq)</sub>, (Acid<sub>2</sub>) is a weak acid (it holds on to its proton-it is stable)

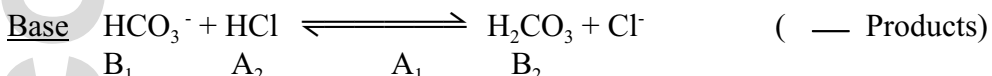


Here, the reactants are favored because the ammonium ion, NH<sub>4</sub><sup>+</sup>, is a stronger acid than water. (That is why solutions of ammonium hydroxide always smell of ammonia, NH<sub>3(g)</sub>.)  
The STRONGEST ACID ALWAYS DISSOCIATES WITH RESPECT TO THE WEAKEST ACID IN THE CONJUGATE PAIR.

e.g. comparing HNO<sub>3</sub> (very strong) with HF (very weak).



The bicarbonate ion, HCO<sub>3</sub><sup>-1</sup>, is both an acid and a base, i.e amphiprotic, depending on the conditions.



### III: Lewis Acids and Bases

Development of Organic Chemistry provided many examples of substances that could act as acids and bases, even if they did not accept or donate protons. Gilbert N. Lewis (of Lewis diagram and valence electron fame) introduced a new definition of acids and bases, even more general than that of Bronsted – Lowry. Lewis' are the most inclusive definitions.

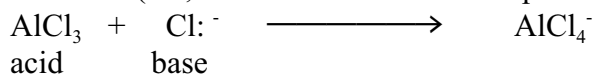
Lewis considered acid base reactions in terms of the exchange of electron pairs, rather than protons (hydrogen ions).

**An acid is a molecule or ion that can accept an electron pair.**

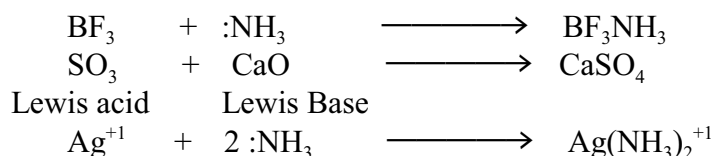
**A base is a molecule or ion that can donate an electron pair.**

The Lewis definition of a base is consistent with the Bronsted – Lowry definition. If an electron pair is available for donation, that electron pair can be used to accept a proton. The definition of an acid was greatly broadened by Lewis. Lewis removed the requirement for a proton, and thus an acid could be anything able to form a covalent bond by accepting an electron pair.

Among the species considered acids, only by the Lewis definition, are substances, such as boron trifluoride, BF<sub>3</sub>, and aluminum chloride, AlCl<sub>3</sub>, which have central atoms without a lone pair, but also without an octet of valence electrons. These substances are able to form coordinate covalent bonds (i.e., where both electrons are provided by one atom/ion):



Other rather different varieties of Lewis acids also exist:



## Strength of Acids and Bases (strong acid vs weak acid)

### Demo:

Up until now we expect or assumed that all acids and bases react completely with water to form hydronium / hydroxide ions respectively. Not so! What do the results of the conductivity test tell you?

The fact that ethanoic acid, (acetic acid), produces a less bright light suggests there are fewer ions in solution.  $\text{CH}_3\text{COOH}$  does not produce ions completely when dissolved.

What are the conjugate acid and bases for the following reactants?



Notice that an equilibrium is set up. This will then have an equilibrium constant which takes the form:

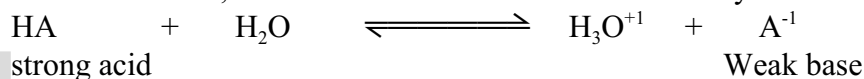
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Water is not shown in the expression because it is a pure liquid, therefore its concentration is constant. The constant is known as the **acid dissociation constant** and is given the designation:  $K_a$

There are also **base ionization constants**,  $K_b$ . This leads to a further classification of acids and bases known as **strong and weak**.

**def: A strong acid or base dissociates almost completely into its ions in solution (100% dissociation).** \*Naturally, strong acids or bases are strong electrolytes.

\*Conversely, weak acids or bases do NOT dissociate to any great extent when dissolved in water. Therefore, weak acids and bases are weak electrolytes.



The  $K_a$  is very \_\_\_\_\_ for strong acids. The equilibrium lies very far to the \_\_\_\_\_. The strong acid, HA, really wants to donate its protons. The conjugate base, \_\_\_\_\_, is very weak because it really does not want to take in, accept protons.

**A strong acid yields a weak conjugate base.**

NEVER confuse the strength of an acid (or base) with its concentration.

\*One can have

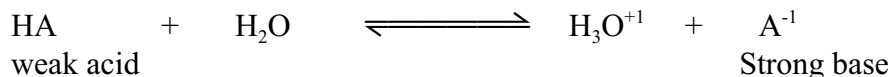
- (i) a concentrated strong acid (dangerous)
- (ii) a dilute strong acid
- (iii) a concentrated weak acid
- (iv) a dilute weak acid (vinegar)

\*Whether an acid is strong or weak depends on its chemical formula and is thus a property of that acid

\*Concentrations depends simply on how much one dissolves. Generally, anything above  $2 \text{ mol dm}^{-3}$  is concentrated and anything below  $0.2 \text{ mol dm}^{-3}$  is dilute. (Completely arbitrary numbers).

## Weak Acids

A weak acid is one in which the acid is only partially ionized in solution. The  $K_a$  is very \_\_\_\_\_. Generally the COOH group associated with organic acids is weak.



