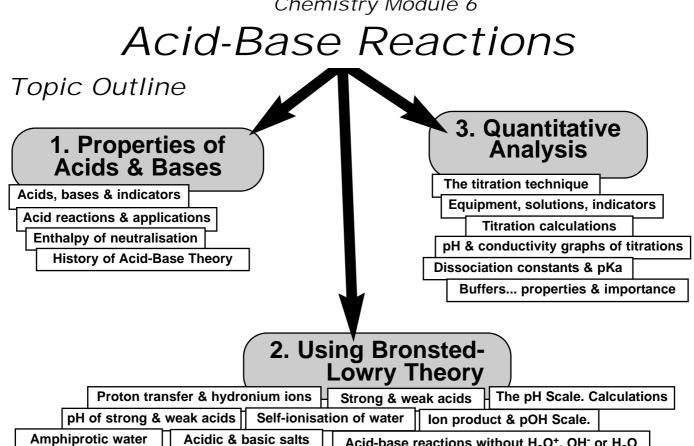
Acid-base reactions without H<sub>2</sub>O<sup>+</sup>, OH<sup>-</sup> or H<sub>2</sub>O



#### KEEP IT SIMPLE SCIENCE

PhotoMaster Format Chemistry Module 6



### What is this topic about?

To keep it as simple as possible, (K.I.S.S. Principle) this topic covers:

### 1. Properties of Acids & Bases

Introduction to acids, bases & indicators. Acid reactions: neutralisation, acid-metal, acid-carbonate. Applications of neutralisation. Enthalpy of neutralisation. A brief history of Acid-Base Theory.

### 2. Using Bronsted-Lowry Theory

Proton-transfer. Definitions of acid & base. Strong & weak acids. Mathematics of pH Scale. pH of strong & weak acids. Self-ionisation of water. K<sub>w</sub>, pK<sub>w</sub> & pOH Scale. Water is amphiprotic. Acidic & basic salts. Acid-base reactions without hydronium, hydroxide or even water.

### 3. Quantitative Analysis

The technique of titration. Aliquots & titres. Titration calculations. pH & conductivity graphs during titration. Dissociation constants & pKa. Buffers... properties, composition & importance.

pH change in dilution

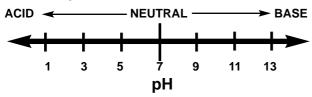


# 1. Properties of Acids & Bases

#### Acid, Base or Neutral?

The chemical definitions of acid and base will come later. For now, you are reminded of what you may have learnt earlier.

Acids and bases are <u>chemical opposites</u>; if you add one to the other they "destroy" (neutralise) each other, and the end product is neutral. Acids and bases are the opposite ends of a chemical property called "acidity", which is measured by a numerical scale called "pH".



The word "acid" comes from the Latin for "sour", and refers to the fact that natural, acidic chemicals (e.g. vinegar) are sour-tasting.

# Practical Work: A Natural Indicator You may have done practical work to prepare and test a natural indicator.



A good example is the common garden plant Hydrangea.

If you collect a flower head and put it through a blender with a little water and ethanol, the filtered liquid extract will work as a simple indicator.

In acid, the Hydrangea flower extract is a bluish colour.
In a base, it turns pink-ish.

### Indicators

Indicators are chemicals which change colour according to the acidity of the solution they are in. The original indicators were natural extracts from plants or other living things. Some, such as <u>litmus</u>, are still in use today, as well as newer, synthetically made chemicals.

#### Modern Laboratory Indicators

In this Module, you will probably become familiar with the common laboratory indicators listed below. You may do experimental work, adding 2 drops of indicator to test tubes of acid, base and pure water (which is neutral) and record the colours produced. Your results should agree with the following:

<u>Acid</u>	<u>Water</u>	<u>Base</u>
pink	purple	blue
clear	clear	red/pink
red	yellow	yellow
yellow	green/blue	blue
	pink clear red	pink purple clear clear red yellow



Choosing an Indicator Why are so many indicators needed?

Litmus is useful for general indentification of acidic or basic substances. However, its colour change is rather indistinct, and can occur over quite a range of pH values... it is not a "sharp" change.

In contrast, Phenolphthalein cannot tell you the difference between a glass of water and sulfuric acid. However, the colour change is very distinctive, and occurs suddenly at a very specific pH value... it is very sharp. This is not much use in general identification of substances, but in certain methods of chemical analysis it is very important.

Everyday Uses of Indicators

Soil Testing. Some plants grow best in acidic soils; others need slightly alkaline (basic) conditions. Farmers and keen gardeners use simple test kits containing an indicator and colour chart, (or an electronic "pH meter") to test the soil. They can then adjust the soil pH to get the best results.

<u>Water Testing</u>. Swimming pools need regular testing for acidity to better maintain their water quality and hygiene. Aquariums must be

maintained at very specific pH levels for the health of their inhabitants.

Now Complete Worksheet 1

Effluent Testing. Acidity is a useful way to assess the levels of certain types of pollution from industries. Industry technicians and Government authorities use indicators to monitor the pH of waste water and natural waterways.





### Acids & Bases... Properties & Naming

#### Laboratory Acids & "Alkalis"

You are reminded that the common laboratory acids are:

**Formula** Solution of **Chemical Name** Name Hydrogen chloride H<sup>+</sup><sub>(aq)</sub>+ Cl<sup>-</sup><sub>(aq)</sub> Hydrochloric acid HCI(ad)

Hydrogen sulfate Sulfuric acid H<sub>2</sub>SO<sub>4(aq)</sub>

Hydrogen nitrate H<sup>+</sup><sub>(aq)</sub>+ NO<sub>3</sub>-<sub>(aq)</sub> HNO<sub>3(aq)</sub> Nitric acid

Typical Properties of Acids

- · mostly water soluble
- sour taste
- corrosive & chemically reactive
- 2H<sup>+</sup><sub>(aq)</sub>+ SO<sub>4</sub><sup>2-</sup><sub>(aq)</sub> react with bases to neutralise them

The most familiar laboratory bases are soluble hydroxide compounds which are sometimes called "alkalis".

**Formula Chemical Name** Sodium hydroxide Sodium hydroxide NaOH<sub>(ag)</sub>

Typical Properties of Bases Solution of Na<sup>+</sup><sub>(aq)</sub> + OH<sup>-</sup><sub>(aq)</sub> • bitter taste & "slippery" feel • corrosive & chemically reactive • react with acids to neutralise

them

K<sup>+</sup><sub>(aq)</sub>+ OH<sup>-</sup><sub>(aq)</sub> Potassium hydroxide

### The Acid-Base Reaction: Neutralisation

You should be already familiar with this reaction: **Example:** 

Potassium hydroxide KOH(aq)

sulfuric + potassium ---- water + potassium hydroxide

$$H_2SO_{4(aq)} + 2KOH_{(aq)} \longrightarrow 2H_2O_{(I)} + K_2SO_{4(aq)}$$

**lonic equation:** 

$$2H^{+}_{(aq)} + SO_{4}^{2-}_{(aq)} + 2K^{+}_{(aq)} + 2OH^{-}_{(aq)}$$

$$\longrightarrow 2H_{2}O_{(1)} + 2K^{+}_{(aq)} + SO_{4}^{2-}_{(aq)}$$

If you study this equation you will see that the potassium and sulfate ions are spectators. You can leave them out to form the net ionic equation:

$$2H^{+}_{(aq)} + 2OH^{-}_{(aq)} \longrightarrow 2H_{2}O_{(1)}$$

or more simply:

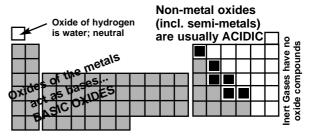
$$H^+_{(aq)} + OH^-_{(aq)} \longrightarrow H_2O_{(l)}$$

All the familiar laboratory acids are solutions containing hydrogen ions (H+). The laboratory "alkali" bases are solution's containing hydroxide ions (OH-). These will always react to form water, so the acid and base have neutralised each other.

