The Acidic Environment

HSC ENRICHMENT DAY

Artchaki Chandrasegar & Alexander Comerford

Key points of the acidic environment

TODAY, WE WILL FOCUS ON:

1. **Definitions**: Lavoisier / Davy; Arrhenius; Brønsted-Lowry; conjugate pairs; salts – acidic/basic/neutral; neutralisation; titrations; standard solutions; pH; and buffers

2. **Indicators**: natural, common lab-based; identification of acidic / basic / neutral substances; and the Arrhenius definition

3. **Acids in the air**: equilibria; Le Chatelier's Principle; and chemical equations

4. **Acids in Biological Systems**: Brønsted-Lowry definitions; simple organic acids; strong/weak-dilute/concentrated distinctions; degree of ionisation – weak/strong/equilibria

Antoine Lavoisier

THE OXYGEN THEORY OF ACIDS

- Defined an acid as a non-metal compound which contained oxygen.
- He attempted to define acid in terms of their composition.

- **Limitations** of the oxygen theory:
    - Could not explain why some substances that did not contain oxygen displayed acidic properties.
    - Could not explain why metal oxides were basic (e.g. NaOH)

1743 - 1794

Humphry Davy

THE HYDROGEN THEORY OF ACIDS

- All acids contain **hydrogen** (as opposed to oxygen) - again attempting to define acids in terms of their composition.
- HCl (then called muriatic acid), by undergoing electrolysis, decomposed into hydrogen and chlorine – no oxygen was present.

- **Limitations** of the Hydrogen Theory of Acids:
  - Could not explain why other compounds containing hydrogen were not acidic (e.g. CH_4)
  - Did not make connection with bases

1778- 1829

Arrhenius definition

IONISATION OF H+ AND OH-

- An **acid** is a substance that provides H^+ ions* in aqueous solution
  - *e.g.* $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
  - *e.g.* $H_2SO_4(aq) \rightarrow 2\,H^+(aq) + SO_4^{2-}(aq)$
- A **base** is a substance that provides OH^- (hydroxide) ions in aqueous solution:
  - *e.g.* $NaOH(aq) \rightarrow Na^+(aq) + HO^-(aq)$

1859 - 1929

Problems with Arrhenius' definition

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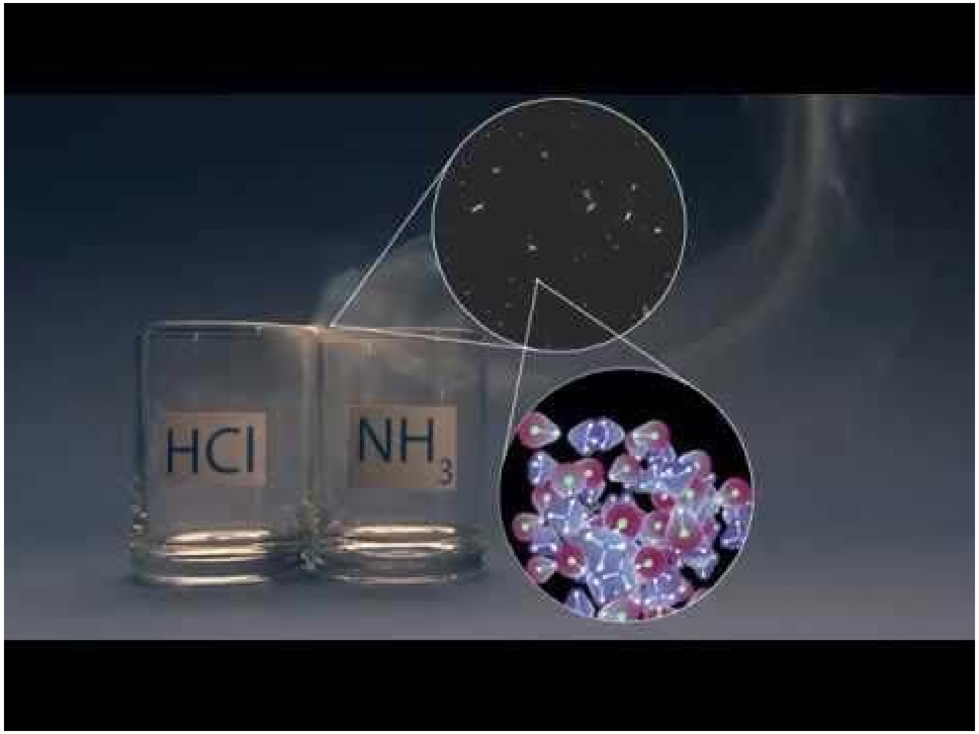
ASKED IN Q8 OF THE 2008 HSC PAPER