Here the equilibrium lies far to the \_\_\_\_\_. Most of the acid is still there as HA. This time the conjugate base  $\text{A}^{-1}$  is better at accepting a proton than water. Hence the **weak acid has a strong conjugate base** (stronger than water).

**Strong Acids:** HI, HBr, HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$

\*All these compounds dissociate practically completely into ions when dissolved to make an aqueous solution.

**Weak Acids:**  $\text{CH}_3\text{COOH}$ , (ethanoic acid),  $\text{C}_6\text{H}_5\text{COOH}$ , (benzoic acid), HF,  $\text{H}_3\text{PO}_4$

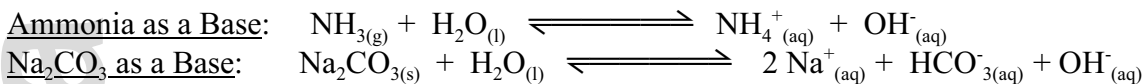
\*These compounds do not ionize very much in water, but exist primarily in the form of molecules. The latter, phosphoric acid, could be considered as a medium strength acid.

**Strong Bases:** NaOH, KOH,

Group 2 elements form the strong hydroxides;  $\text{Mg}(\text{OH})_2$ ,  $\text{Ca}(\text{OH})_2$ ,  $\text{Ba}(\text{OH})_2$ , and  $\text{Sr}(\text{OH})_2$

**Weak Bases:**  $\text{Al}(\text{OH})_3$ ,  $\text{NH}_3$ ,  $\text{Na}_2\text{CO}_3$

\*NB: Ammonia and sodium carbonate do not have an  $\text{OH}^-$  ion, but they are Bronsted-Lowry bases because they are proton acceptors.



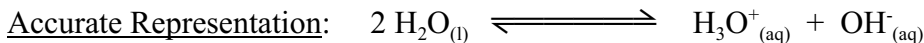
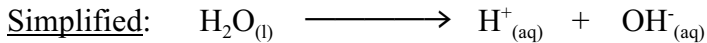
\*There is an increase in the concentration of  $\text{OH}^-$ .  $\text{HCO}_3^-$  is known as the hydrogen carbonate ion or bicarbonate ion. Sodium carbonate is a salt which acts as a weak base in water and it was used as a water softener (washing soda).

## Summary

Definition	Acid	Base
Arrhenius	produces $\text{H}^{+1}$	produces $\text{OH}^{-1}$
Bronsted-Lowry	proton donor	proton acceptor
Lewis	electron-pair acceptor	electron-pair donor

The Bronsted-Lowry description of acids and bases lends itself readily to a quantitative treatment of the strengths of acids and bases. No such quantitative treatment is possible for Lewis acids and bases.

## THE AUTO - IONIZATION OF WATER



\*Water is AMPHIPROTIC, which means it can act as an Acid or a Base. i.e. One of the water molecules acts as a Bronsted-Lowry acid (proton donor), while the second water molecule acts as a Bronsted-Lowry base (proton acceptor).  
Water will “self-ionize”, i.e undergo auto-ionization to a small extent:



(1) the equilibrium expression for this process is thus:

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

(2) however, in pure water and dilute solutions, the water concentration (and the value of  $[\text{H}_2\text{O}]^2$ ) is essentially constant:  $55.5 \text{ mol dm}^{-3}$ ,  $(55.5 \text{ mol dm}^{-3})^2$ . { $1000 \text{ g L}^{-1}$  or  $55.49 \text{ mol dm}^{-3}$ }

The value of  $K_c \times [\text{H}_2\text{O}]^2$  is called the **ionic product constant of water, or  $K_w$** .

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

(3) as with any other equilibrium constant,  $K_w$  is temperature dependent.

At **25°C** (standard temperature), the value of  **$K_w$  is  $1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$**

(4)  $\text{p}K_w = -\log_{10} K_w = -\log_{10} (1.0 \times 10^{-14}) = 14$

What is the effect of an increase of temperature on (a) the equilibrium, (b)  $[\text{H}^+]$  (c)  $[\text{OH}^-]$ , (d) pH and (e)  $K_w$

\*The concentration of hydrogen ion  $[\text{H}^+]$ , in pure water is very small being  $1.00 \times 10^{-7} \text{ mol dm}^{-3}$ . The Hydroxide concentration in pure water is also  $1.0 \times 10^{-7} \text{ mol dm}^{-3}$ . This is at 25 °C. Thus water is a very weak electrolyte and with  $[\text{H}^+] = [\text{OH}^-] = 1.0 \times 10^{-7}$  is practically a NON-electrolyte.

For neutral water,  $K_w = 1.0 \times 10^{-14} \text{ mol}^2\text{dm}^{-6}$   
 $= [\text{H}_3\text{O}^+][\text{OH}^-]$   
 $= (1.0 \times 10^{-7} \text{ mol dm}^{-3})(1.0 \times 10^{-7} \text{ mol dm}^{-3})$

i.e.  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$

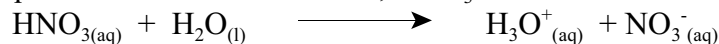
Since:  $K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$

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

Thus, for dilute solutions of strong acids and bases, the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  can be easily calculated:



**Example 1:** What are the hydronium and hydroxide ion concentrations in a 0.040 mol dm<sup>-3</sup> aqueous solution of nitric acid, HNO<sub>3</sub> at 25°C.