The spectator ions remain in solution. If the solution is evaporated, a solid ionic compound crystalises. (potassium sulfate in the example above) Compounds like this are known collectively as "salts".

### Acid-Base Properties of the Oxide Compounds

The common laboratory acids and alkali-bases are not the whole story. Most of the oxide compounds of the elements show some acid-base behaviour too, and the periodic table reveals another pattern.



#### Basic Oxides of the Metals

Most of the oxides of the metallic elements are considered basic because they can neutralise acids, forming water and a "salt".

hydrochloric + magnesium 
$$\longrightarrow$$
 water + magnesium acid oxide chloride

$$2HCI_{(aq)} + MgO_{(s)} \longrightarrow H_2O_{(l)} + MgCI_{2(aq)}$$

$$sulfuric + copper(II) \longrightarrow water + copper(II)$$

$$acid oxide sulfate$$

$$H_2SO_{4(aq)} + CuO_{(s)} \longrightarrow H_2O_{(l)} + CuSO_{4(aq)}$$

Continued...



### Acid-Base Reactions (cont.)

#### Acidic Oxides of the Non-Metals

Many of the oxide compounds of the non-metal elements are acidic because they will:

- react with water to form an acid and/or
  - react with a base by neutralising it, to form water and a "salt".

#### **Examples**:

carbon dioxide + water ----- carbonic acid

$$CO_{2(g)}$$
 +  $H_2O_{(l)}$   $\longrightarrow$   $H_2CO_{3(aq)}$ 

$$CO_{2(g)} + 2NaOH_{(aq)} \longrightarrow 2H_2O_{(l)} + Na_2CO_{3(aq)}$$

#### Metals React With Acids

This reaction pattern was covered in Module 3. Here is a quick revision.

The different activity levels of the metals is clearly seen when metals are reacted with dilute acids. You may do experimental work to observe how vigorously different metals react with a dilute acid.

Metals like calcium and magnesium react vigorously. Zinc and iron are slower. Lead is very slow indeed. Copper does not react at all.

When there is a reaction, the gas produced is hydrogen. (Confirm with a "pop test")

The metal is "eaten away" and dissolves into the liquid. This is because it forms a soluble ionic compound. Exactly what the compound is, depends on which acid is used.

#### Examples

magnesium + nitric acid $\rightarrow$  hydrogen + magnesium nitrate Mg + 2HNO<sub>3</sub>  $\longrightarrow$  H<sub>2</sub> + Mg(NO<sub>3</sub>)<sub>2</sub>

iron + sulfuric acid 
$$\longrightarrow$$
 hydrogen + iron(II) sulfate Fe +  $H_2SO_4$   $\longrightarrow$   $H_2$  +  $FeSO_4$ 

For all reactions encountered, you need to be able to write full ionic equations, including states.

The soluble ionic compounds formed are collectively known as "salts", so the general pattern of the reactions is



#### Acid-Carbonate Reaction

Acids react with any compounds containing the <u>polyatomic ion</u> carbonate, CO<sub>3</sub><sup>2-</sup>.

The products are always carbon dioxide gas, water and "a salt".

#### Example

$$2\mathsf{HCl}_{(\mathsf{aq})} \quad + \quad \mathsf{CaCO}_{3(\mathsf{s})} \quad \longrightarrow \quad \mathsf{CO}_{2(\mathsf{g})} \qquad + \; \mathsf{H}_2\mathsf{O}(\mathsf{I}) \quad + \quad \; \mathsf{CaCl}_{2(\mathsf{aq})}$$

Full ionic equation:

$$2H^{+}_{(aq)} + 2CI^{-}_{(aq)} + Ca^{2+}_{(s)} + CO_{3}^{2-}_{(s)} \longrightarrow CO_{2(g)} + H_{2}O_{(I)} + Ca^{2+}_{(aq)} + 2CI^{-}_{(aq)}$$

Net ionic equation: (subtract spectators)

$$2H^{+}_{(aq)} + CO_{3}^{2-}_{(s)} \longrightarrow CO_{2(g)} + H_{2}O_{(l)}$$

**Now Complete Worksheet 2** 



### Applications of the Neutralisation Reaction

#### In Agriculture & Industry

One of the most important industrial processes for our civilisation is the production of chemical fertilisers.

Generally, these are made by the neutralisation of the base ammonia (NH<sub>3</sub>) by an acid.

One of the most important fertilisers is made by reacting ammonia with sulfuric acid:

ammonia + sulfuric acid ---- ammonium sulfate

$$NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

You might not yet recognise that this is an acidbase neutralisation, but you will soon.

#### In Everyday Life

Your stomach produces hydrochloric acid to help digest the food you eat. Sometimes, it may produce excessive amounts of acid which can cause discomfort... "indigestion".

The simple solution is to swallow a harmless chemical which will act as a base and neutralise the excess acid.

"Antacid" tablets often contain a non-toxic, non-alkaline metal hydroxide, such as Al(OH)<sub>3</sub>.

3HCI + AI(OH)<sub>3</sub> 
$$\longrightarrow$$
 3H<sub>2</sub>O + AICI<sub>3</sub>

You should be able to figure this out as a neutralisation reaction.

### Enthalpy of Neutralisation

The syllabus requires that you carry out an experiment to measure the "enthalpy of neutralisation".

This is easily done with a simple laboratory calorimeter, a thermometer and solutions of acid & base.

#### Typical Method

- 1. Measure 50mL of 2.0 molL<sup>-1</sup> HCl and (separately) 50mL of 2.0 molL<sup>-1</sup> KOH solution.
- 2. Measure the temperature of each solution. If they are NOT the same, let them sit together until they equilibrate to the same temp. This is the starting temp. for the calorimetry calculation.
- 3. When ready, simply pour both solutions into the calorimeter. Stir, then record the final temperature.

Typical Results

Starting temp. = 18°C

Final temp. = 31°C

 $\Delta T = 13^{\circ}C$ 

Mass of liquid in calorimeter  $\cong 0.1$  kg (measure this for greater precision)

Specific Heat Capacity = 4,183 Jkg<sup>-1</sup>K<sup>-1</sup> (assumed the same as water)

Calculation

Q = m.c.
$$\Delta$$
T = 0.1 x 4,183 x 13  
= 5,438 J of heat released.



#### Reaction

The reaction has released heat energy, (exothermic) but to find the "Enthalpy of Neutralisation" you must express this as the amount of energy released <u>per mole</u> of reactants.

The reaction is:

$$HCI_{(aq)} + KOH_{(aq)} \longrightarrow H_2O_{(l)} + KCI_{(aq)}$$

The quantity of each reactant was 50mL of 2.0 molL<sup>-1</sup> solution.

Since 
$$C = n/V$$
 then  $n = C.V$   
= 2.0 x 0.05  
= 0.1 mol.

Enthalpy of Neutralisation
Therefore, the energy release per mole

Therefore, the energy release per mole = 54,380 J

$$\Delta H_{\text{neut}} = -54.4 \text{ kJmol}^{-1}$$

#### Further Discussion

The "accepted" enthalpy for this reaction is about -56 kJmol<sup>-1</sup>, so a result close to this is outstanding. Is that the enthalpy just for that exact reaction?

Well, no.

If you write the equation in ionic form

$$H^+ + Cl^- + K^+ + OH^- \longrightarrow H_2O_{(1)} + K^+ + Cl^-$$

then eliminate the "spectators":

$$H^+ + OH^- \longrightarrow H_2O_{(1)}$$

it is obvious that the "essential" reaction is between hydrogen & hydroxide ions. With minor variations, this enthalpy will be the same for all acid-base neutralisations.



### History of Acid-Base Theory

1923.

