Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

Acids, Bases and pH

Preliminary Course

Steffi Thomas
ssthomas@tcd.ie
14/09/2017

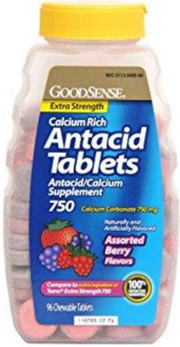
Outline

- What are acids and bases?
- Can we provide a general definition of acid and base?
- How can we quantify acidity and basicity?
- Can we classify acid and base strength?
- pH concept and pH scale.
- Acid/base reactions: neutralization
- How can we monitor an acid/base reaction in real time?

Acids and Bases: Common examples

Acids

Bases



Uses of Common Acids and Bases

18.1 Some Common Acids and Bases and Their Household Uses

Substance	Formula	Use
Acids		
Acetic acid (vinegar)	CH_3COOH (or $HC_2H_3O_2$)	Flavoring, preservative
Citric acid	$H_3C_6H_5O_7$	Flavoring
Phosphoric acid	H_3PO_4	Rust remover
Boric acid	$B(OH)_3$ (or H_3BO_3)	Mild antiseptic; insecticide
Aluminum salts	$NaAl(SO_4)_2 \cdot 12H_2O$	In baking powder, with sodium hydrogen carbonate
Hydrochloric acid (muriatic acid)	HCl	Brick and ceramic tile cleaner
Bases		
Sodium hydroxide (lye)	$NaOH$	Oven cleaner, unblocking plumbing
Ammonia	NH_3	Household cleaner
Sodium carbonate	Na_2CO_3	Water softener, grease remover
Sodium hydrogen carbonate	$NaHCO_3$	Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid
Trisodium phosphate	Na_3PO_4	Cleaner for surfaces before painting or wallpapering

Acids and Bases

Acids

1. Have sharp or sour taste
2. React with metals to produce hydrogen gas
3. React with (bi)carbonates to produce CO_2 gas

➢ This results in weathering of buildings, etc.

Bases

1. Have bitter taste
2. React with acids to make salts
3. React with oil to make soaps

➢ They feel slippery on your hands

Classical Acid-Base definition

- An **acid** is a neutral substance that contains hydrogen and dissociates or ionizes in water to yield hydrated protons or hydronium ions H_3O^+.

$$HCl \rightarrow H^+ (aq) + Cl^- (aq)$$

- A **base** is a neutral substance that contains the hydroxyl group and dissociates in water to yield hydrated hydroxide ions OH^-.

$$NaOH \rightarrow Na^+ (aq) + OH^- (aq)$$

- **Neutralization** is the reaction of an H^+ (H_3O^+) ion from the acid and the OH^- ion from the base to form water, H_2O.

$$\underset{acid}{HCl (aq)} + \underset{base}{NaOH (aq)} \rightarrow \underset{salt}{NaCl (aq)} + \underset{water}{H_2O (aq)}$$

- These definitions although correct are limited in that they are not very general and do not give a comprehensive idea of what acidity and basicity entails.

A note on "hydronium"

The H_3O^+ hydronium ion is often represented simply as "H^+"

This is simpler and easier to write, but "H^+" is simply a proton – and an isolated proton simply cannot exist by itself in solution.

However, "H_3O^+" is also a simplification – acidified water is EXTREMELY complicated, with large and dynamic conglomerates of water molecules really stabilising the extra protons.

It's probably best to write "H_3O^+", but don't be confused if you see "H^+".

Defining acids and bases

1. Arrhenius (1884)

- **Acid**: a species that dissolves to give proton concentration
- **Base**: a species that dissolves to give hydroxide concentration

2. Brønsted-Lowry (1923)

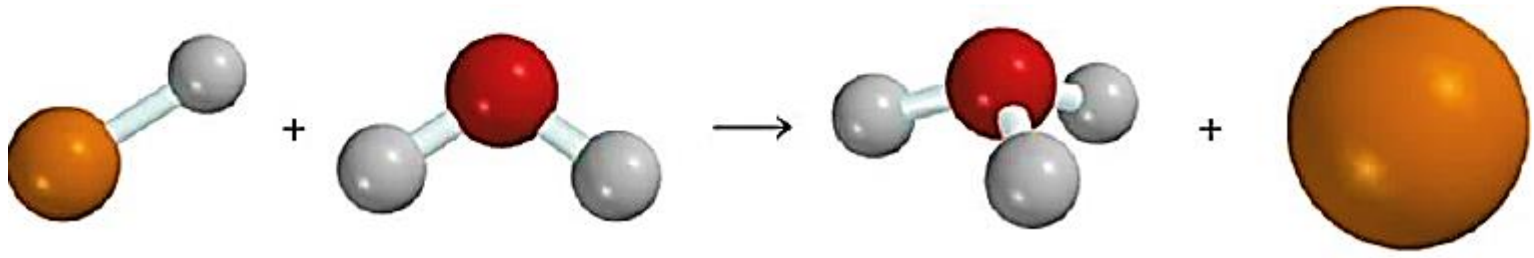
- **Acid**: a species that donates a proton
- **Base**: a species that accepts a proton

3. Lewis (1923)

- **Acid**: a species able to accept an electron pair
- **Base**: a species able to donate an electron pair

Arrhenius Acid-Base definition

Arrhenius acid is a H-containing substance that dissociates in water to produce hydronium ions (H_3O^+)



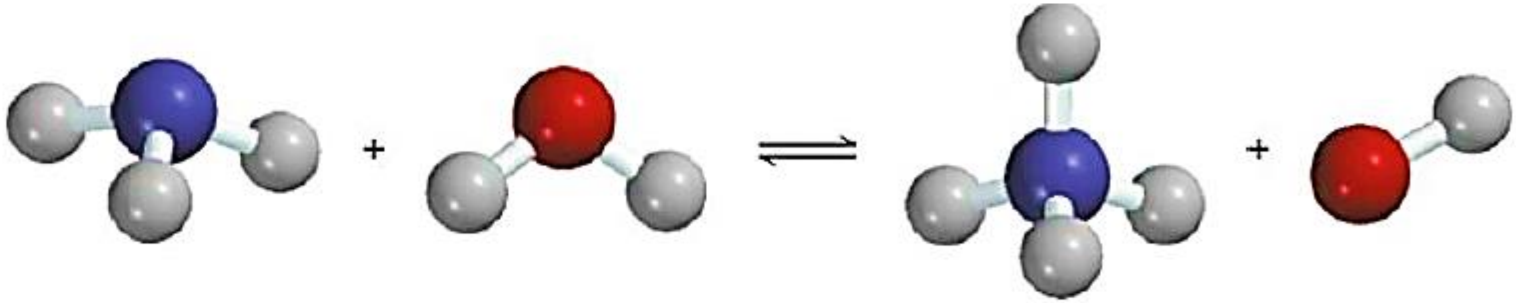
$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Arrhenius base is an OH-containing substance that dissociates in water to produce hydroxide ions, OH^-

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

The problems with Arrhenius

For example, ammonia (NH_3) has all the properties of a base, but doesn't contain any OH groups, so doesn't fit Arrhenius's definition