- Arrhenius definition explains properties of many acids and bases in the presence of water, but not all
  - For example:
    - Only accounts for substances which already have H^+ or $OH^–$ in their structure (e.g. NH_3 is basic)
    - Does not explain the behaviour of some salts ($ZnCl_2$: acidic, NaS: basic)
    - Cannot explain how some substances can act as both an acid and a base (amphoteric substances like H_2O, $HCO_3^–$, $HSO_4^–$, $H_2PO_4^–$

ACID-BASE REACTION

LIMITATIONS OF ARRHENIUS' DEFINITION



Source:
https://www.youtube.com/watch?v=cz87YmRYwhU

Brønsted –Lowry Definition

OF ACIDS AND BASES PROPOSED INDEPENDENTLY IN 1923

- An acid is a proton (H^+) donor molecule or ion
- A base is a proton acceptor molecule or ion
- Acid-base reactions happen simultaneously - A substance cannot behave as an acid without another behaving as a base (this fact is important in understanding the formation of conjugates).

(Johannes Brønsted)

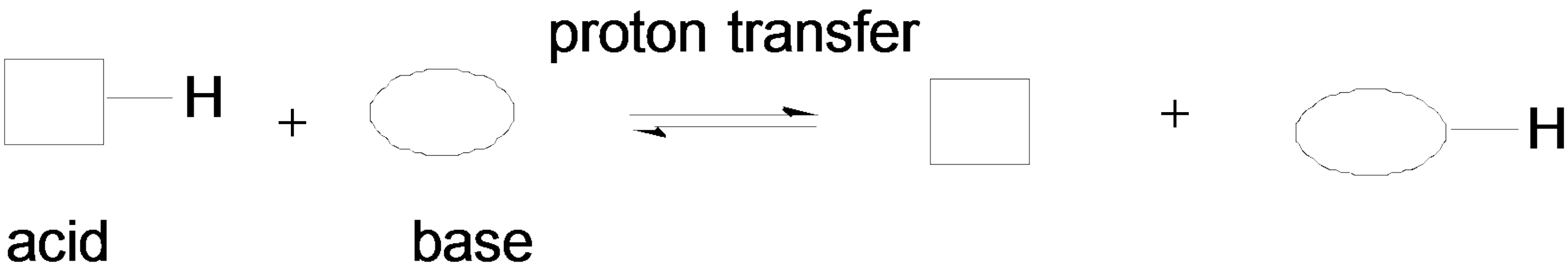
(1879-1947)

(Thomas Lowry)

(1874-1936)

Brønsted –Lowry Definition

APPLIED



EXAMPLE QUESTION:

- *e.g.* NaOH (*aq*) + HCl (*aq*) ➔ H_2O (*l*) + NaCl (*aq*)

ANSWER:

- HCl is a Bronsted-Lowry Acid as it **donates** a proton (H+)
- NaOH is a Bronsted-Lowry Base as it **accepts** a proton (H+)

Summary of acid base definitions

FOR THE HSC COURSE

- **Lavoisier** - noticed that many oxides were acidic (*e.g.* nitrous oxide, sulfur trioxide)
- **Davy** - noticed many hydrides were acidic (*e.g.* hydrogen sulfide, hydrogen chloride)
- **Arrhenius** - acids dissociate to H^+ and bases to OH^-
- **Brønsted/Lowry** - acids are proton (H^+) donors, bases are proton acceptors

2005 HSC had the question "Analyse how knowledge of the composition and properties of acids has led to changes in the definition of acids."