Early Ideas About Acids & Bases
Naturally occurring acids, like ethanoic acid in
vinegar, have been known for thousands of years,
and described by their simple, observable properties
such as their sour taste.

Chemistry became a modern Science just over 200 years ago, and one of the earliest scientific theories about acids was put forward by

Antoine Lavoisier (French, 1780's)
Lavoisier used simple plant-extract indicators
(e.g. litmus) to identify acids and bases. He found by
experiment that all the non-metal oxide compounds
he tested produced acid solutions. He concluded
that acids must contain oxygen.

Humphry Davy (English, 1820's)
Forty years later and armed with more chemical knowledge, Davy realised that Lavoisier was wrong about acids. While some acids do NOT contain oxygen (e.g. HCI), he found that all known acids contain hydrogen.

Davy also discovered that metal oxides are basic and described the patterns in the way acids react with metals to form hydrogen gas.

These early ideas were all <u>empirical descriptions</u> of properties; they described the properties of acids discovered by experiment, but did not include a general theory to explain or predict chemical behaviour.

That had to wait for *Svante Arrhenius* (Swedish, 1880's) The <u>Arrhenius Theory</u> of acidsbase behaviour is still generally used in years 7-10 High School Science.

Acids produce H<sup>+</sup> ions in water solution. Bases produce OH<sup>-</sup> ions (or oxide ions).

The Arrhenius Theory was very successful in accounting for simple acid-base behaviour in water solution. It explained the neutralisation reaction, and could explain strong and weak acids as being due to complete or partial ionisation.

However, the Arrhenius Theory had some deficiences:

- It could not account for acid-base behaviour that was not in water solution.
- It could not explain why some ions (which do NOT contain any hydrogen, hydroxide or oxide) showed acid-base behaviour in water solution.

You will soon learn that the main reason for all these deficiencies was that Arrhenius failed to consider the <u>role of the solvent itself</u>, and in water solutions this is critical.

The Bronsted-Lowry Theory was developed independently by Johannes Bronsted (Danish) and Thomas Lowry (English) in

The basic concepts of this theory are not obvious. You will need to read on into the next section, then come back here as needed to understand it fully.

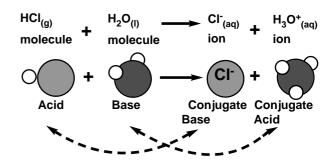
Acid-Base reactions involve transfer of Protons. ( = hydrogen ions, H<sup>+</sup>)
Acids are Proton Donors.
Bases are Proton Acceptors.

Central to the Bronsted-Lowry (B-L) Theory is the concept of "conjugate" species. For example, when ethanoic acid dissolves in water:

The CH<sub>3</sub>COO<sup>-</sup> ion is the <u>conjugate base</u> of Ethanoic acid, because if this reaction was to run in reverse, the ion could act as a base and accept a proton to form ethanoic acid again.

In the forward reaction, the water molecule is acting as a base, because it accepts a proton to become the  $\rm H_3O^+$  ion. The  $\rm H_3O^+$  ion is the <u>conjugate acid</u> because, if the equilibrium shifts left, it can donate a proton and become a water molecule again.

Another Example: Dissolving of HCl in water:



In this case, the reaction is very unlikely to ever run in reverse, but Cl<sup>-</sup> is still considered the <u>conjugate</u> <u>base</u>.

As before, water has acted as a base, and its conjugate acid is the hydronium ion.



# 2. Using Bronsted-Lowry Theory

#### Acids as Proton Donors

What defines all acids is their ability to donate a hydrogen ion (H+) to another species. Since a hydrogen ion is really just a "naked" proton from the nucleus of the hydrogen atom, the formal definition of an acid is:

An acid is a chemical species which DONATES PROTONS

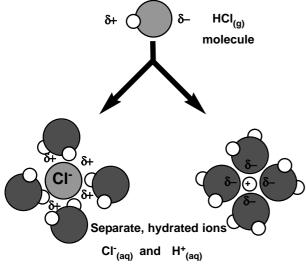
#### Acids in Ageous Solution

When acids dissolve in water, we often just imagine an ionisation such as this example:

Hydrochloric acid:  $HCl_{(g)} \longrightarrow H^+_{(aq)} + Cl^-_{(aq)}$ 

However, this is NOT the full story!

In a previous module you learnt about how ions are "hydrated" by polar water molecules when in solution. The dissolving of HCl in water could be represented



Although there may be many water molecules clinging to a H<sup>+</sup> ion, for simplicity we imagine there is just one, and it forms a special ion, called the "hydronium ion", H<sub>3</sub>O<sub>+</sub>\*.

"hydronium ion", 
$$H_3O^+$$
.

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

HCl is an acid because it has "donated" a proton to a water molecule. The hydronium ion in the solution is an acid because it can, in turn, donate a proton to other species.

In water solution, all acids produce hydronium ions.

# Formation of Hydronium Ions More examples:

Nitric acid:

$$HNO_{3(I)} + H_2O_{(I)} \longrightarrow H_3O^+_{(aq)} + NO_3^-_{(aq)}$$

Sulfuric acid:

$$H_2SO_{4(I)} + 2H_2O_{(I)} \longrightarrow 2H_3O_{(aq)}^+ + SO_4^{2-}(aq)$$

Phosphoric acid:

$$H_3PO_{4(1)} + 3H_2O_{(1)} \longrightarrow 3H_3O_{(aq)}^+ + PO_4^{3-}$$

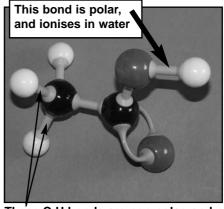
#### Some useful words:

MONOPROTIC = donating 1 proton (e.g. HCl) DIPROTIC = donating 2 protons (e.g.  $H_2SO_4$ ) TRIPROTIC = donating 3 protons (e.g.  $H_2PO_4$ )

#### The "Organic" Acids

Many naturally-occurring, biological molecules are acids too. These are carbon-compounds, made by living things and most contain a special chemical group you should become familiar with: the "-COOH" group.

Perhaps the most important is <u>ethanoic acid</u>, CH<sub>3</sub>COOH:



—C

This group is usually abbreviated as "-COOH" and is always acidic.

These C-H bonds are non-polar, and never ionise.

When this molecule is dissolved in water the O-H bond ionises, and donates a proton to a water molecule:

$$\mathsf{CH_3COOH_{(aq)}} + \, \mathsf{H_2O_{(l)}} \; \Longrightarrow \; \mathsf{H_3O^+_{(aq)}} + \, \mathsf{CH_3COO^-_{(aq)}}$$

ethanoic + water 
$$\longrightarrow$$
 hydronium + ethanoate

Notice that this reaction is reversible and typically reaches a dynamic equilibrium which "lies to the left", favouring the reactants.

**Now Complete Worksheet 3** 



### Strong & Weak Acids

In everyday usage, a "strong" solution might mean the same as "concentrated" (i.e. having a lot of solute) and "weak" can mean the same as "dilute".

FROM HERE ON, YOU MUST NOT USE THESE TERMS THAT WAY. "Strong" & "weak" have particular meanings with regard to acids.

For example, HCl is a <u>STRONG acid</u>; when added to water the reaction goes fully to completion.

$$HCI_{(g)} + H_2O_{(I)} \longrightarrow H_3O^+_{(aq)} + CI^-_{(aq)}$$

100% of the HCl molecules are ionised.

If the concentration of HCl was (say) 1 molL<sup>-1</sup>, then the concentration of hydronium ions will also be 1 molL<sup>-1</sup>.