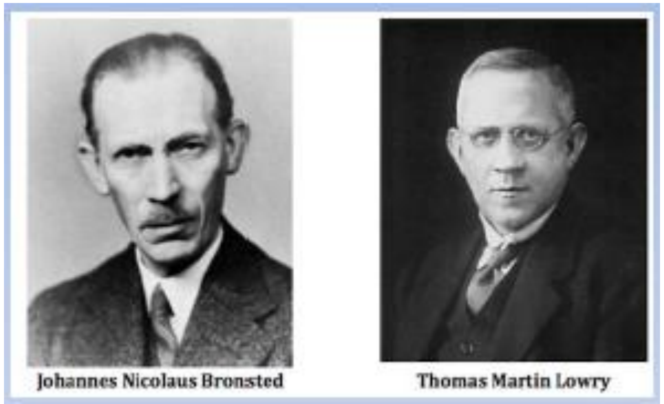
$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

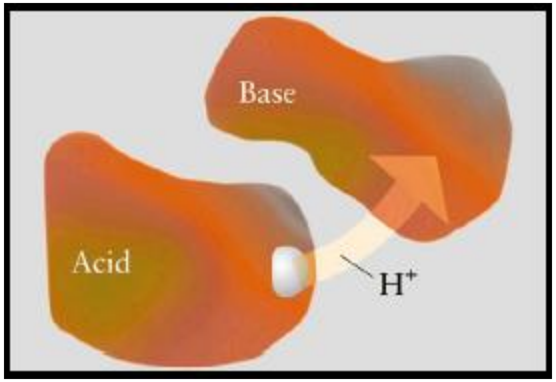
Similarly, Boric Acid (BO_3H_3) produces hydronium ions, but by taking on an OH, not by losing a H, so it doesn't fit Arrhenius's definition

$$BO_3H_3 + H_2O \rightarrow BO_4H_4^- + H_3O^+$$

Bronsted – Lowry definition

- Bronsted – Lowry Acid (HA): An acid is a species which donates a proton.
- Bronsted – Lowry Base (B): A base is a species which accepts a proton.
- These definitions are quite general and refer to the reaction between an acid and a base.
- An acid must contain H in its formula; HNO_3 and $H_2PO_4^-$ are two examples
- A base must contain a lone pair of electrons to bind the H^+ ion; a few examples are NH_3, CO_3^{2-}, F^-, as well as OH^-.





In the Bronsted-Lowry perspective: one species donates a proton and another species accepts it: an acid-base reaction is a proton transfer process.

General Definition

Does this match Arrhenius's definition?

If I put an acid in water, it can donate a proton to form hydronium:

$$HA + H_2O \rightarrow A^- + H_3O^+$$

If I put an base in water, it can accept a proton to form hydroxide:

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

So Bronsted and Lowry repeat Arrhenius's observations, but with more general rules:

- Water does not need to be present

- More things fit the definitions of acid and base (eg. NH_3 and BO_3H_3)

General Definition

How does water fit in to these definitions of acid/base?

With acid: $HA + H_2O \rightarrow A^- + H_3O^+$ — So water is acting as a base

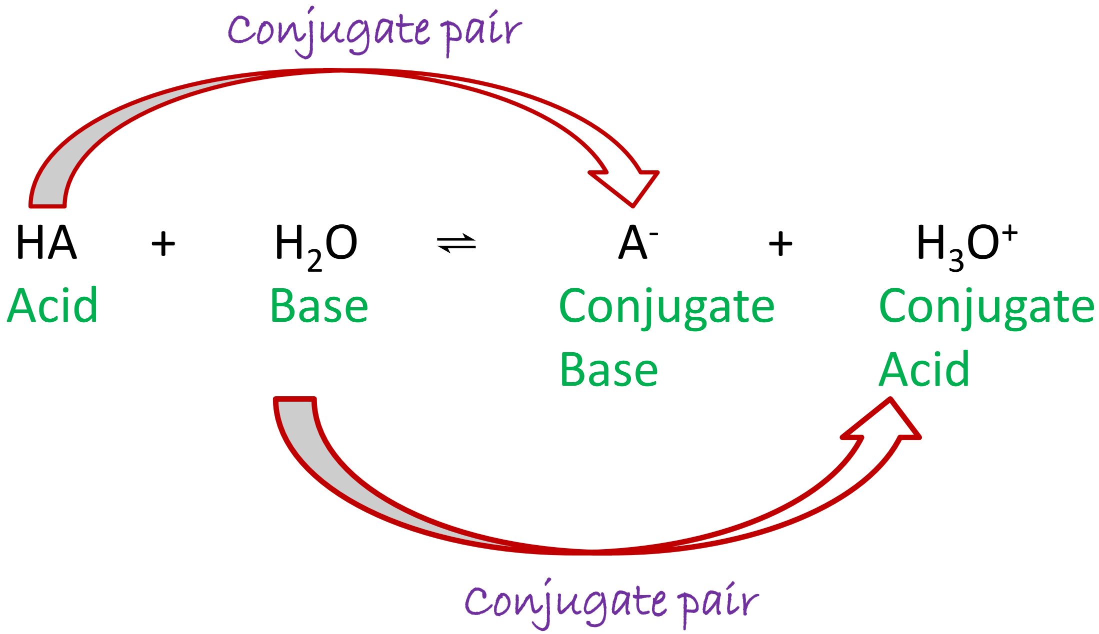
Accepted a proton

And with base: $B + H_2O \rightarrow BH^+ + OH^-$ — So water is acting as an acid

Donated a proton

Water is known as an **AMPHOTERIC** or **AMBIPROTIC** substance, since it can act as an acid and as a base.

- Proton donation and acceptance are dynamic processes for all acids and bases. Hence a proton transfer equilibrium is rapidly established in solution.
- They are not one way streets – the products can turn back into the reactants. This is known as an **EQUILIBRIUM PROCESS**, denoted by $\rightleftharpoons$



Therefore:

After an acid donates its proton, it is known as a **CONJUGATE BASE**

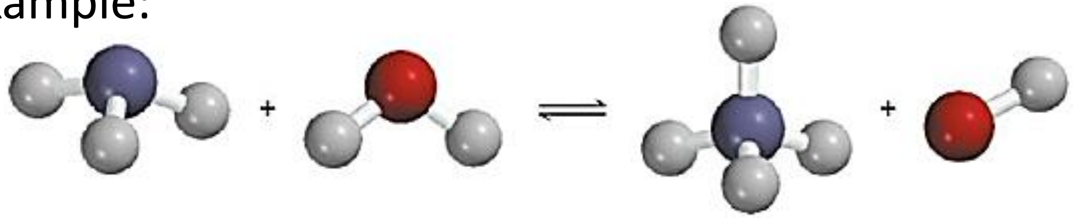
After an base accepts its proton, it is known as a **CONJUGATE ACID**

- A conjugate acid has one more proton than the base has, and a conjugate base one less proton than the acid has.
- If the acid of a conjugate acid/base pair is strong (good tendency to donate a proton) then the conjugate base will be weak (small tendency to accept a proton) and vice versa.