Sample Question

Q3 2014 HSC Final Exam

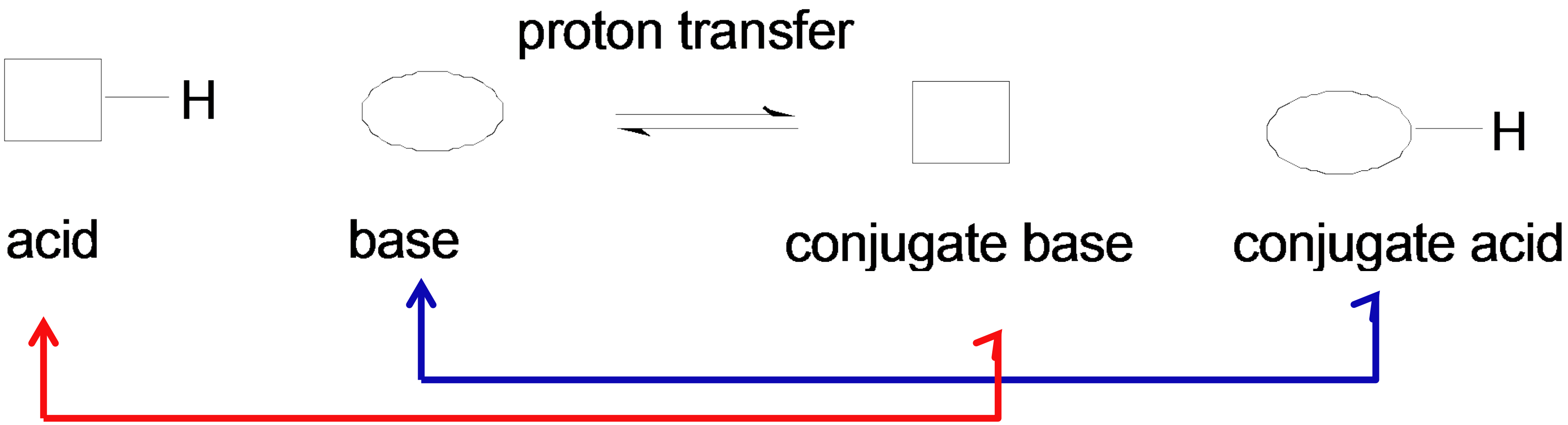
Which row of the table correctly matches the scientist(s) with their theory of acids?

	Scientist(s)	*Theory*
(A)	Arrhenius	Acids contain oxygen
(B)	Brönsted and Lowry	Acids are proton donors
(C)	Davy	Acids are able to produce hydrogen ions in water
(D)	Lavoisier	Acids contain hydrogen

Conjugate pairs

FOR ACIDS AND BASES

- An acid gives up a proton (H^+) to form its conjugate base
- A base accepts a proton (H^+) to form its conjugate acid



Conjugate pairs

EXAMPLES

Conjugate base = acid – H^+
Conjugate acid = base + H^+
Remember charges and atoms must balance on both sides of the equation!

Acid ------------------------Conjugate base

$$H_2SO_4\,(aq) \quad + \quad H_2O(l) \quad \rightarrow \quad HSO_3^-\,(aq) + \quad H_3O^+\,(aq)$$

Base ---------------------- Conjugate acid

Conjugate pairs

EXAMPLES

Base ---------------------- Conjugate acid

e.g. $NH_3(g) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$

Acid ---------------------Conjugate base

Conjugate pairs

EXAMPLES

Acid ------------------------ Conjugate base

e.g. $NH_3(g) + {}^{-}OCH_3(aq) \rightarrow NH_2^{-}(aq) + CH_3OH(l)$

Base ------------------------ Conjugate acid

Conjugate bases

OF STRONG ACIDS AND WEAK ACIDS

- The conjugate base of a strong acid is a very weak base
  - (*e.g*. HCl ➔ Cl^-)
- The conjugate base of a weak acid is a weak base
  - (*e.g.* NH_4^+ ➔ NH_3)
- The conjugate bases of very weak acids (*e.g.* water, methanol and ethanol) are strong bases

Q7, 2009 asked about the conjugate base of HSO_4^-

Strong and weak acids and bases

IMPORTANT POINTS

- Strong acids and bases are completely ionised
- Weak acids and bases are partially ionised
- H_2SO_4, HCl, HBr, HI and HNO_3 are strong acids
- Most other acids (*e.g.* ethanoic acid (acetic acid), citric acid, NH_4^+ and carbonic acid) are weak acids
- Metallic oxides and hydroxides are generally strong bases (remember Lavoisier?)
- Ammonia, ethanoate (acetate) and carbonate ions are examples of weak bases