In contrast, ethanoic acid is a <u>WEAK acid</u>; when added to water, the reaction...

$$CH_3COOH_{(aq)} + H_2O_{(l)}$$
  $\Rightarrow$   $H_3O^+_{(aq)} + CH_3COO^-_{(aq)}$ 

...reaches an equilibrium with only about 1% of the molecules ionised. (i.e. the equilibrium lies well to the left, favouring the reactant molecules.) If the concentration of the solution was 1 molL<sup>-1</sup>, then the hydronium ion concentration would be only about 0.01 molL<sup>-1</sup>.

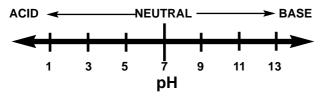
It is quite possible to have a "concentrated solution of a weak acid" or a "dilute solution of a strong acid"... just be careful with these precise meanings!

STRONG Acid = Total Ionisation in Solution

**WEAK Acid = Partial Ionisation in Solution** 

### The pH Scale

You are already familiar with the pH scale in a descriptive way.



Where do these numbers come from?

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

pH is the negative logarithm of the molar concentration of hydronium ions

#### Notes:

- 1. You must know that [square brackets] around any chemical species means "molar concentration".
- 2. " $\log_{10}$ " means the "logarithm to base 10". This is a mathematical function, best understood by example:

If 
$$100 = 10^2$$
, then  $\log_{10}(100) = 2$   
 $1,000 = 10^3$ , then  $\log_{10}(1,000) = 3$   
 $500 = 10^{2.699}$ , then  $\log_{10}(500) = 2.699$   
pH values are therefore, powers of 10.

3. Different calculators may handle log functions differently. You must find out or figure out how to do log functions on <u>your</u> calculator.

### More about pH

Since the numbers on the pH scale are powers of 10, it follows that if an acid solution has a pH one unit lower than another, it is actually 10 times more acidic. Two units on the pH scale represents 100 times ( $10^2$ ) difference in [ $H_3O^+$ ].

Example Calculations: pH and [H<sub>3</sub>O+]

1. If the concentration of hydronium ions is  $[H_2O^+] = 0.500 \text{molL}^{-1}$ , what is the pH?

Solution: 
$$pH = -log_{10}[H_3O^+]$$
  
=  $-log_{10}[0.500]$   
=  $-(-0.301)$   
∴  $pH = 0.301$ 

2. If the concentration of hydronium ions is

[H<sub>3</sub>O<sup>+</sup>] = 0.00252molL<sup>-1</sup>, what is the pH?  
Solution: pH = 
$$-\log_{10}[H_3O^+]$$
  
=  $-\log_{10}[0.00252]$   
=  $-(-0.2.60)$   
∴ pH = 2.60 Now Complete Worksheet 4

3. If the pH = 3.75, what is  $[H_3O^+]$ ? <u>Solution</u> pH =  $-log_{10}[H_3O^+]$ so  $[H_3O^+]$  = Inverse(log(-3.75))

so 
$$[H_3O^+]$$
 = inverse(log(-3.75)  
∴  $[H_3O^+]$  = 0.000178 molL<sup>-1</sup>.

Example:

Acid "P":  $[H_3O^+] = 10^{-5} \text{molL}^{-1}$ . pH = 5 Acid "Q":  $[H_3O^+] = 10^{-3} \text{molL}^{-1}$ . pH = 3 Acid "R":  $[H_3O^+] = 10^{-2} \text{molL}^{-1}$ . pH = 2

In the examples above, acid "Q" has a  $[H_3O^+]$  value 100 times larger than "P", and its pH is 2 units lower. Acid "R" has a  $[H_3O^+]$  value 10 times higher than "Q", and its pH is 1 unit lower.

The ph scale is said to be "<u>logarithmic</u>", because the values are logarithms... powers of 10.



### pH of Strong & Weak Acids

Remember the special meanings of "strong" and "weak" with regard to acids. You may have used a pH meter to measure the pH of several different acids of exactly the same concentration.

#### 1.00 molL<sup>-1</sup> Hydrochloric Acid

When HCI<sub>(q)</sub> dissolves in water:

$$HCI_{(g)} + H_2O_{(I)} \longrightarrow H_3O^+_{(aq)} + CI^-_{(aq)}$$

Since HCI is a STRONG ACID, the ionisation is 100%.

If [HCI] = 1.00 molL<sup>-1</sup>,  
then 
$$[H_3O^+]$$
 = 1.00 molL<sup>-1</sup>

$$pH = -log_{10}[H_3O^+] = -log_{10}[1.00]$$

Sure enough, by experiment you will have found that a 1  $molL^{-1}$  HCl solution has a pH = 0.

#### 1.00 molL<sup>-1</sup> Sulfuric Acid

When H<sub>2</sub>SO<sub>4(1)</sub> dissolves in water:

$$H_2SO_{4(I)} + 2H_2O_{(I)} \longrightarrow 2H_3O^+_{(aq)} + SO_4^{2-}_{(aq)}$$

Since  $H_2SO_4$  is a STRONG ACID, the ionisation is 100%. It is DIPROTIC, so each mole of  $H_2SO_4$  produces 2 moles of  $H_3O^+$ .

If 
$$[H_2SO_4] = 1.00 \text{ molL}^{-1}$$
,  
then  $[H_3O^+] = 2.00 \text{ molL}^{-1}$ 

pH = 
$$-\log_{10}[H_3O^+]$$
  
=  $-\log_{10}[2.00]$   
=  $-(0.301)$   
∴ pH =  $-0.30$ 

Sure enough, by experiment you will have found that a 1  $molL^{-1}$   $H_2SO_4$  solution has a pH = -0.30. (below zero)

#### 1.00 molL<sup>-1</sup> Ethanoic Acid

When CH<sub>3</sub>COOH dissolves in water:

$$CH_3COOH_{(aq)}+H_2O_{(l)}$$
  $\Longrightarrow$   $H_3O^+_{(aq)}+CH_3COO^-_{(aq)}$ 

Since this is a WEAK ACID, the ionisation is incomplete.

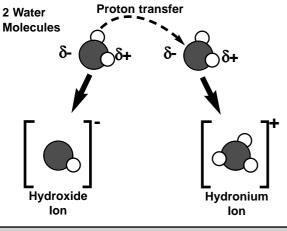
If 
$$[CH_3COOH] = 1.00 \text{ molL}^{-1}$$
, then  $[H_3O^+] << 1.00 \text{ molL}^{-1}$ 

and the pH can be expected to be well above the values found for HCl or H2SO4.

By experiment you will have found that a 1 molL<sup>-1</sup> CH<sub>3</sub>COOH solution has a pH  $\cong$  2.

### Self-Ionisation of Water

Water itself can be considered as an extremely weak acid, since in pure water a few water molecules ionise and donate a proton to another molecule.



$$2 H_2 O_{(I)} \longrightarrow OH_{(aq)}^- + H_3 O_{(aq)}^+$$

In pure water, at 25°C, it turns out that the concentration of hydronium ions,  $[H_3O^+] = 1.00 \times 10^{-7} \text{ molL}^{-1}$ .

So the pH of pure water:

pH = 
$$-\log_{10}[H_3O^+]$$
  
=  $-\log_{10}[1.00 \times 10^{-7}]$   
=  $-(-7.00)$   
∴ pH = 7.00

- That's why pH = 7 is <u>neutral</u> on the pH scale!
- In an acid solution,  $[H_3O^+] > 1.00 \times 10^{-7} \text{ molL}^{-1}$ , so pH < 7
- In a basic solution,  $[H_3O^+] < 1.00 \times 10^{-7} \text{ molL}^{-1}$ , so pH > 7



### [OH-] & the pOH Scale

#### Ion-Product of Water

When pure water undergoes self-ionisation...

$$2 H_2O_{(I)} \rightarrow OH_{(aq)} + H_3O_{(aq)}^+$$

...the concentrations of OH and H<sub>2</sub>O are equal and both have the value of 1.00x10<sup>-7</sup> molL<sup>-1</sup> at 25°C.