As nitric acid is a strong acid, it dissociates 100%. The hydronium ion concentration, [H<sub>3</sub>O<sup>+</sup>], is thus that of the nitric acid, 0.040 mol dm<sup>-3</sup>.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Rearranging and substituting:

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.0 \times 10^{-14} (\text{mol dm}^{-3})^2}{0.040 \text{ mol dm}^{-3}} = 2.5 \times 10^{-13} \text{ mol dm}^{-3}$$

therefore, a 0.040 mol dm<sup>-3</sup> nitric acid solution has a [OH<sup>-</sup>] of 2.5 x 10<sup>-13</sup> mol dm<sup>-3</sup>

**NOTE:**

- (1) as illustrated in the example above, addition of small amounts of acid (and similarly for base) has a dramatic effect on hydronium ion and hydroxide ion concentrations. Adding acid dramatically lowers the OH<sup>-</sup> concentration; adding base dramatically lowers the H<sub>3</sub>O<sup>+</sup> concentration.
- (2) Hydronium and hydroxide ion concentrations are extremely important in many contexts (e.g., a relatively minor change of [H<sub>3</sub>O<sup>+</sup>] is not compatible with life). As seen above, these concentrations can vary over very broad ranges. In 1909, the Danish biochemist Soren P. Sorenson introduced the **pH scale**. The analogous pOH scale followed.

**The pH of a solution is “the negative logarithm, to the base ten, of the hydronium ion concentration”:**

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

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

- (3) since a neutral solution at 25°C has a hydronium ion concentration, [H<sub>3</sub>O<sup>+</sup>] of 1.0 x 10<sup>-7</sup> mol dm<sup>-3</sup>, a neutral solution has pH = 7

$$\text{pH} = -\log_{10} [1.0 \times 10^{-7} \text{ mol dm}^{-3}] = \mathbf{7.00}$$

- (4) solutions with pH less than 7 are acidic; solutions with pH greater than 7 are basic.
- (5) the pH of most aqueous solutions fall in the range 0 to 14. However, pH values of highly acidic solutions may be negative; pH values of highly basic/alkaline solutions can be greater than 14.

**Example 1:** What is the pH of **0.040 mol L<sup>-1</sup>** nitric acid solution?

$$\text{pH} = -\log_{10} [0.040 \text{ mol L}^{-1}] = -(-1.40) = \mathbf{1.4}$$

**Example 2:** What is the hydronium ion concentration of a solution with pH = 12.50 (i.e., an alkaline/basic solution)?

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} \text{ mol} \cdot \text{L}^{-1} = 10^{-12.50} \text{ mol} \cdot \text{L}^{-1} = 3.16 \times 10^{-13} \text{ mol} \cdot \text{L}^{-1}$$

## Concept of pOH

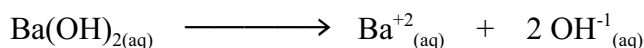
Just as pH is a compact way of presenting the hydronium ion concentration, pOH is a compact way of presenting the hydroxide ion concentration.

**The pOH of a solution is “the negative logarithm, to the base ten, of the hydroxide ion concentration.”**

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

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

**Example 1:** What is the pOH of a solution containing  $0.0050 \text{ mol} \cdot \text{L}^{-1} \text{ Ba(OH)}_2$ , barium hydroxide. (Note: barium hydroxide is rather insoluble, but completely dissociates at concentrations of 0.010 M or less.)



$$[\text{Ba(OH)}_2] = 0.0050 \text{ mol} \cdot \text{L}^{-1} \therefore [\text{OH}^-] = 2 \times 0.0050 \text{ mol} \cdot \text{L}^{-1} = 0.010 \text{ mol} \cdot \text{L}^{-1}$$
$$\text{pOH} = -\log_{10} [\text{OH}^-] = -\log_{10} [0.010 \text{ mol} \cdot \text{L}^{-1}] = -(-2.00) = 2.00$$

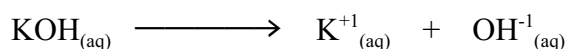
therefore, the pOH of a  $0.0050 \text{ mol} \cdot \text{L}^{-1} \text{ Ba(OH)}_2$  barium hydroxide solution (i.e., a  $0.010 \text{ mol} \cdot \text{L}^{-1} \text{ OH}^-$  solution) is 2.00.

Manipulation of the equations and use of the relationship between  $[\text{H}_3\text{O}^+]$  &  $[\text{OH}^-]$  reveals:

$$\text{pH} + \text{pOH} = \text{pK}_w = 14.00 \quad \text{at } 25^\circ\text{C}$$

This relationship is true of aqueous solutions as well as for water.

**Example 2:** Calculate the pOH and pH of a solution of the strong base KOH with a concentration of  $5.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ .

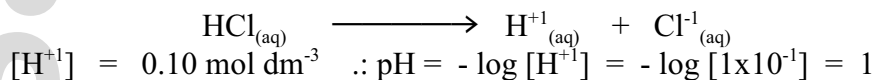


$$\text{pOH} = -\log_{10} [\text{OH}^-] = -\log_{10} [5.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}] = -(-2.30) = 2.30$$

$$\text{pH} + \text{pOH} = 14.00 \therefore \text{pH} = 14.00 - 2.30 = 11.70$$

therefore, this alkaline solution would have a pOH of 2.30 and a pH of 11.70

**Example 3:** What is the pH of a solution of hydrochloric acid of concentration  $0.10 \text{ mol dm}^{-3}$  ?



**Example 4:** What is the pH of a solution of sulphuric acid if 0.098 g of it are dissolved to make  $250 \text{ cm}^3$  solution? ( $\text{H}_2\text{SO}_4 \longrightarrow 2 \text{H}^+ + \text{SO}_4^{2-}$ )