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

$$\mathrm{CH_3COOH}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3COO^-}(aq) + \mathrm{H_3O^+}(aq)$$

The pH scale

AND ITS USE IN CALCULATIONS

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

In chemistry, when you see "p", think "$-\log_{10}$"

A neutral solution has a pH of 7 ($[H_3O^+] = [^-OH]$)

An acidic solution has a pH < 7 ($[H_3O^+] > [^-OH]$)

A basic solution has a pH > 7 ($[^-OH] > [H_3O^+]$)

At 25 °C:

$$[HO^-] = \frac{1.00 \times 10^{-14}}{[H_3O^+]} \qquad \textbf{OR} \qquad pOH = 14 - pH$$

Why does water have pH of 7?

PURE WATER AROUND ROOM TEMPERATURE

Around room temperature in pure water:

$[H^+] = 10^{-7}$

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

$pH = -\log_{10} [10^{-7}]$

Therefore pH = 7

Degree of ionisation in water

FOR ACIDS (HA) OR BASES (B)

Ionisation of any acid (HA) in water:

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

aka: $HA(aq) \rightarrow H^+(aq) + A^-(aq)$

The **degree of ionisation for acids** $= \dfrac{[H_3O^+]}{[HA]} \times 100\%$

Ionisation of base (B) in water:

$$B(aq) + H_2O(l) \rightarrow HB^+(aq) + {}^-OH(aq)$$

The **degree of ionisation for bases** $= \dfrac{[{}^-OH]}{[B]} \times 100\%$

$[H_3O^+]$ = concentration of H_3O^+ produced, calculated from pH ($[H_3O^+] = 10^{-pH}$)

[HA] or [B] = concentration as made up in mol/L

Degree of ionisation

SAMPLE QUESTION

Example: Calculate the pH of a 0.10 mol/L solution of ascorbic acid. Note the solution is 2.8% ionised.

Degree of ionisation

EXAMPLE QUESTION

Example: Calculate the pH of a 0.10 mol/L solution of ascorbic acid. Note the solution is 2.8% ionised.

i) Degree of ionisation $= \dfrac{[H_3O^+]}{[\text{ascorbic acid}]} \times 100\% = 2.8\%$

ii) $2.8 = \dfrac{[H_3O^+]}{0.1 \text{ mol/L}} \times 100\%$

iii) $\dfrac{2.8\ (0.1 \text{ mol/L})}{100\%} = [H_3O^+]$

iv) $[H_3O^+] = 2.8 \times 10^{-3}$ mol/L

v) $\text{pH} = -\log_{10}[2.8 \times 10^{-3}] = \mathbf{2.6}$

Exams generally have a question on calculation of pH.