A useful way to describe the equilibrium is called the "lon-Product" for water.

$$K_w = [OH^-][H_3O^+] = 1x10^{-14} \text{ at } 25^{\circ}\text{C}.$$

If each part of this expression is manipulated by taking the negative logarithm (-log), you get

$$pK_w = pOH + pH = 14$$

(Note that the lower case "p" in front of an expression is taken to mean "-log" of that value.)

#### Example Calculations: pH and pOH

- 1. In a water solution at 25C, the concentration of hydroxide ions  $[OH^{-}] = 5.0 \times 10^{-5} \text{ molL}^{-1}$ .
- a) What is the pOH?
- b) What is the pH?
- c) What is [H<sub>2</sub>O+]?

#### Solution

a)  $pOH = -log[OH^{-}] = -log(5 \times 10^{-5}) = 4.30$ 

This expression at left contains the item "pOH". This refers to the negative logarithm of the concentration of hydroxide ions, and is entirely analogous to pH.

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

**Notice that** pOH + pH = 14 (at 25°C).

This means that in a water solution, if the pH is (say) 3, then pOH = 14 - 3 = 11This allows you to calculate the concentration of hydroxide ions, as well as hydronium ions from pH.

(Mathematical note: In the expression for  $K_w$  the concentrations are multiplied, but this becomes an addition when log functions are applied. This is because logs are index numbers (powers) which must be added when multiplying expressions.)

#### Solution (cont.)

b) 
$$pOH + pH = 14$$
, so  $pH = 14 - pOH$   
= 14 - 4.30

= 9.7

c) 
$$pH = -log_{10}[H_3O^+]$$
  
so  $[H_3O^+] = Inverse(log(-9.7))$ 

$$\therefore$$
 [H<sub>3</sub>O+] = 2.0 x 10<sup>-10</sup> molL<sup>-1</sup>.

To check that this is correct, you could use the expression for K<sub>w</sub>.

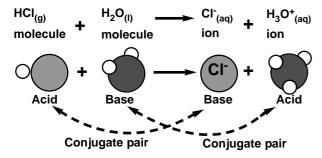
$$K_w = [OH^-][H_3O^+] = 5x10^{-5} \times 2x10^{-10} = 1.0x10^{-14}$$



## Water is Amphiprotic

#### Water Can Act as a Base

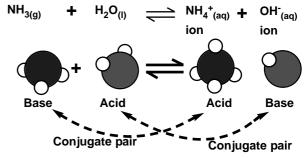
Previously, we explained the formation of hydronium ions in water solution using this example:



Note that the water molecule acts as a base (in terms of B-L Theory) because it accepts a proton from the HCI molecule.

Chemical species (like water) which can both donate and accept protons are called "AMPHIPROTIC". More Amphiprotic species later.

Water Can be an Acid, Too Water can also act as an acid and donate a proton. For example, when ammonia, NH<sub>3</sub> dissolves:



In this reaction the water molecule acts as an acid by donating a proton. Its conjugate base is the hydroxide ion, OH<sup>-</sup>.

This equation explains why ammonia is a base, and why a solution of ammonia  $(NH_{3(aq)})$  can be considered as a solution of ammonium hydroxide, NH<sub>4</sub>OH<sub>(an)</sub>. **Now Complete Worksheet 5** 



#### Acidic and Basic Salts

One of the weaknesses of the Arrhenius Theory was that it could not explain the results of simple experiments you may have done:

#### **Practical Work:**

### Testing the pH of Various Salt Solutions

You may have done simple experiments using a pH meter, or Universal Indicator, to test the pH of solutions of various ionic "salts", none of which seem to be obviously acids or bases, from their formulas.

You may have tested many, but they probably included...

sodium chloride, NaCl sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>

sodium hydrogen sulfate,  $NaHSO_4$ 

...all at the same concentration, in pure water.



### **Typical Results**

<u>Salt</u>	Нq	Conclusion
NaCl	7	Neutral
Na <sub>2</sub> CO <sub>3</sub>	11	Basic
NaHSO <sub>₄</sub>	2	Acidic

The reasons WHY some salts show acid-base behaviour is explained below. The Arrhenius Theory failed to account for the acid-base of the solvent, water.

Note: Due to CO<sub>2</sub> from the air dissolving in the solution, the pH of the NaCl solution may be slightly acidic.

#### Acidic Salts

As some ions dissolve in water they react as acids, forcing the water molecule to be a base. An example is the "hydrogen sulfate ion", HSO<sub>4</sub>-.

$$HSO_{4 (aq)}^{-} + H_2O_{(I)} \longrightarrow SO_4^{2-}(aq) + H_3O^{+}(aq)$$

If the salt used was sodium hydrogen sulfate there would also be some sodium ions in the solution. In terms of acid-base behaviour, they would be merely spectators.

#### Basic Salts

dissolve in water and react as bases, forcing the water molecule to be the acid. An example is the carbonate ion:

$$CO_3^{2-}_{(aq)} + H_2O_{(l)} \longrightarrow HCO_3^{-}_{(aq)} + OH^{-}_{(aq)}$$

Once again, if sodium carbonate was used, there would be sodium ion "spectators" in the solution as well.

A few worth remembering					
Acidic Salts	Neutral Salts	Basic Salts			
NaHSO <sub>4</sub>	NaCl	Na <sub>2</sub> CO <sub>3</sub>			
NH₄CI	KNO <sub>3</sub>	CH <sub>3</sub> COONa			
NH <sub>4</sub> NO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	(sodium			
ethanoate) (There is a pattern to help you remember these later)					

### Neutralisation... Again

Now that you know about B-L Theory, we can go back to look again at the simple acid-alkali neutralisation.

#### **Example**

$$HCI_{(aq)} + NaOH_{(aq)} \longrightarrow H_2O_{(l)} + NaCI_{(aq)}$$

However, now we know that what makes HCI an acid is really the formation of  $\rm H_3O^+$  ions in water, and the CI<sup>-</sup> ions are spectators, as are the Na<sup>+</sup> ions from the NaOH.

Leaving out the spectators, the net ionic equation is...

$$H_3O^+_{(aq)} + OH^-_{(aq)} \longrightarrow 2H_2O_{(l)}$$

The reaction involves a proton transfer

... and this is the net reaction for ALL the simple acid-alkali reactions, regardless of which acid or which alkali are used.



### Salts from Acid-Base Neutralisations

Although we might view all neutralisations as essentially the same reaction and ignore the "spectator ions" which form the "salt", this prevents us noticing a useful pattern which was mentioned on the previous page.

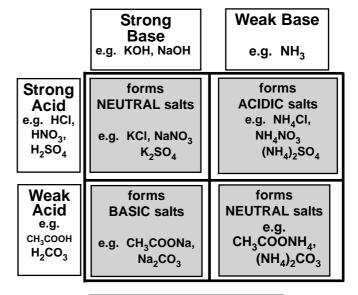
The nature of the "salt" formed depends on whether the acid and base were "strong" or "weak", as shown at right... see the pattern?

Why is Ammonia (NH<sub>3</sub>) a "Weak Base"?

#### Simple!

Because when it reacts with water, the reaction does NOT ionise fully, but reaches an equilibrium with a significant concentration of un-ionised molecules present.

$$NH_{3(aq)} + H_2O_{(I)}$$
  $\longrightarrow$   $NH_4^+_{(aq)} + OH_{(aq)}^-$ 



**Now Complete Worksheet 6** 

### Acid-Base Reactions without H<sub>3</sub>O+, OH or H<sub>2</sub>O

Although most of the simple examples of neutralisation involve the reaction

$$H_3O^+_{(aq)} + OH^-_{(aq)} \longrightarrow 2H_2O_{(I)}$$

and usually we study reactions taking place in water, be aware that this is not always the case.