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

HA	H_2O	A^-	H_3O^+
Acid	Base	Conjugate Base	Conjugate Acid

Another example:



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

NH_3	H_2O	NH_4^+	OH^-
Base	Acid	Conjugate acid	Conjugate base

Acid: Proton donor
Base: Proton acceptor

Quantifying acid/base strength

Strong acid or base

Weak acid or base

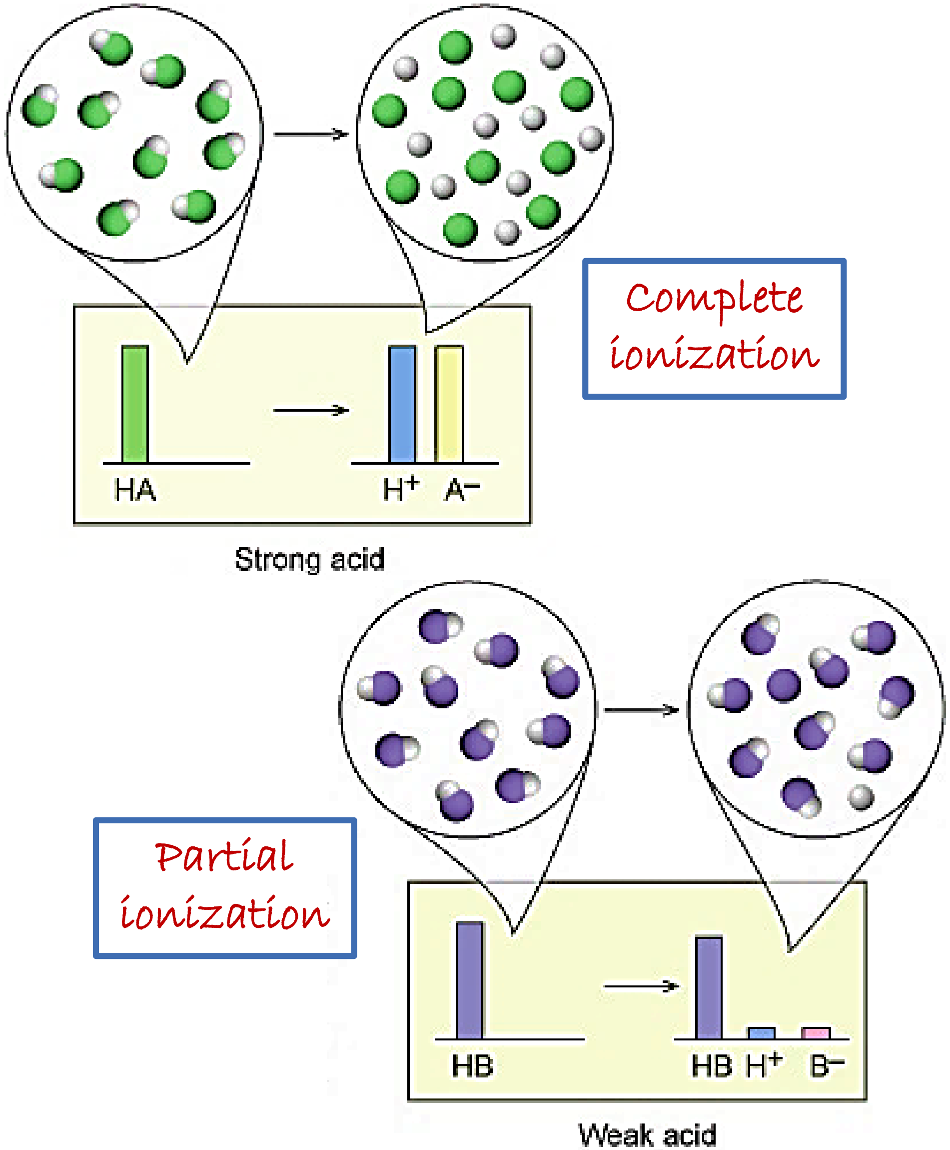
- Key concept is degree of ionization or dissociation
- Correlation exists between acid/base strength, degree of ionization in solution and extent to which solution exhibits ionic conductivity.

Degree of dissociation

1. Acid/base strength quantified in terms of degree of dissociation

2. **Strong acid/base**: An acid or base is classified as strong if it is fully ionized in solution (e.g. HCl, NaOH).

3. **Weak acid/base:** An acid or base is classified as weak if only a small fraction is ionized in solution (e.g. CH_3COOH, NH_3).



Examples

Strong Electrolyte : 100% dissociation

$$NaCl\ (s) \rightarrow Na^{+}\ (aq) + Cl^{-}\ (aq)$$

Weak Electrolyte: not completely dissociated

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

Strong Acids are strong electrolytes

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

$$HNO_3(aq) + H_2O\ (l) \rightarrow H_3O^{+}\ (aq) + NO_3^{-}\ (aq)$$

Nitric acid

Weak Acids are weak electrolytes

$$HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^{+}\ (aq) + F^{-}\ (aq)$$

$$HNO_2\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^{+}\ (aq) + NO_2^{-}\ (aq)$$

Nitrous acid

Strong bases are strong electrolyte

$$NaOH\ (s) + H_2O\ (l) \rightarrow Na^{+}(aq) + OH^{-}(aq)$$

$$KOH\ (s) + H_2O\ (l) \rightarrow K^{+}(aq) + OH^{-}(aq)$$

Weak Bases are weak electrolytes

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

$$F^{-}\ (aq) + H_2O\ (l) \rightleftharpoons OH^{-}\ (aq) + HF\ (aq)$$

Dissociation constant, K

We can quantify the extent of dissociation of a weak acid or a weak base in aqueous solution by introducing:

The acid dissociation constant K_a

or

The base dissociation constant K_b

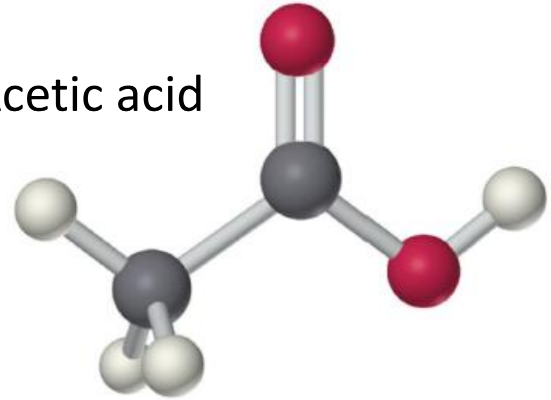
These are numbers which reflect acid or base strength and are computed by determining the equilibrium concentrations of all relevant species in the solution, and inputting this data into a theoretical expression for the relevant dissociation constant.