**Example 5:** Calculate the hydroxide ion concentration in a  $0.25 \text{ mol dm}^{-3} \text{ HI}$  solution.  
(Answer:  $4.0 \times 10^{-14} \text{ mol dm}^{-3}$ )

**Example 6:** Calculate the hydroxide concentration in a solution prepared by dissolving 0.37 g of HCl in water to form 250 cm<sup>3</sup> of solution. (Ans.: 2.5 x 10<sup>-13</sup> mol dm<sup>-3</sup>)

**Example 7:** A household cleaner contains 5.00 g of KOH in 2.00 dm<sup>3</sup> of solution. Calculate the [H<sub>3</sub>O<sup>+</sup>] of the cleaning solution. (Ans.: 2.24 x 10<sup>-13</sup> mol dm<sup>-3</sup>)

**Example 8:** Calculate the pH of a solution with a [H<sub>3</sub>O<sup>+</sup>] of 4.7 x 10<sup>-11</sup> mol dm<sup>-3</sup>  
(Ans: The solution has a pH of 10.33)

**Example 9:** Calculate the pOH of a solution with a hydroxide concentration of 3.0 x 10<sup>-6</sup> mol dm<sup>-3</sup>. (Ans. 5.52)

**Example 10:** What is the pOH of a solution whose pH is measured to be 6.4. (Ans. 7.6)

**Example 11:** Calculate the pH, pOH, and [OH<sup>-1</sup>] of each of the following solutions:  
a) 0.0020 mol dm<sup>-3</sup> HBr (b) 0.006 mol dm<sup>-3</sup> HI (c) 0.025 mol dm<sup>-3</sup> HNO<sub>3</sub>  
(Ans: (a) 2.70, 11.30, 5.0 x 10<sup>-12</sup> (b) 2.2, 11.8, 2 x 10<sup>-12</sup> (c) 1.60, 12.40, 4.0 x 10<sup>-13</sup>)

**Example 12:** What mass of KOH is contained in 500 cm<sup>3</sup> of solution that has a pH of 11.5? (Ans: 0.09 g)

**Example 13:** Calculate the pH of a solution prepared by dissolving 4.30 g of Ba(OH)<sub>2</sub> in water to form 1.5 dm<sup>3</sup> of solution. (Ans: 12.53, 1.47)

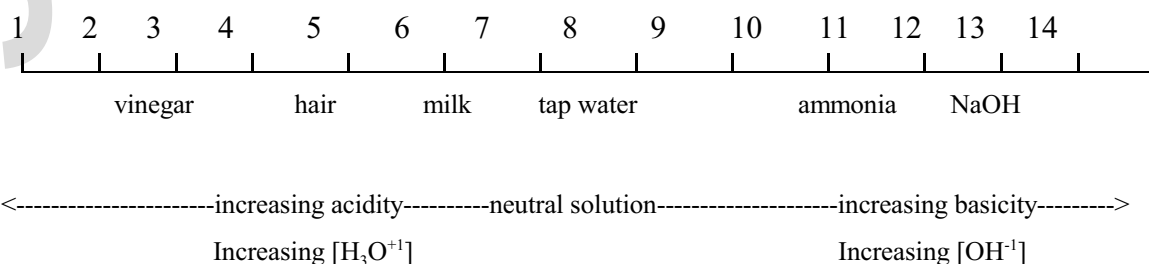
## Acids and Bases : pH

In 1909 a Danish chemist, Soren Sorenson, developed a simplified system for referring to the degree of acidity of a solution. He used the term pH for potenz (power) of hydrogen thus pH refers to the concentration of hydronium (hydrogen) ions in solution. H<sub>3</sub>O<sup>+</sup><sub>(aq)</sub> ranges from about 10 mol dm<sup>-3</sup> down to 1.0 x 10<sup>-15</sup> mol dm<sup>-3</sup> in common aqueous solutions. A range on the order of a quadrillion-to-one can only be expressed by using powers of ten, so pH was based on the following formula:

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

For solutions 1.0 mol/L or less in concentration, pH values range from 0.0 to 14.0. Pure water is considered neutral with a pH of 7.0. pH values lower than 7.0 are acidic, while pH values higher than 7.0 are basic.

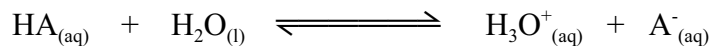
The pH values of some common solutions are given in the pH scale below:



## Approximate pH of Some Common Substances

Substance	$[\text{H}_3\text{O}^+_{(\text{aq})}]$ ( $\text{mol dm}^{-3}$ )	$[\text{OH}^-_{(\text{aq})}]$ ( $\text{mol dm}^{-3}$ )	$[\text{H}_3\text{O}^+_{(\text{aq})}]$ $[\text{OH}^-_{(\text{aq})}]$ [( $\text{mol dm}^{-3}$ ) <sup>2</sup> ]	Typical pH	Actual pH range
1.0 mol/L $\text{HCl}_{(\text{aq})}$	1.0	$1.0 \times 10^{-14}$	$1.0 \times 10^{-14}$	0.0	0.0
limes	$1.3 \times 10^{-2}$	$7.7 \times 10^{-13}$	$1.0 \times 10^{-14}$	1.9	1.8-2.0
gastric juice	$1.0 \times 10^{-2}$	$1.0 \times 10^{-12}$	$1.0 \times 10^{-14}$	2.0	1.0-3.0
lemons	$5.0 \times 10^{-3}$	$2.0 \times 10^{-12}$	$1.0 \times 10^{-14}$	2.3	2.2-2.4
vinegar	$1.3 \times 10^{-3}$	$7.7 \times 10^{-12}$	$1.0 \times 10^{-14}$	2.9	2.4-3.4
Pop	$1.0 \times 10^{-3}$	$1.0 \times 10^{-11}$	$1.0 \times 10^{-14}$	3.0	1.8-4.0
Rhubarb	$8.0 \times 10^{-4}$	$1.3 \times 10^{-11}$	$1.0 \times 10^{-14}$	3.1	3.1-3.2
Apples (and cider)	$8.0 \times 10^{-4}$	$1.3 \times 10^{-11}$	$1.0 \times 10^{-14}$	3.1	2.9-3.3
Wines		$2.5 \times 10^{-11}$	$1.0 \times 10^{-14}$	3.4	2.8-3.8
Beers	$3.2 \times 10^{-5}$	$3.2 \times 10^{-10}$	$1.0 \times 10^{-14}$	4.5	4.0-5.0
Bread (white)	$3.1 \times 10^{-8}$	$3.2 \times 10^{-9}$	$1.0 \times 10^{-14}$	5.5	5.0-6.0
Asparagus	$2.5 \times 10^{-6}$	$4.0 \times 10^{-9}$	$1.0 \times 10^{-14}$	5.6	5.4-5.8
Potatoes	$1.6 \times 10^{-6}$	$6.3 \times 10^{-9}$	$1.0 \times 10^{-14}$	5.8	5.6-6.0
Salmon	$6.3 \times 10^{-7}$	$1.6 \times 10^{-8}$	$1.0 \times 10^{-14}$	6.2	6.1-6.3
Corn	$6.3 \times 10^{-7}$	$1.6 \times 10^{-8}$	$1.0 \times 10^{-14}$	6.2	6.0-6.5
Rain water	$6.3 \times 10^{-7}$	$1.6 \times 10^{-8}$	$1.0 \times 10^{-14}$	6.2	4.0-6.5
Milk (cow)	$3.2 \times 10^{-7}$	$3.2 \times 10^{-8}$	$1.0 \times 10^{-14}$	6.5	6.3-6.6
Saliva	$1.0 \times 10^{-7}$	$1.0 \times 10^{-7}$	$1.0 \times 10^{-14}$	7.0	6.5-7.5
Pure water	$1.0 \times 10^{-7}$	$1.0 \times 10^{-7}$	$1.0 \times 10^{-14}$	7.0	7.0
Blood	$4.0 \times 10^{-8}$	$2.5 \times 10^{-7}$	$1.0 \times 10^{-14}$	7.4	7.35-7.45
Swimming pool water	$4.0 \times 10^{-8}$	$2.5 \times 10^{-7}$	$1.0 \times 10^{-14}$	7.4	7.2-7.6
Eggs (white)	$3.2 \times 10^{-9}$	$3.3 \times 10^{-7}$	$1.0 \times 10^{-14}$	7.8	7.6-8.0
Sea water	$1.0 \times 10^{-11}$	$3.2 \times 10^{-6}$	$1.0 \times 10^{-14}$	8.5	8.0-9.0
Household ammonia	$1.0 \times 10^{-11}$	$1.0 \times 10^{-3}$	$1.0 \times 10^{-14}$	11.0	10.6-11.6
1.0 mol/L $\text{NaOH}_{(\text{aq})}$	$1.0 \times 10^{-14}$	1.0	$1.0 \times 10^{-14}$	14.0	14.0

## THE ACID IONIZATION EQUILIBRIUM CONSTANT, ( $K_a$ )



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \quad \text{p}K_a = -\log_{10} K_a$$

The expression for  $K_a$  does not include  $[\text{H}_2\text{O}]$  because the concentration of water remains constant in dilute solutions. The acid dissociation constant can be calculated from the pH of a solution of the acid of known concentration.

**\*\* For Strong Acids**, which are essentially 100% dissociated,  $K_a$  is VERY LARGE, and  $\text{p}K_a$  is very small. (Products predominated, no undissociated acid).

For STRONG ACIDS ( $K_a$  large),  $\text{A}^-$ , the conjugate base, will be very STABLE in solution and can exist without the proton.

For WEAK ACIDS ( $K_a$  small),  $\text{A}^-$ , the conjugate base will be very UNSTABLE in solution and will cling to its protons.

If  $K_a$  is greater than  $10^{-2}$  the acid is strong, while if it is less than  $10^{-2}$  the acid is considered to be weak.

$$\% \text{ Ionization} = \frac{[\text{H}^+]_{\text{eq}}}{[\text{HA}]_{(\text{INITIAL})}} \times 100$$

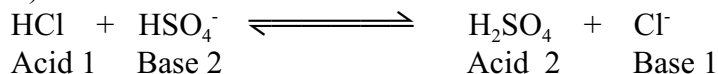
N.B. Except for strong acids, it is not always easy to identify a compound as an acid or a base.

A compound may be classified as an acid, but in the presence of a STRONGER ACID, it acts as a BASE.

e.g. The hydrogen sulfate ion, (a.k.a bisulphate),  $\text{HSO}_4^-$ , is a moderately strong acid:

$\text{HSO}_4^-$  has a  $K_a$  of  $1.3 \times 10^{-2}$  (See page for position.)

■ However, in the presence of HCl, a very strong acid,  $\text{HSO}_4^-$  has to act as a BASE (a proton donor.)



The equilibrium lies to the RIGHT (favours products) because HCl is a stronger acid than  $\text{H}_2\text{SO}_4$ .