For example, if you add together the <u>dry gases</u>  $HCl_{(g)}$  and  $NH_{3(g)}$  they will react

hydrogen + ammonia 
$$\longrightarrow$$
 ammonium chloride  $HCI_{(g)} + NH_{3(g)} \longrightarrow NH_4CI_{(s)}$ 

Proton transfer

Although there is no water present, and no H<sub>3</sub>O<sup>+</sup> or OH<sup>-</sup> ions are formed at any time, this is clearly an acid-base reaction, according to the B-L definition.

### Changes in pH When Solutions are Diluted

What happens to the pH of a solution if it is diluted? This is best understood with some worked examples.

#### Diluting an Acid Solution

- a) What is the pH of a 0.25 molL<sup>-1</sup> solution of HCI?
- b) If 5.0mL of this solution was diluted to 100mL with pure water, what is the new pH?

Solution

a) 
$$HCI_{(g)} + H_2O_{(I)} \longrightarrow H_3O^+_{(aq)} + CI^-_{(aq)}$$

Since HCl is a strong acid, then  $[H_3O^+] = 0.25 \text{ molL}^{-1}$ .

pH = 
$$-\log_{10}[H_3O^+]$$
  
=  $-\log_{10}[0.25]$   
=  $-(-0.602)$   $\therefore$  pH = 0.60

b) Can use  $c_1V_1 = c_2V_2$ , or apply logic:

Diluting 5mL to 100mL is a dilution factor of 20.

$$\therefore$$
 [H<sub>3</sub>O<sup>+</sup>] will be 20 times lower = 0.25 / 20 = 0.0125

$$pH = -log_{10}[H_3O^+] = -log_{10}[0.0125]$$

#### Diluting a Base Solution

- a) What is the pH of a 0.50 molL<sup>-1</sup> solution of KOH? b) If 1.0mL of this solution was diluted to 250mL
- with pure water, what is the new pH?

#### Solution

a) 
$$KOH_{(g)} + H_2O_{(I)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$$
  
Since KOH is a strong base, then  $[OH^-] = 0.50$  molL<sup>-1</sup>.

pOH = 
$$-\log_{10}[OH^{-}] = 0.30$$
. Now pOH + pH = 14  
  $\therefore$  pH = 13.7

- b) Can use  $c_1V_1 = c_2V_2$ , or apply logic:
- Diluting 1mL to 250mL is a dilution factor of 250.
- $\therefore$  [OH-] will be 250 times lower = 0.5 / 250 = 0.002

pOH = 
$$-\log_{10}[OH^-] = 2.70$$
.  $\therefore$  pH = 11.3 (lower pH means less basic)



# 3. Quantitative Analysis

### **Titration**

Titration has been one of the most important techniques in Chemical Analysis for over a century. Its use has diminished as electronic "probes" have become more widespread, but it remains a "must-know" part of Chemistry.

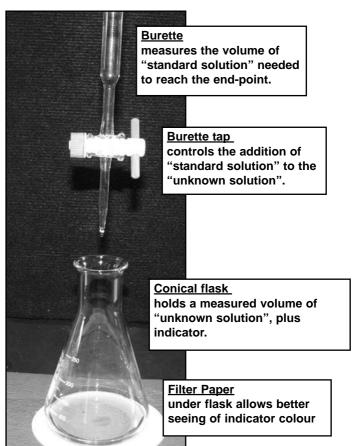
The purpose of titration is <u>Chemical Analysis</u>. It allows the concentration of an "<u>unknown</u>" solution to be determined by calculation, after measuring the volume of a known-concentration "<u>standard solution</u>" which reacts with a sample to reach the "<u>equivalence-point</u>" (end-point). This is the point where the reactants have been consumed in exactly the molar ratio specified by the balanced equation.

Titration can be used for any reaction for which you can determine the "end-point". Acid-base neutralisations are ideal because indicators (or pH probes) can identify the end-point.

#### Titration Technique

- You must have a "standard solution" (next page)
- The burette should be rinsed with small quantities of the standard solution, then filled with it. The level is then adjusted to the zero mark, ensuring that there are no air bubbles in the tap and delivery spout.
- An exact, measured volume of "unknown" solution is placed in the reaction flask by pipette. ("Aliquot")
- 1-2 drops of suitable indicator are added to the flask. (See "Choosing the Indicator", next page)
- The reaction proceeds by careful addition, with mixing, of solution from the burette. Add drop-bydrop approaching the end-point, until the indicator just changes colour.
- Record the volume of solution delivered by burette. Repeat 3 times, and average the "titres" (= burette volumes). It is common to discard any values which are not in close agreement.

  The rest is calculation.



Example Titration Calculation Titration of an "unknown" solution of KOH.

"Aliquot" (volume of samples) = 25.00 mL (by pipette)

Standard solution; H<sub>2</sub>SO<sub>4</sub> solution, C = 0.04252 molL<sup>-1</sup>. Indicator used: Bromothymol Blue (see next page)

"<u>Titres</u>" (volumes from burette)
measured (in mL): 34/25, 33.90, 33.85, 33.95.
The first titre is discarded (not in close agreement with the others). Average titre = 33.90 mL

Titration Formula:  $\frac{\text{Ca x Va}}{\text{a}} = \frac{\text{Cb x Vb}}{\text{b}}$ 

Ca, Cb = concentrations (molL-1) of acid & base solns Va, Vb = volumes (mL) of each solution used.
a, b = molar co-efficients (balancing numbers) from balanced equation for reaction.

Step 1: Balanced equation (ALWAYS!!)

$$H_2SO_4 + 2KOH \longrightarrow 2H_2O + K_2SO_4$$

Step 2: Titration Formula

$$Ca \times Va = Cb \times Vb$$

ı b

Step 3: Re-arrange and substitute.

We are trying to find the concentration of the "unknown" base, so make "Cb" the subject:

 $Cb = b \times Ca \times Va$  $a \times Vb$ 

= 2 x 0.04252 x 33.90 1 x 25.00

= 0.1153

∴ Concentration of KOH solution = 0.1153 molL<sup>-1</sup>.



### Titration Technique (cont.)

### Preparing a Standard Solution

The key to titration is to have available a suitable "standard solution".

The problem is to get a substance which is of very high purity and stability to use as a "Primary Standard" to make the solution from.

The common acids like  $\rm H_2SO_4$ , and bases like NaOH, cannot be obtained in the pure state due to the way they rapidly absorb water and/or  $\rm CO_2$  from the atmosphere.

Suitable primary standard substances are:

- Base: anhydrous sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>
- Acid: oxalic acid, COOHCOOH (diprotic)

Calculate the mass of pure, dry <u>Primary Standard</u> solute required for solution, and weigh out accurately

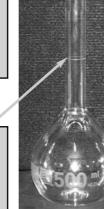


Dissolve Solute in a small amount of (pure) water in a clean beaker





Carefully transfer solution into a Volumetric Flask. Rinse beaker with small amounts of water & add washings to flask



Add water to flask to fill it to the mark.
(Use a dropper to avoid overshooting)
Insert stopper & mix well.

In the example (previous page) the standard solution was  $\rm H_2SO_4$ . This would <u>not</u> have been a primary standard solution.

It may have been "<u>standardised</u>" by titration against a primary standard Na<sub>2</sub>CO<sub>3</sub> solution, so that its exact concentration is known. Then it can be used, in turn, as the titration standard solution.

#### Selecting the Indicator

Choosing the best indicator to use is not just a matter of which colour change you'd prefer looking at.

Each indicator changes colour over a range of pH values, and the trick is to choose an indicator which will change colour as close to the "end-point" as possible.