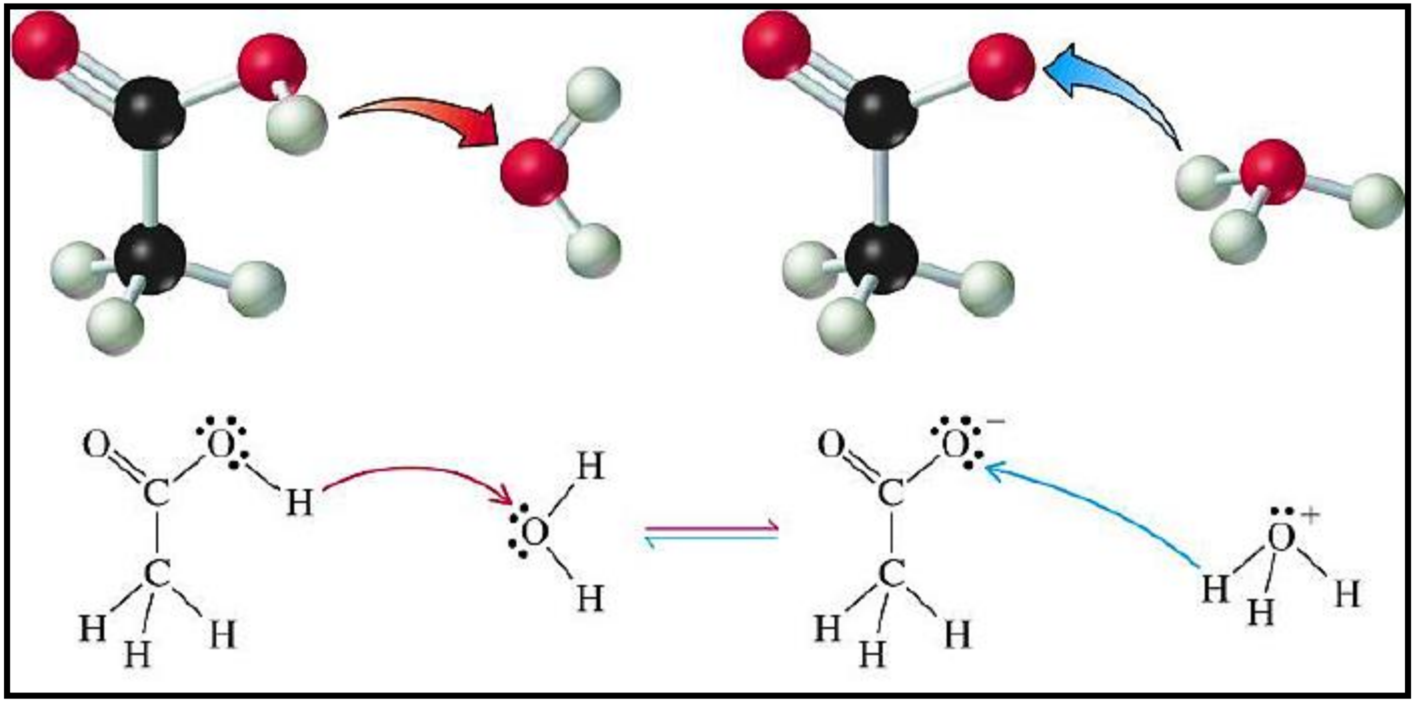
Acid strength: the acid dissociation constant, K_a

- It is easy to quantify the strength of strong acids since they fully dissociate to ions in solution.
- The situation with respect to weak acids is more complex since they only dissociate to a small degree in solution.
- The question is how small is small?
- We quantify the idea of incomplete dissociation of a weak acid HA by noting that the dissociation reaction is an equilibrium process and introducing the acid dissociation constant, K_a.

Weak acids

Acetic acid





$$CH_3COOH \quad + \quad H_2O \quad \rightleftharpoons \quad CH_3COO^- \quad + \quad H_3O^+$$

Weak acids

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

But, $[H_2O]$ = constant

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

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

[…] represents the concentration of relevant species in Molar (can be represented as mol/L, mol/dm^3 or M)

Therefore:

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

$$K_a = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

$[H_2O]$ =Constant

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

- K_a is a measure of the acid strength.
- When K_a is large there is considerable dissociation and the acid is strong.
- When K_a is small there is a small degree of dissociation, and the acid is weak.

K_a values vary over a wide range so it is best to use a log scale.

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

Acid Name (Formula)	**K_a at 298 K**	**pK_a**
Hydrogen Sulfate ion (HSO_4^-)	1.02×10^{-2}	1.99
Nitrous acid (HNO_3)	7.1×10^{-4}	3.15
Acetic acid (CH_3COOH)	1.8×10^{-5}	4.74
Hypobromous acid (HBrO)	2.3×10^{-9}	8.64
Phenol (C_6H_5OH)	1.0×10^{-10}	10.00

K_A ↓ pK_A ↑

When K_a is small pK_a is large and the acid does not dissociate in solution to a large extent. A change in 1 pK_a unit implies a 10 fold change in K_a value and hence acid strength.

The ion product of water

$$H_2O\ (l) \rightleftharpoons H^+\ (aq) + OH^-\ (aq)$$

$$K_C = \frac{[H^+][OH^-]}{[H_2O]}$$; K_C = Equilibrium constant and $[H_2O]$ = constant

$$K_C[H_2O] = [H^+][OH^-]$$

$$K_W = [H^+][OH^-]$$

The **ion-product constant** (K_W) is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.

At 25˚C:

$$K_W = [H^+][OH^-] = 1.0 \times 10^{-14}$$

	Solution is
$[H^+] = [OH^-]$	Neutral
$[H^+] > [OH^-]$	Acidic
$[H^+] < [OH^-]$	Basic

Basicity Constant, K_b

- The proton accepting strength of a base is quantified in terms of the basicity constant K_b
- The larger the value of K_b, the stronger the base.
- If K_b is large then pK_b will be small, and the stronger will be the base.
- Solve weak base problems like weak acids **except** solve for $[OH^-]$ instead of $[H^+]$.

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

$$K_b = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

$[H_2O]$ =Constant

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

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

$$K_aK_b = K_w$$

$$pK_a + pK_b = K_w$$

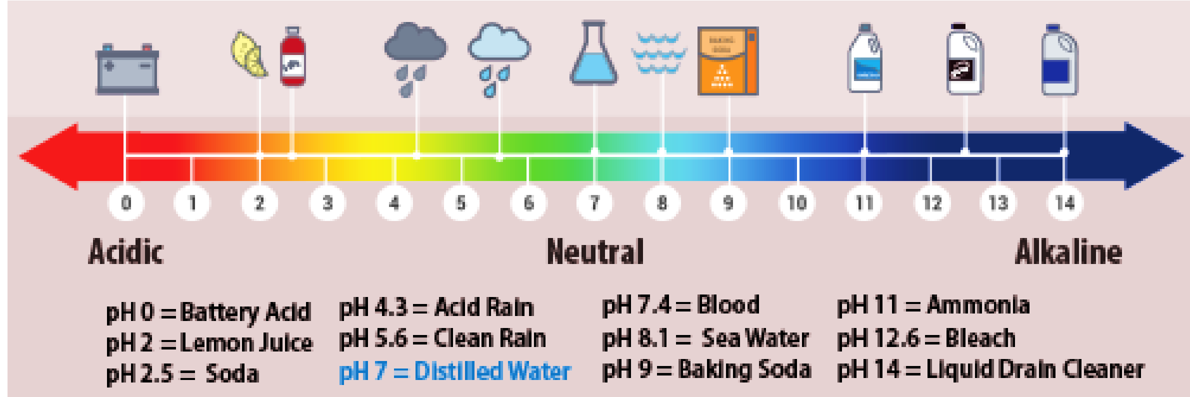
The pH concept

- The best quantitative measure of acidity or alkalinity rests in the determination of the concentration of hydrated protons $[H_3O^+]$ present in a solution.
- The $[H_3O^+]$ varies in magnitude over quite a large range in aqueous solution, typically from 1 M to 10^{-14} M.
- Hence to make the numbers meaningful $[H_3O^+]$ is expressed in terms of a logarithmic scale called the **pH scale**.
- The higher the $[H_3O^+]$, the more acidic the solution and the lower is the solution pH.
- The pH of a solution can be defined as the negative base 10 logarithm of the hydronium ion concentration.