## Calculations Involving ionization Constants for Acids and Bases

### **K<sub>a</sub>, K<sub>b</sub> Problems**

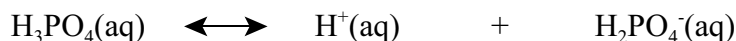
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$\% \text{ Ionization} = \frac{[\text{H}^+]_{\text{eq}}}{[\text{HA}]_{\text{(INITIAL)}}} \times 100$$

$$\% \text{ Ionization} = \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100\% \quad \text{or} \quad \frac{\text{Change}}{\text{Initial}} \times 100\%$$

$$K_w = K_a \times K_b$$

Example1: Given a solution of 0.082 mol/L phosphoric acid, upon reaching equilibrium, testing with indicators showed a hydrogen ion concentration of 0.021 mol/L. Find the K<sub>a</sub> for phosphoric acid.

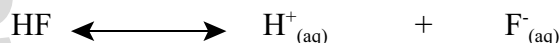


	[H <sub>3</sub> PO <sub>4</sub> ] (mol/L)	[H <sup>+</sup> ] (mol/L)	[H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ] (mol/L)
Initial	0.082	-----	-----
Change	-0.021	+0.021	+ 0.021
Equil <sup>m</sup>	0.061	0.021	0.021

$$\begin{aligned} K_a &= \frac{[\text{H}^+][\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} \\ &= \frac{(0.021)(0.021)}{(0.061)} \\ &= 7.2 \times 10^{-3} \end{aligned}$$

Example2: Determine the pH of a 0.050 mol/L solution of hydrofluoric acid.

(Given: K<sub>a</sub> of HF(aq) is 6.7 x 10<sup>-4</sup>)



	[HF] (mol/L)	[H <sup>+</sup> ] (mol/L)	[F <sup>-</sup> ] (mol/L)
Initial	0.050	-----	-----
Change	- x	+ x	+ x
Equil <sup>m</sup>	0.050 - x	x	x

Let x represent the [H<sup>+</sup>]<sub>E</sub> in mol/L, then x represents [F<sup>-</sup>]<sub>E</sub> in mol/L

$$K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$$

$$6.7 \times 10^{-4} = \frac{(x)(x)}{(0.050 - x)}$$

$$K_a < 1.0 \times 10^{-3}$$

$$6.7 \times 10^{-4} = x^2 / 0.050$$

$$0.050 \gg x$$

$$x = 5.79 \times 10^{-3}$$

$$0.050 - x = 0.050$$

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

$$\text{pH} = -\log(5.79 \times 10^{-3})$$

$$\text{pH} = 2.2$$

## Practice Calculations

**Example 1:** Acetylsalicylic acid (aspirin) is a weak monoprotic acid which can be abbreviated as HAsp. A  $0.100 \text{ mol dm}^{-3}$  solution has a pH of 2.24, calculate the acid ionization constant.

**Example 2:** Ascorbic acid, vitamin C, is a weak monoprotic acid which can be abbreviated as Hasc. It has an acid ionization constant of  $8.0 \times 10^{-5}$ . Calculate the pH of a  $0.100 \text{ mol dm}^{-3}$  solution.

**Example 3:** An acid whose  $K_a$  is  $4.3 \times 10^{-6}$  has a pH of 4.7. Find the concentration of the acid.

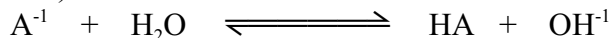
**Example 4:** Calculate the pH of a  $1.00 \times 10^{-2} \text{ mol dm}^{-3}$  solution of butanoic acid,  $\text{C}_3\text{H}_7\text{COOH}$ , for which  $K_a = 1.51 \times 10^{-5} \text{ mol dm}^{-3}$  (Answer: pH = 3.42)

**Example 4:** The pH value of  $0.100 \text{ mol dm}^{-3}$  solutions of  $\text{HCl}_{(\text{aq})}$  and ethanoic acid,  $\text{CH}_3\text{COOH}$ , are 1 and approximately 3 respectively. How does this difference arise?

**Example 5:** If two acids, HA and HB, have  $\text{p}K_a$  values of 3.4 and 4.4, what can you say about the relative strengths of the two acids?

## Calculations Involving Base Ionization Constants $K_b$

In the same way, it is possible to write a  $K_b$  expression for a base,  $\text{A}^{-1}$ , (since the acid is represented by HA) :



$$K_b = \frac{[\text{HA}][\text{OH}^{-1}]}{[\text{A}^{-1}]} \quad \text{p}K_b = -\log_{10} K_b$$

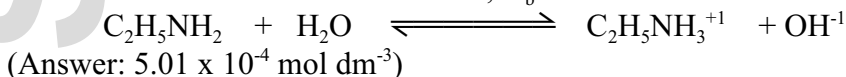
The concentration  $[\text{H}_2\text{O}]$  remains constant and is not included in the equation. The basic dissociation constant can be calculated from the pH of a solution of the base of known concentration.

**The higher the value of  $K_b$ , the lower the value of  $\text{p}K_b$ , and the stronger the base.**

The quantitative measure of strengths of acids and bases provided by the  $K_a$  and  $K_b$  values is an excellent feature of the Bronsted-Lowry treatment of acids and bases. No such quantitative treatment can be made of Lewis acids and bases.

**Example 1:** Caffeine is a weak base that is related to ammonia. For the purposes of this example we can abbreviate its formula to CafN. It has a base ionization constant,  $K_b$ , of  $4.1 \times 10^{-4}$ . Calculate the pH of a  $0.70 \text{ mol dm}^{-3}$  solution

**Example 2:** If the pH of a  $0.100 \text{ mol dm}^{-3}$  solution of ethylamine,  $\text{C}_2\text{H}_5\text{NH}_2$ , is 11.85, what is its basic dissociation constant,  $K_b$ ?