e.g. Q8 2005; Q10 2007; Q21 2008; Q21 2010; Q14 2014 HSC exam; Q12 2016 HSC

Be practical

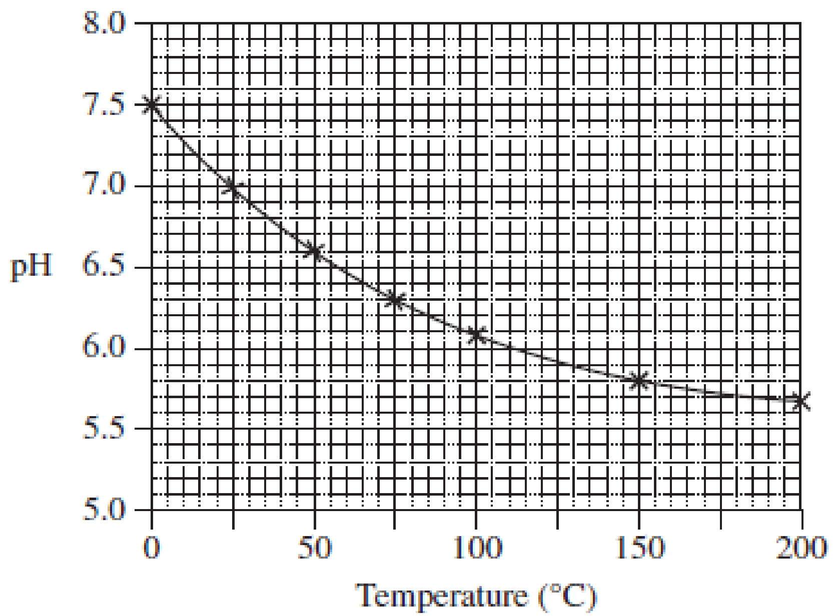
WHEN APPROACHING ACID BASE QUESTIONS

- Acid strength is not the same as concentration
- Different substances of the same concentration (mol/L), may have different pH values
- A solution of a strong acid (100% ionised) has a lower pH value (*i.e.* higher [H_3O^+]) than the pH of a similar concentrated solution of a weak acid (not fully ionised)
  - See hydrochloric acid versus ascorbic acid in 2001 exam (Q20), 2002 (Q22) and hydrochloric versus ethanoic (acetic) acid in 2010 (Q21).

Q8 2014 HSC Final

SAMPLE QUESTION

The graph shows the pH of a solution of a weak acid, HA, as a function of temperature.



ANSWER: B

What happens as the temperature decreases?

(A) HA becomes less ionised and the H^+ concentration increases.

(B) HA becomes less ionised and the H^+ concentration decreases.

(C) HA becomes more ionised and the H^+ concentration increases.

(D) HA becomes more ionised and the H^+ concentration decreases.

Acid + base

= SALT + WATER

Generally the reaction of an acid and base produces a salt and water

e.g. $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

$HNO_3(aq) + LiOH(aq) \rightarrow LiNO_3(aq) + H_2O(l)$

$H_2SO_4(aq) + Ca(OH)_2(aq) \rightarrow CaSO_4(aq) + 2\ H_2O(l)$

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

The reaction of an acid and base to give salt and water is often referred to as a **neutralisation** reaction

The reaction is **exothermic**, *i.e.* releases heat

pH of salt solutions

PRODUCED BY ACID BASE REACTIONS

A salt solution may be acidic, basic or neutral

Depends on strength of parent acid and base:

- Strong Acid + Strong Base = Neutral Salt
- Strong Acid + Weak Base = Acidic Salt
- Weak Acid + Strong Base = Basic Salt

$HCl + NaOH \rightarrow NaCl + H_2O$	Neutral
$HCl + NH_3 \rightarrow NH_4Cl$	Acidic
$NaOH + CH_3COOH \rightarrow CH_3COONa + H_2O$	Basic

Think of if it in steps, neutralisation happens first and then consider the salt produced afterwards

Neutralisation occurs on the left side and the products is what comes after

Le Chatelier's Principle

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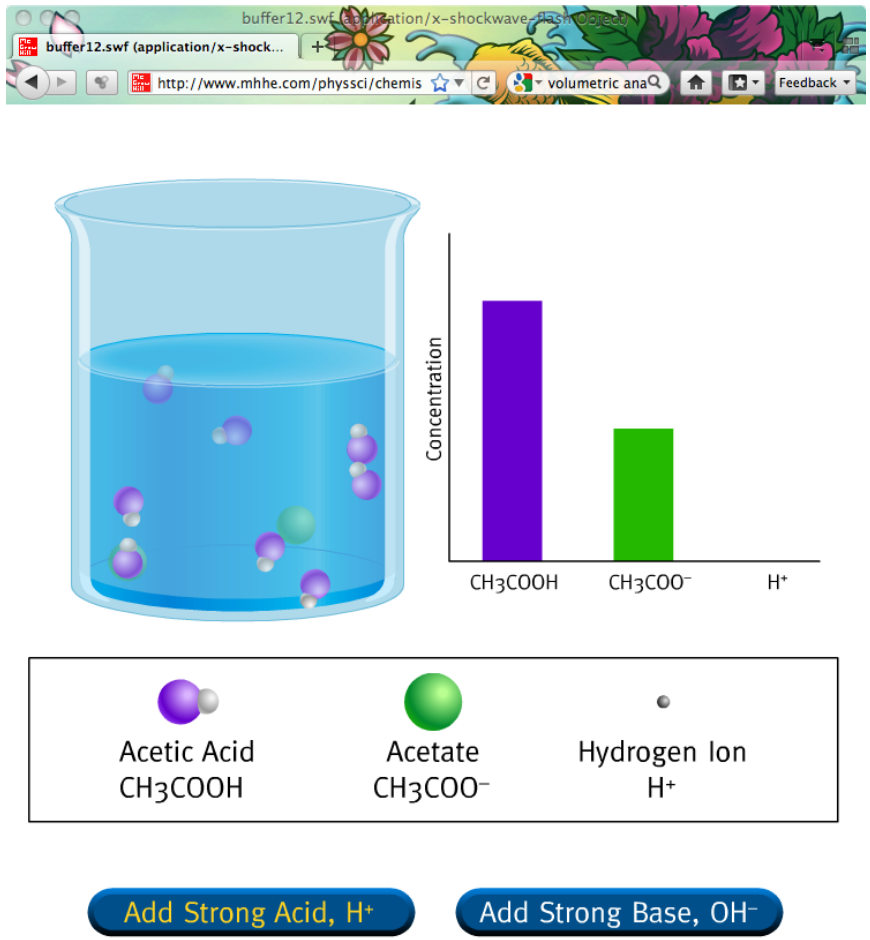
DEFINITION