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

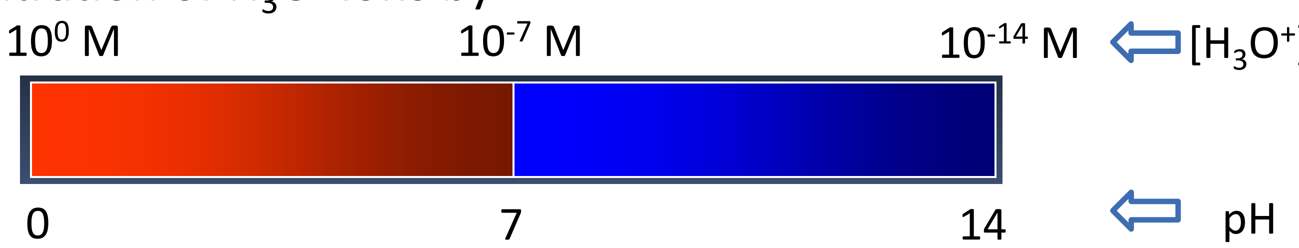
$$[H_3O^+] = 10^{-pH}$$

pH scale

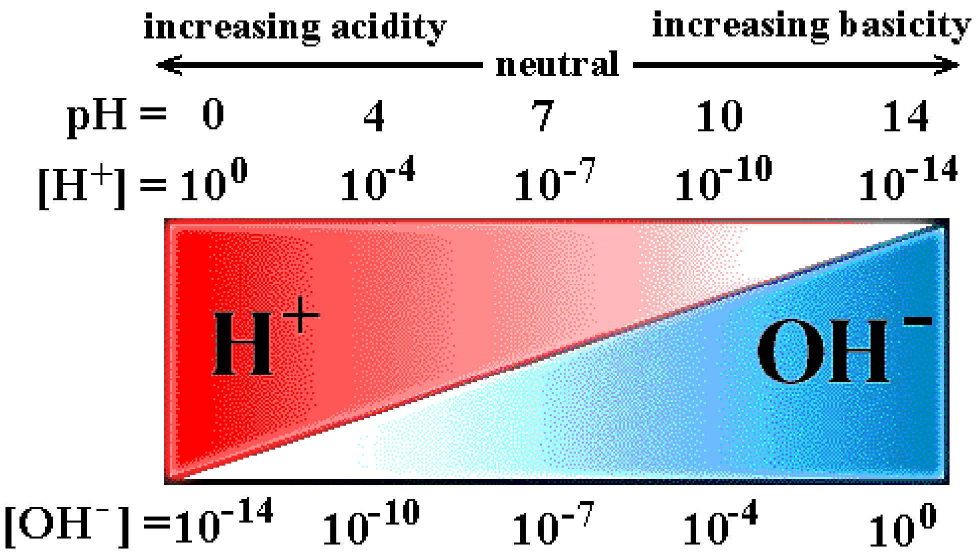


- pH is expressed on a numerical scale from 0 to 14.
- When $[H_3O^+]$ = 1.0 M (i.e. 10^0 M), pH = 0.
- When $[H_3O^+] = 10^{-14}$ M, pH = 14.
- Hence a change in one pH unit represents a change in concentration of H_3O^+ ions by a factor of 10.

pH = 7	**Neutral**
pH < 7	**Acidic**
pH > 7	**Alkaline**



pH and pOH scale



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

Similarly:

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

Therefore:

$$\boldsymbol{pH + pOH = 14}$$

Summary: pH – a measure of acidity

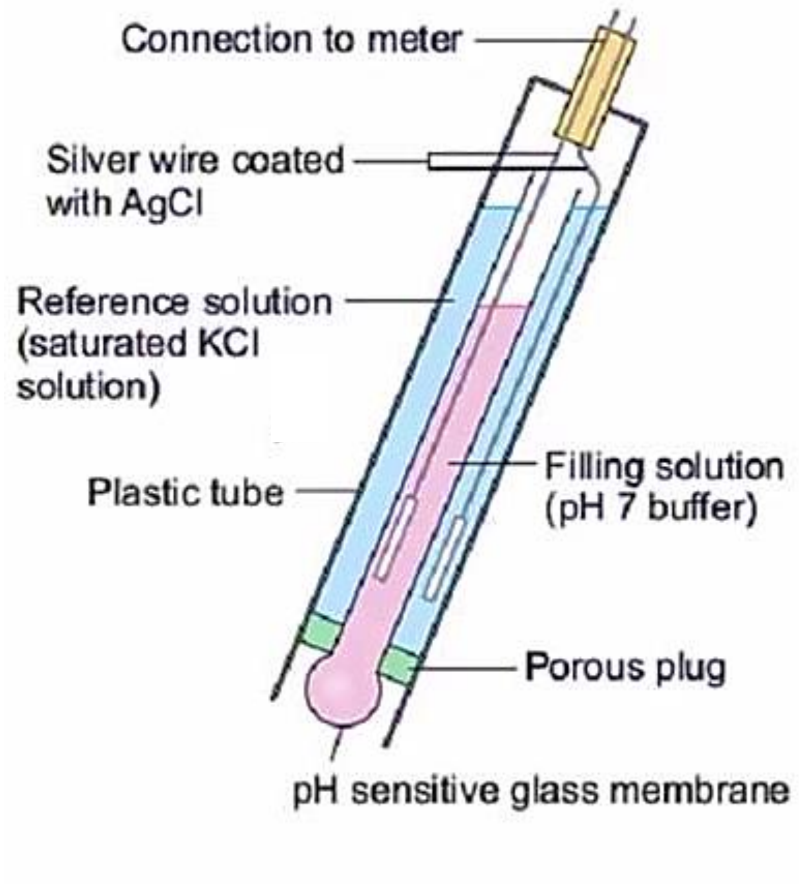
$$pH = -log_{10}\,[H_3O^+] = -log_{10}\,[H^+]$$