	Colour in		<u>Changes</u>
<u>Indicator</u>	<u>Acid</u>	<u>Base</u>	at pH
1.9			
Litmus	red	blue	6 - 8
Bromothymol blue	yellow	blue	6.2 - 7.6
Methyl orange	red	yellow	3.1 - 4.4
Phenolphthalein	clear	pink	8.3 - 10.0

Isn't the end-point always at neutral, pH = 7 ?? (I hear you ask)

No, its not! Remember (see p.12) that the "salts" formed by different combinations of strong or weak acids and bases may have acidic or basic properties. This means that, at the exact end point, the pH might not be neutrality.

Strong Acid - Strong Base
If titrating (say) H<sub>2</sub>SO<sub>4</sub> against KOH,
you can expect the salt K<sub>2</sub>SO<sub>4</sub> to be neutral.

Therefore, choose Bromothymol blue, which changes colour near pH = 7.

(Actually, it doesn't really matter, because the last drop of chemical at the end point causes a huge pH change.) See graph next page.

Strong Acid - Weak Base If titrating (say)  $H_2SO_4$  against  $NH_3$ , you can expect the salt  $(NH_4)_2SO_4$  to be acidic.

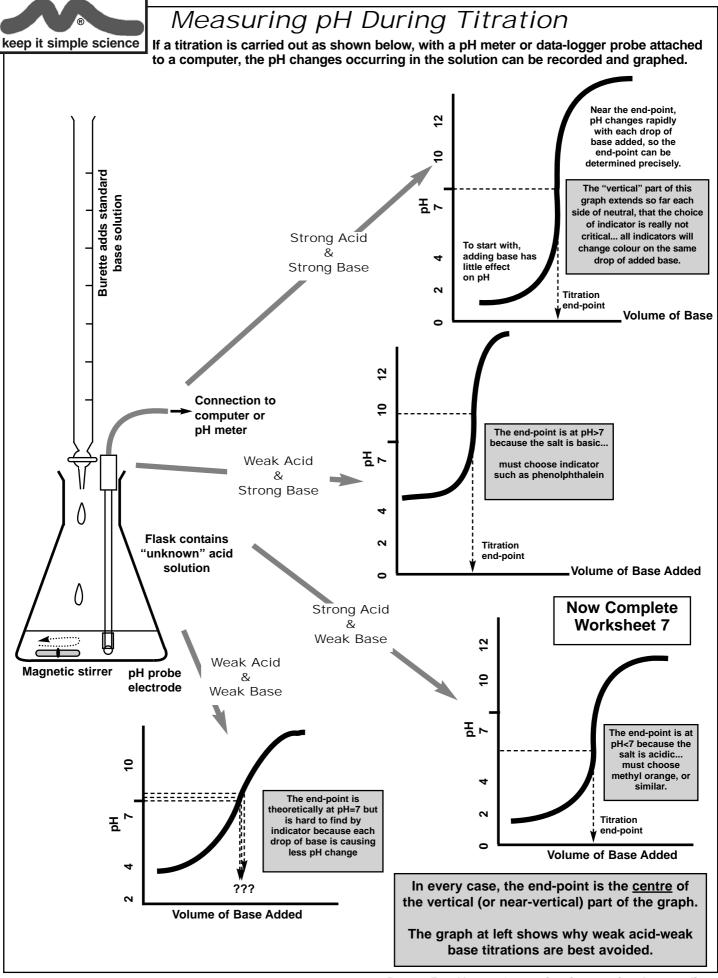
Therefore, choose Methyl orange, which changes colour around pH = 3-4.

Weak Acid - Strong Base If titrating (say) CH<sub>3</sub>COOH against KOH, you can expect the salt (potassium ethanoate,CH<sub>3</sub>COOK) to be basic.

Therefore, choose <u>Phenolphthalein</u>, which changes colour around pH = 8-10.

Weak Acid - Weak Base
Titrations with this combination are to be avoided,

Titrations with this combination are to be avoided, because the end-point is not very "sharp".



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### More About Titration Graphs

All the titration graphs on the previous page were examples of a titration where the "unknown" solution (in the flask) was an acid. It was titrated by adding known "standard" base solution from the burette.

You can tell from the graphs, because the pH starts low (acidic) and ends high (basic) as it proceeds beyond the end point.

Of course, a titration can be done in the reverse way.

Look at the graph at right. It begins high (basic) and ends low (acidic). This means the "unknown" in the flask was a base and acid was added from the burette to move through the end point.

You can also look for clues as to whether the acid & base were "strong" or "weak". The precise pH depends on concentrations of solutions, but generally speaking:

- if the "acid end" of the graph begins or ends near ph = 0, then the acid must be strong.
- if the "acid end" of the graph begins or ends near ph = 3-4, then the acid must be weak.
- if the "base end" of the graph begins or ends near ph = 14, then the base must be strong.
- if the "base end" of the graph begins or ends near ph = 10-11, then the base must be weak.

Compare the starting and ending pH values of these 2 graphs.

Don't forget that, before electronic pH-measuring devices, the end point was determined solely by the colour change of an indicator.

#### Conductivity Graphs

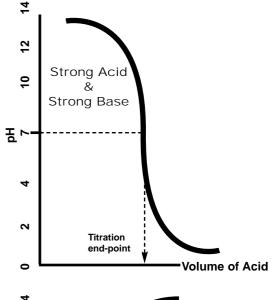
Measuring the pH is not the only graphical method for finding the end point of a titration. Another way is to measure the electrical conductivity of the solution.

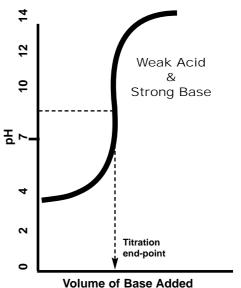
Conductivity of aqueous solutions is mainly dependant upon the concentration of ions in the solution. This reaches a minimum at the end-point because:

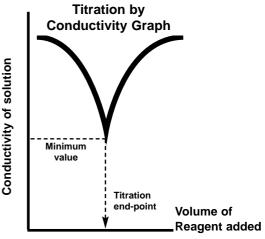
$$H_3O^+_{(aq)} + OH^-_{(aq)} \longrightarrow 2H_2O_{(l)}$$

...neutralisation consumes these ions and the conductivity of molecular water is essentially zero.

Of course, the presence of other "spectator ions" guarantees that there is always some degree of conductivity, but the endpoint of the titration is marked by a distinct minimum-value point on a conductivity graph.







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## Dissociation Constants & pKa

You were previously introduced to the...

Ion-Product of Water

When pure water undergoes self-ionisation...

$$2 H_2O_{(l)} \rightarrow OH_{(aq)}^- + H_3O_{(aq)}^+$$

...the concentrations of  $OH^-$  and  $H_3O^+$  are equal and both have the value of  $1.00 \times 10^{-7}$  molL<sup>-1</sup> at 25°C.

A useful way to describe the equilibrium is called the "lon-Product" for water.

$$K_w = [OH^-][H_3O^+] = 1x10^{-14} \text{ at } 25^{\circ}\text{C}.$$

If each part of this expression is manipulated by taking the negative logarithm (-log), you get

$$pK_w = pOH + pH = 14$$

(Note that the lower case "p" in front of an expression is taken to mean "-log" of that value.)

Perhaps you didn't realise it then, but this expression arises from the <u>equilibrium constant</u> for the dynamic equilibrium.

#### Equilibrium Constant

When pure water undergoes self-ionisation the equilibrium constant expression is:

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

However, in any aqueous solution, the concentration of water molecules is essentially the same. ie, it has a constant value.

To simplify the expression, this value is "absorbed" into  $K_{react}$  to give the useful expression " $K_{w}$ " shown at left

#### Dissociation Constant for an Acid

Similarly, we can write a general equation for the dissociation of any acid as:

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

and its equilibrium constant as:

$$K_a = [H_3O^+][A^-]$$
 $[HA][H_2O]$ 

Once again, the concentration of water can be taken as a constant value and "absorbed" into "K<sub>a</sub>", the "acid-dissociation constant".