**Example 3:** a solution of dimethylamine,  $(\text{CH}_3)_2\text{NH}$ , of concentration  $1.00 \times 10^{-2} \text{ mol dm}^{-3}$  has a pH of 7.64 at  $25^\circ\text{C}$ . Calculate the dissociation constant,  $K_b$  of the base.  
(Answer:  $K_b = 1.91 \times 10^{-11} \text{ mol dm}^{-3}$ )

**RELATIVE STRENGTHS OF ACIDS IN AQUEOUS SOLUTION AT ROOM TEMPERATURE**

The equation for the ionization is  $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$ .

Since all ions and molecules in water solution are aquated, the (aq) is assumed in the notation. We then write:  $K_a = [H^+][A^-]/[HA]$

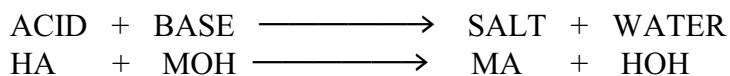
Acid	Strength	Reaction	$K_a$
Perchloric acid	Very strong	$HClO_4 \rightleftharpoons H^+ + ClO_4^{-1}$	Very large
Hydroiodic acid		$HI \rightleftharpoons H^+ + I^-$	Very large
Hydrobromic acid		$HBr \rightleftharpoons H^+ + Br^-$	Very large
Hydrochloric acid		$HCl \rightleftharpoons H^+ + Cl^-$	Very large
Nitric acid		$HNO_3 \rightleftharpoons H^+ + NO_3^-$	Very large
Sulfuric acid	Very strong	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	Very large
Hydronium ion		$H_3O^+ \rightleftharpoons H^+ + H_2O$	1
Oxalic acid		$HOOC-COOH \rightleftharpoons H^+ + HOOC-COO^-$	$5.4 \times 10^{-2}$
Sulfurous acid ( $SO_2 + H_2O$ )		$H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$	$1.7 \times 10^{-2}$
Hydrogen sulfate ion	Strong	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	$1.3 \times 10^{-2}$
Phosphoric acid		$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$	$7.1 \times 10^{-3}$
Ferric ion		$Fe(H_2O)_6^{+3} \rightleftharpoons H^+ + Fe(H_2O)_5(OH)^{+2}$	$6.0 \times 10^{-3}$
Hydrogen Telluride acid		$H_2Te \rightleftharpoons H^+ + HTe^-$	$2.3 \times 10^{-3}$
Hydrofluoric acid	Weak	$HF \rightleftharpoons H^+ + F^-$	$6.7 \times 10^{-4}$
Nitrous acid		$HNO_2 \rightleftharpoons H^+ + NO_2^-$	$5.1 \times 10^{-4}$
Hydrogen selenide		$H_2Se \rightleftharpoons H^+ + HSe^-$	$1.7 \times 10^{-4}$
Chromic ion		$Cr(H_2O)_6^{+2} \rightleftharpoons H^+ + Cr(H_2O)_5(OH)^{+3}$	$1.5 \times 10^{-4}$
Benzoic acid		$C_6H_5COOH \rightleftharpoons H^+ + C_6H_5COO^{-1}$	$6.6 \times 10^{-5}$
Hydrogen oxalate ion		$HOOC-COO^- \rightleftharpoons H^+ + OOC-COO^-$	$5.4 \times 10^{-5}$
Acetic acid	Weak	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	$1.8 \times 10^{-5}$
Aluminum ion		$Al(H_2O)_6^{3+} \rightleftharpoons H^+ + Al(H_2O)_5(OH)^{+2}$	$1.4 \times 10^{-5}$
Carbonic acid ( $CO_2 + H_2O$ )		$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$	$4.4 \times 10^{-7}$
Hydrogen sulfide		$H_2S \rightleftharpoons H^+ + HS^-$	$1.0 \times 10^{-7}$
Dihydrogen phosphate ion		$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$	$6.3 \times 10^{-8}$
Hydrogen sulfite ion		$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$	$6.2 \times 10^{-8}$
Ammonium ion	Weak	$NH_4^+ \rightleftharpoons H^+ + NH_3$	$5.7 \times 10^{-10}$
Hydrogen carbonate ion		$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$	$4.7 \times 10^{-11}$
Hydrogen telluride ion		$HTe^- \rightleftharpoons H^+ + Te^{2-}$	$1.0 \times 10^{-11}$
Hydrogen peroxide	Very weak	$H_2O_2 \rightleftharpoons H^+ + HO_2^-$	$2.4 \times 10^{-12}$
Monohydrogen phosphate ion		$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$	$4.4 \times 10^{-13}$
Hydrogen sulfide ion		$HS^- \rightleftharpoons H^+ + S^{2-}$	$1.2 \times 10^{-15}$
$5.4 \times 10^{-2}$ Water		$H_2O \rightleftharpoons H^+ + OH^-$	$1.8 \times 10^{-16}$
Hydroxide ion		$OH^- \rightleftharpoons H^+ + O^{2-}$	$< 10^{-36}$
ammonia	Very weak	$NH_3 \rightleftharpoons H^+ + NH_2^-$	Very small

↖ Very strong base

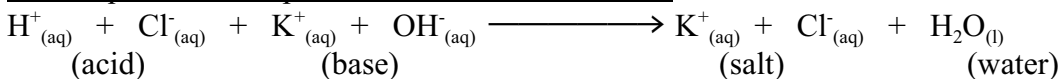


## Neutralization of Acids and Bases

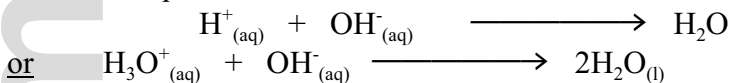
Since the reactive ion of an acid is  $H^+$ , ( $H_3O^+$ ) and the reactive ions of a base is  $OH^-$ , an acid and a base can neutralize each other as follows:



### Ionic Equation for a specific neutralization reaction



### Net Ionic Equation for Neutralization:



Thus, when the hydrogen ion concentrations (of the acid) equals the hydroxide ion concentration (of the base), the net result is an aqueous solution of a salt (a neutral solutions).