Solution is		**At 25˚C**	
Neutral	$[H^+] = [OH^-]$	$[H^+] = 1x\ 10^{-7}$	pH = 7
Acidic	$[H^+] > [OH^-]$	$[H^+] > 1x\ 10^{-7}$	pH < 7
Basic	$[H^+] < [OH^-]$	$[H^+] < 1x\ 10^{-7}$	pH > 7

pH ↑ $[H^+]$ ↓

pH measurement: pH meter

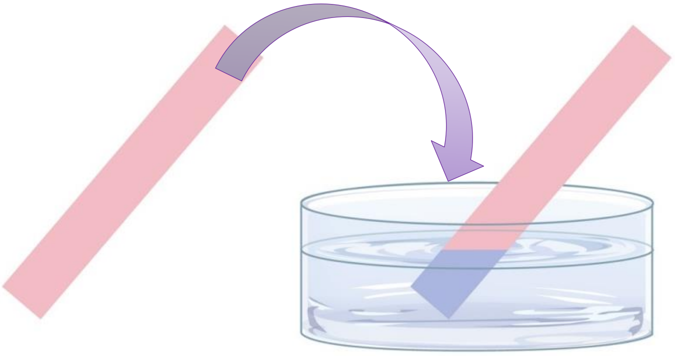
- More accurate pH values determined using an electronic instrument called a pH meter.
- The device (consisting of a probe electrode made of glass and associated electronics) measures the electrical potential generated across a glass membrane (which separates an internal solution of known $[H_3O^+]$ from the external test solution of unknown $[H_3O^+]$) located at the electrode tip.
- This membrane potential is proportional to the pH of the test solution.
- A digital readout of solution pH is obtained.