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

And, (we are sure you saw this coming!) it is often convenient to take the negative logarithm of this value and call it "pK<sub>a</sub>"

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

*K<sub>a</sub> Values for Strong & Weak Acids*Consider a strong acid, such as HCI.

HCI + 
$$H_2O \rightleftharpoons H_3O^+ + CI^ K_a = \frac{[H_3O^+][CI^-]}{[HCI]}$$

Since dissociation is essentially 100%, you can figure out that the value of Ka is very large... in fact is thought to be about  $10^9$ , so pKa  $\cong$  -9.

Now consider a weak acid, such as ethanoic acid.

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

$$K_a = [H_3O^+][CH_3COO^-]$$

$$[CH_3COOH]$$

Since only about 1% of molecules dissociate, you can figure out that the value of  $\rm K_a$  will be much smaller and  $\rm pK_a$  very much larger.

In fact, 
$$pK_a = 4.76$$

Values of pK<sub>a</sub> allow you to calculate the pH of weak acid solutions. (continued over...)



### Using pK<sub>a</sub> values

Example Problem 1: pH from pKa

Hydrofluoric acid (HF) is a weak acid with  $pK_a = 3.17$ 

- a) Write an equation for its B-L dissociation in water.
- b) Identify the conjugate pairs involved.
- c) Write an expression for K<sub>a</sub>.
- d) Calculate the pH of a 0.200 molL<sup>-1</sup> HF solution.

Solution

a) 
$$HF + H_2O \implies H_3O^+ + F^-$$

b) HF acts as an acid; conjugate base is F<sup>-</sup> H<sub>2</sub>O acts as base; conjugate acid is H<sub>3</sub>O<sup>+</sup>

c) 
$$K_a = \frac{[H_3O^+][F^-]}{[HF]}$$

d) Since pKa = 3.17, then  $K_a$  = antilog (-3.17)  $\therefore K_a = 6.76 \times 10^{-4}$ 

let  $[H_3O^+]$  = "x" at equilibrium. So  $[F^-]$  = "x" also. then  $K_a = x^2 / (0.200-x) = 6.76 \times 10^{-4}$ (that may require some discussion)

This last expression is a quadratic equation and can be solved using the "quadratic function", after some re-arrangement.

However, for weak acids the value "x" compared to the initial concentration (0.200) is generally so small as to be insignificant. Therefore, the expression (0.200-x) can be taken to be  $\cong$  0.200.

So, a good approximation is

$$K_a = x^2 / 0.200 = 6.76x10^{-4}$$
  
∴  $x = \sqrt{0.200 \times 6.76x10^{-4}}$   
= 1.35x10<sup>-4</sup> molL<sup>-1</sup>.

$$pH = -log[H_3O^+] = 3.87$$

Let's check on our approximation:

What is 0.200-x? 0.200 - 0.000135 = 0.199865. This so close to 0.200 that our approximation is well within the precision of the question and therefore is justified.

Example Problem 2: pKa from pH

A weak acid solution is of concentration  $[HA] = 0.350 \text{ molL}^{-1}$ . The pH is measured to be 4.50.

- a) Write expressions for the dissociation equilibrium and for  $K_a$ .
- b) Find the value for K<sub>a</sub> and pK<sub>a</sub>.

Solution

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

b) 
$$K_a = [H_3O^+][A^-]$$
 [HA]

Since pH = 4.50, then  $[H_3O^+]$  = antilog (-4.50)  $\therefore [H_3O^+] = 3.16 \times 10^{-5} \text{ molL}^{-1}.$ 

$$\therefore K_a = [H_3O^+][A^-] = (3.16x10^{-5})^2 / 0.350$$
[HA]

Note:

[HA] at equilibrium should really be [HA]= 0.35 - 3.16x10<sup>-5</sup>, but we have applied the same approximation as in problem 1. You may verify the validity of this yourself.

Continuing from above:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = (3.16 \times 10^{-5})^2 / 0.350$$
  
= 2.85 x 10<sup>-9</sup>

and 
$$pK_a = -log(K_a) = 8.54$$

(Comparing this pKa to other values, it shows that this (ficticious) acid is a VERY weak acid compared to most)

Now Complete Worksheet 8



### **Buffers**

A "Buffer", or "buffered solution", is a solution which can absorb significant amounts of acid or base with minimal change in pH.

Biology students will be aware that in all living things it is vital that the conditions within the body/cells are kept very constant. Living things cannot function properly if their "internal environment" undergoes large changes in:

- temperature, water content,
- salt concentration, (and many other chemicals) AND
- pH level.

The fluids inside all living things are buffered, so that pH remains remarkably constant, despite changes in the external environment, eating acidic food, breathing, excreting, etc, all of which could alter the body's pH.

### How do Buffers Work?

All buffers are solutions containing a weak acid and its conjugate base.

This equilibrium constitutes a buffer solution, so long as there are significant amounts of the ethanoate ion (CH<sub>3</sub>COO<sup>-</sup>) present. (e.g. by adding CH<sub>3</sub>COONa)

<u>If acid is added</u> (i.e.  $[H_3O^+]$  increases) (pH lower) then (by Le Chatelier's Principle) the equilibrium shifts left, absorbing  $H_3O^+$  and lowering  $[H_3O^+]$  again.

<u>If base is added</u> (ie  $[H_3O^+]$  decreases) (pH higher) then (by Le Chatelier's Principle) the equilibrium shifts right, making  $H_3O^+$  and raising  $[H_3O^+]$  again.

This way, the pH remains quite constant, despite acid or base being added.

#### A Natural Buffer System

The classic example of a natural buffer system is the way our blood is maintained at a pH = 7.4, despite the fact that we keep exchanging CO<sub>2</sub> (acidic), excreting wastes, absorbing foods, etc.

The main chemical buffer in our blood is a solution containing both the bicarbonate ion  $(HCO_3^-)$  and its conjugate base, the carbonate ion  $(CO_3^{-2})$ .

#### *HCO*<sub>3</sub><sup>-</sup> is Amphiprotic

The bicarbonate ion is amphiprotic, which adds a further dimension to its buffering ability.

If the environment is acidic, HCO<sub>3</sub> acts as a base:

$$H_3O^+_{(aq)} + HCO_3^-_{(aq)} \longrightarrow H_2CO_{3(aq)} + H_2O_{(aq)}$$

If the environment is basic, HCO<sub>3</sub> acts as an acid:

$$OH_{(aq)}^{-} + HCO_{3(aq)}^{-} \longrightarrow CO_{3}^{2-}_{(aq)} + H_{2}O_{(aq)}$$

So, the total buffering system can be summarised as:

$$H_2CO_3 \xrightarrow{\frac{-H^+}{2H^+}} HCO_3 \xrightarrow{\frac{-H^+}{2H^+}} CO_3^2$$

This system is highly effective at maintaing the pH of our blood. Be aware that it is not the only buffer operating.

As you'll learn below, Amphiprotic substances are useful in emergencies, too.

# Using Neutralisation on a Chemical Spill

Whether its a small vinegar spill at home, or a sulfuric acid tanker leaking after a road accident, a knowledge of neutralisation can help damage control and safety.



Finish-off by Completing Worksheets 9 & 10 So, if someone gets splashed with a strong base, neutralise it by throwing a bucket of acid over them, right?

Wrong! Unless you can guarantee to apply the exact molar quantity for titration-like precision, then using an acid on an alkali spill (or vice-versa) can do more harm than good, and would be extremely dangerous as a first-aid method.

The best thing to do is use an <u>Amphiprotic</u> substance such as bicarbonate ion (e.g. sodium bicarbonate, NaHCO<sub>3</sub>).

As shown by the reactions above, it can react and neutralise either an acid or a base, and once the neutralisation is achieved, it stops working and poses no further threat in its own right.

It does its job, and then stops automatically... perfect!