If the  $H^+$  concentration is GREATER than the  $OH^-$  concentration, the solution will be acidic.

If the  $H^+$  concentration is LESS than the  $OH^-$  concentration, the solution will be basic.

## Neutralization Reactions: Titration

**Titration** is a volumetric technique used to determine the concentration of a solution.

One solution is used to analyze another.

A titration is a volumetric technique where the concentration of an acid or base is determined using an acid-base indicator:

### Method

A known amount (# moles) of one substance is placed in an **Erlenmeyer flask**. We can calculate the amount either by knowing the mass of a solid reactant, or by knowing the concentration and volume of a reactant in solution.

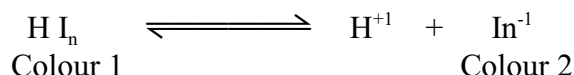
A few drops of an appropriate **indicator** are added to the **Erlenmeyer flask**.

The solution of unknown concentration, also referred to as the **sample**, is placed in a **buret**. A **buret** is a device that can deliver precise volumes of solution. The initial volume reading on the **buret** is taken. Burets can be read to  $\pm 0.02 \text{ cm}^3$ .

The unknown solution is added to the **Erlenmeyer flask**, containing a solution of known solute concentration, called the **titrant**, until the two reactants have been combined in the stoichiometric ratio, which is the ratio given by the chemical equation. This point is called the **equivalence point**. If a good **indicator** has been chosen it should change colour at this point. The point at which the indicator changes colour is call the **end point**.

The final volume reading on the **buret** is taken. The two volume readings (initial and final are used to calculate the total volume of the unknown solution that had been added.) Since most acids and bases are colourless, the EQUIVALENCE POINT and END POINT cannot be determined without the use of an INDICATOR.

INDICATORS are usually weak organic acids or bases that are sensitive to acidity and change COLOR as the solution changes,; because they have different colours in their undissociated and dissociated states:



Example: The molecules  $HIn$  are red, and the anions are,  $In^{-1}$  are blue for litmus indicator. However, if  $[HIn] = [In^{-1}]$ , the indicator appears purple.

Adding  $H^{+1}$  shifts equilibrium to the left,  $\therefore$  colour 1

Adding  $OH^{-1}$  removes  $H^{+1}$  and  $\therefore$  shifts equilibrium to the right, thus colour 1 observed. Indicators are used in low concentrations and therefore do not significantly alter the equivalence point.

If the indicator is chosen well, so that the point at which the indicator actually changes colour is the equivalence point, then the volume difference and therefore the error between the end point and the equivalence point is usually small and may be corrected for, or ignored.

The dissociation constant of the indicator is:  $K_a = \frac{[H^{+1}][In^{-1}]}{[HIn]}$

If  $[HIn] = [In^{-1}]$  then:  $[H^{+1}] = K_a \frac{[HIn]}{[In^{-1}]} = K_a$

Or:  $pH = pK_a$

Thus, if the ratio:  $[HIn] / [In^{-1}] \geq 10 / 1$ , the solution will appear as Colour 1.

If the ratio:  $[HIn] / [In^{-1}] \leq 1 / 10$ , the solution will appear as Colour 2.

Hence the indicator changes colour within a range of  $pH \pm 1$

Before the sample can be analyzed, it is important that we know, to a considerable degree of accuracy, the concentration of the titrant, because this concentration is used to calculate the concentration of the sample. Measuring the titrant's concentration is called "**standardizing**" the titrant, and is often the first stage of a titration.

A **primary standard** is a chemical available in a pure and stable form, for which an accurate concentration can be prepared, the solution is then used to determine precisely, by means of titrating, the concentration of a titrant. Primary standards are solids at standard temperature and pressure and form colourless solutions, they are not hygroscopic, (fyi: it gains mass by absorbing water from the air, such as NaOH), and they do not vaporize like HCl, (especially concentrated HCl solution.)

Common primary standards are sodium carbonate, (a base used to standardize an acid titrant), and potassium hydrogen phthalate,  $KHC_7H_4O_4(s)$ , (an acid used to standardize a basic titrant).

### Calculations

- Calculate the number of moles of the known substance. ( $n = m/M$  or  $n = cv$ )
- Calculate the number of moles of the unknown substance, using the ratio given in the chemical equation.
- Calculate the concentration of the unknown solution. ( $c = n/V$ )

**Stoichiometry is the key to solving these problems!!!**

[Note: The simplest way of determining the concentration or volumes is by using the simplified formula:

$$M_a V_a = M_b V_b \quad \text{or} \quad x M_a V_a = y M_b V_b$$

\* Where  $M_a$  is the acid concentration and  $V_a$  the volume used.

$M_b$  is the concentration of the base and  $V_b$  is the volume of base used to reach the end point.  $x$  is # of  $H^{+1}$  in the formula of the acid,  $y$  is # of  $OH^{-1}$  in the formula of the base.]

SavitaPall.com