Methods for Measuring the pH of an Aqueous Solution

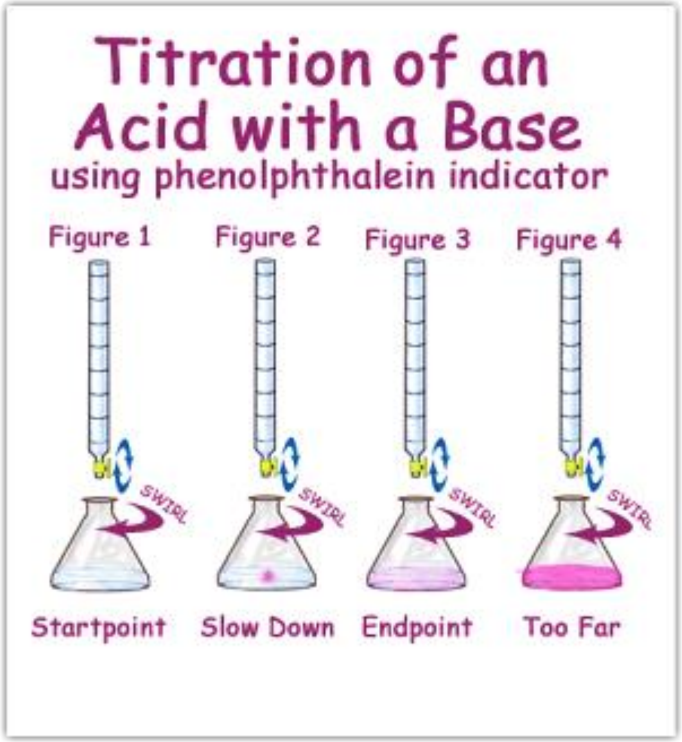
pH meter

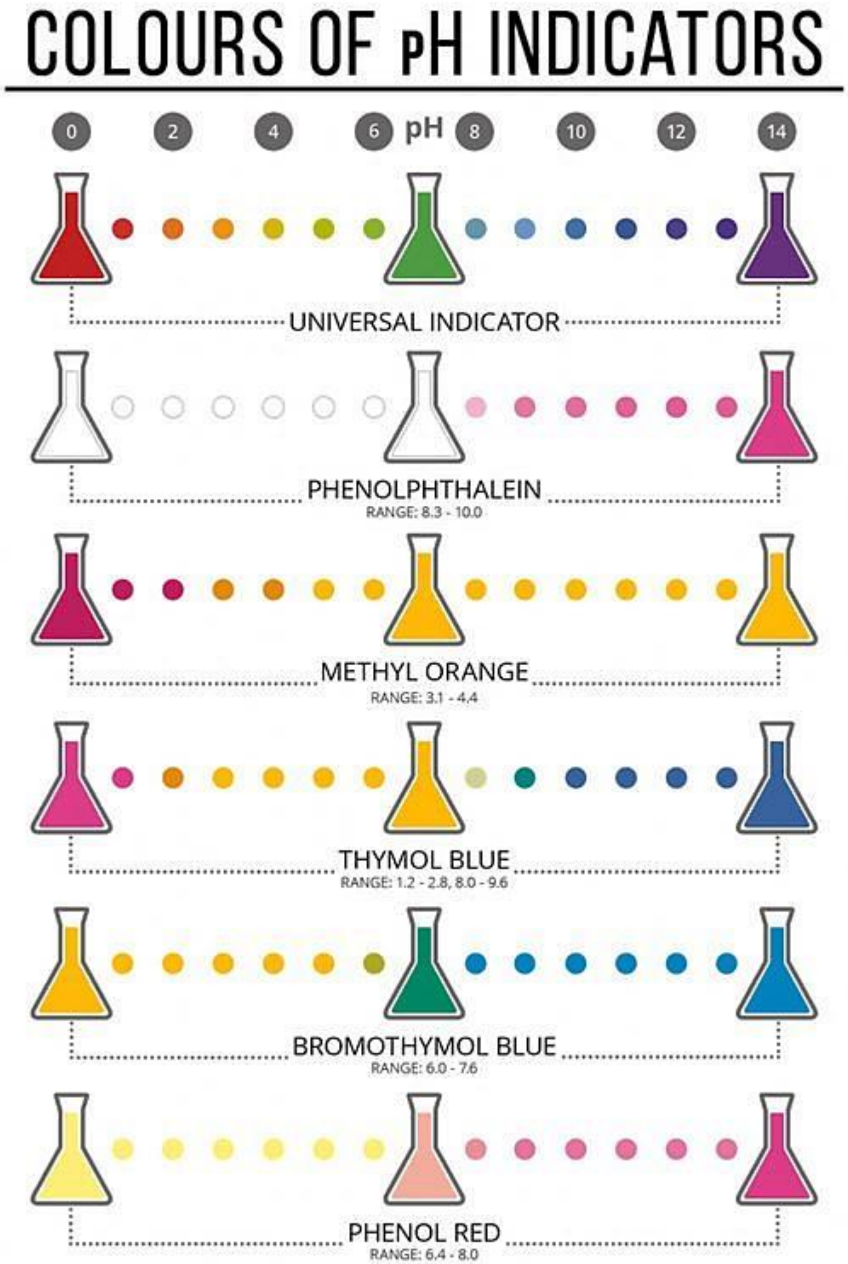
Litmus papers



pH measurements: Indicators

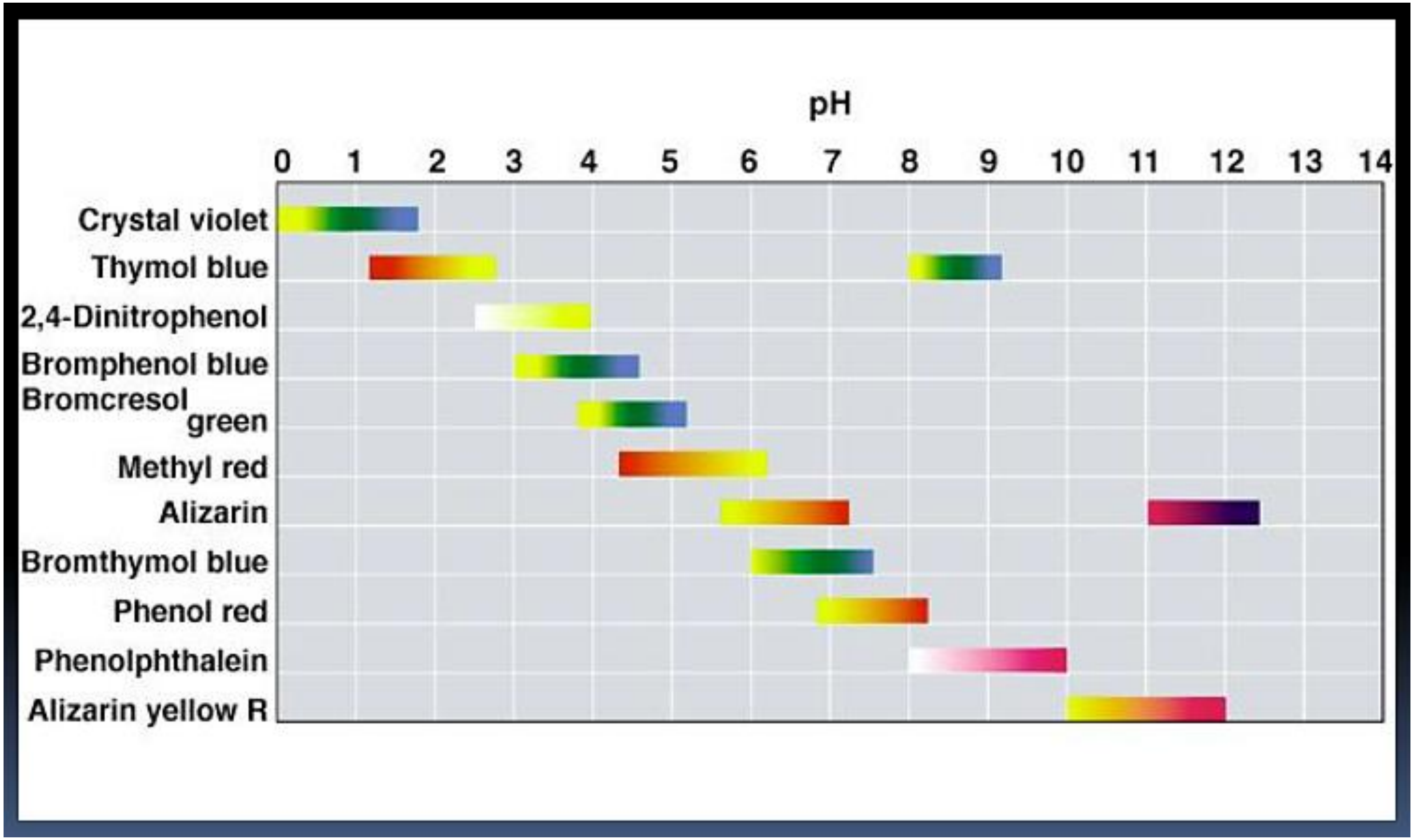
- Approximate pH of a solution determined by use of acid/base indicators.
- Indicators are substances (weak acids) which change colour over a specific pH range when they donate protons.
- We add a few drops of indicator (which changes colour over the required pH range) to the test solution and record the colour change produced.
- This procedure is utilized in acid/base titrations. Universal indicator (mixture of pH indicators) often used for making approximate pH measurements in range 3 – 10.
- As solution pH increases, the indicator changes colour from red to orange to yellow to green to blue, and finally to purple.




COLOURS OF pH INDICATORS
0
2
4
6
pH
8
10
12
14
UNIVERSAL INDICATOR
PHENOLPHTHALEIN
RANGE: 8.3 - 10.0
METHYL ORANGE
RANGE: 3.1 - 4.4
THYMOL BLUE
RANGE: 1.2 - 2.8, 8.0 - 9.6
BROMOTHYMOL BLUE
RANGE: 6.0 - 7.6
PHENOL RED
RANGE: 6.4 - 8.0

Colors and Approximate pH Range of Some Common Acid-Base Indicators

Universal indicator is a mixture of indicators to give a full range of pH values



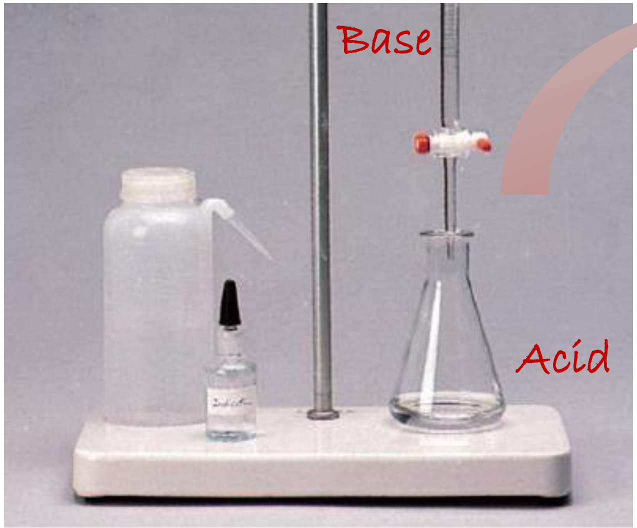
Titrations

In a **titration,** a solution of accurately known concentration is added gradually added to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

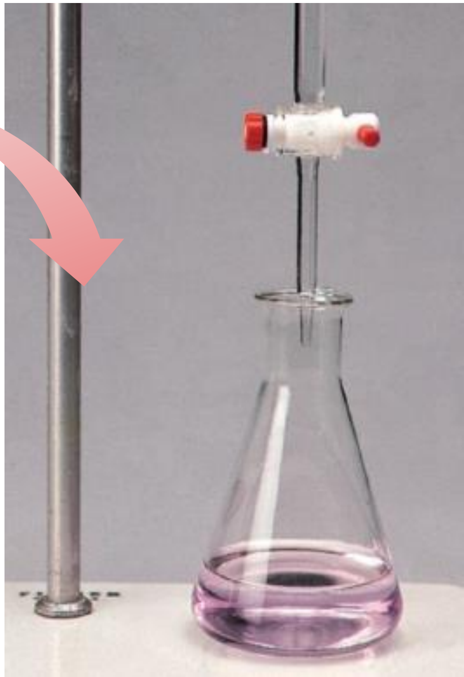
$$HA + MOH \rightarrow MA + H_2O$$

Indicator: Substance that changes color at (or near) the equivalence point

Equivalence point or Stoichiometric point: The point at which the reaction is complete



Slowly add base to unknown acid UNTIL The indicator changes color (pink)



Strong acid – strong base titrations

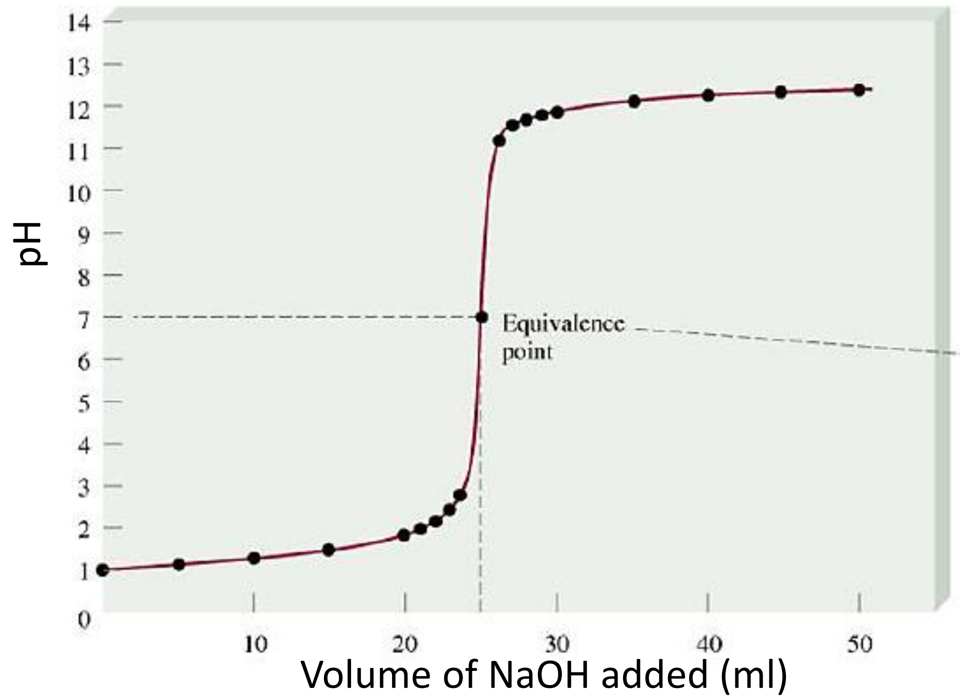
$HCl\ (aq) + NaOH\ (aq) \rightarrow NaCl\ (aq) + H_2O\ (aq)$

At equivalence point:

Amount of acid = Amount of base

$$n_A = n_B$$
$$c_A V_A = c_B V_B$$

<u>*0.1 M NaOH added to 25 ml of 0.1 M HCl*</u>



Volume NaOH added (mL)	pH
0.0	1.00
5.0	1.18
10.0	1.37
15.0	1.60
20.0	1.95
22.0	2.20
24.0	2.69
25.0	7.00
26.0	11.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

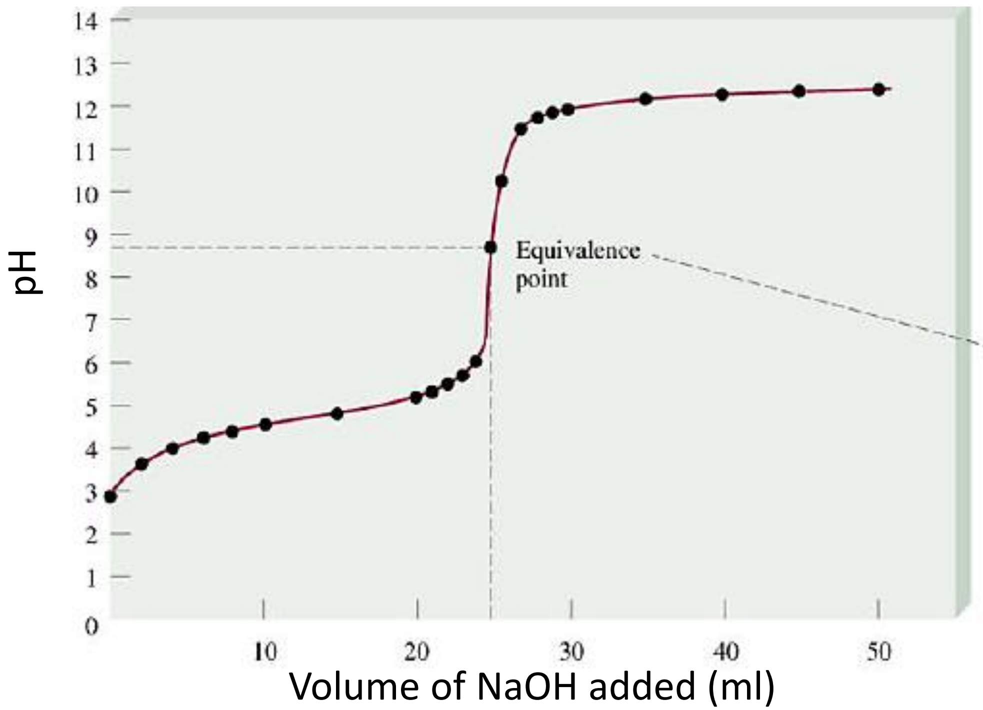
Weak acid – strong base titrations

$$CH_3COOH\ (aq) + NaOH\ (aq) \rightarrow CH_3COONa\ (aq) + H_2O\ (l)$$

$$CH_3COOH\ (aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O\ (l)$$

At equivalence point (pH > 7):

$$CH_3COO^-(aq) + H_2O\ (l) \rightleftharpoons OH^-(aq) + CH_3COOH\ (aq)$$



Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

Summary

- The process involves the transfer of a hydrated proton from a donor species (the acid) to an acceptor species (the base).
- The degree of proton transfer can be quantified and enables a distinction between strong and weak acids/bases to be made.
- The degree of acidity or alkalinity of a solution may be quantified in terms of the logarithmic pH scale.
- Acidic solutions have a low pH and basic solutions have a high pH.
- The solution pH can be measured via use of indicators or via use of pH meter.
- An acid/base reaction is termed a neutralization reaction and can be monitored by measuring the pH during the reaction.

Reading Materials

1. Silberberg, Chemistry, 4th edition.

- Chapter 18 → Acid/base equilibria. pp.766 – 813.
- Chapter 19 → Ionic equilibria in aqueous systems. pp.814 – 862.

2. Kotz, Treicheland Weaver, 7th edition.

- Chapter 17&18, pp.760 – 859.

3. Burrows et al. Chemistry^3(OUP), 2009.Ch.6, pp.263 – 300.

4. Lecture notes available after course on School of Chemistry website located at: http://www.tcd.ie/Chemistry/outreach/prelim/

Useful websites

1. http://www.shodor.org/unchem/basic/ab/
2. http://chemistry.about.com/od/acidsbases/
3. http://www.chem.neu.edu/Courses/1221PAM/acidbase/index.htm
4. http://dbhs.wvusd.k12.ca.us/webdocs/AcidBase/AcidBase.html
5. http://www.sparknotes.com/chemistry/acidsbases/fundamentals/section1.html

Trinity College Dublin
Coláiste na Tríonóide, Baile Átha Cliath
The University of Dublin

Good luck!!