The principle: *When a system in equilibrium is disturbed, the system adjusts itself to counteract the change and establish a new equilibrium.*

- A system 'adjusts itself' by increasing the rate of either the forward or reverse reactions until equilibrium is established again.
- The new equilibrium that is established is different to the original – the position of the equilibrium is said to have shifted.

Le Chatelier’s Principle

IN ACTION



Buffer Solutions

TO UNDERSTAND BUFFER SOLUTIONS

- A buffer is a solution that maintains **approximately constant pH** when small amounts of acids or bases are added.
- Mixtures of a weak acid and weak base - usually conjugate pairs
- Both components are weak and readily accept protons added to the solution if they are a base or have protons to donate to added bases if they are an acid - Le Chatelier's Principle

Acetic acid & sodium acetate

$$CH_3COOH + B \rightleftharpoons CH_3COO^- + BH^+$$

$$CH_3COO^- + HA \rightleftharpoons CH_3COOH + A^-$$

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

Natural / biological buffer situations

COMMONLY SEEN IN HSC CHEMISTRY EXAMS

Important biological buffer systems:

- **dihydrogen phosphate** system – internal fluid of all cells

$$H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$$

- **carbonic acid** system – sea water and blood

$$H^+(aq) + HCO_3^-(aq) \rightleftharpoons CO_2(g) + H_2O(l)$$

- pH of ocean has dropped from 8.1 to 7.9 in the last 20 years
- Both bicarbonate and hydrogenphosphate are amphiprotic (a substance that can **donate** or **accept** a proton, H^+)

This was asked in 2004 and 2006 HSC

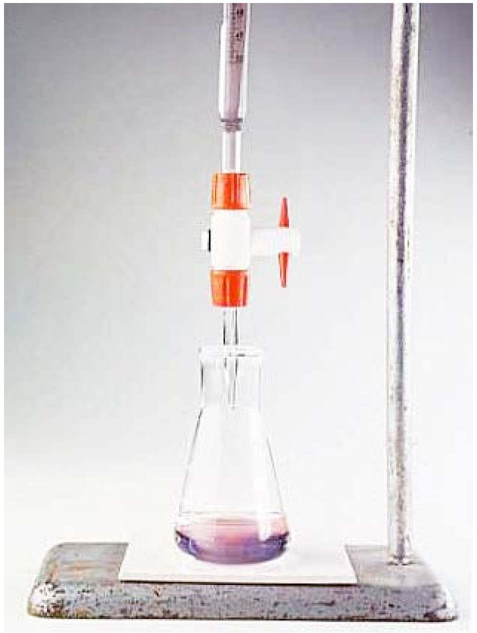
Volumetric analysis

USED TO DETERMINE CONCENTRATION OF UNKNOWN ACID OR BASE

Equivalence Point:

•Where amounts of acid & base are sufficient to cause complete consumption of both

•Measure equivalence point with indicator, pH meter or by electrical conductivity



Example of a Volumetric Acid–Base Analysis

From 2008 HSC exam, Q28:

- A standard solution was prepared by dissolving 1.314 g of sodium carbonate in water. The solution was made up to a final volume of 250.0 mL

(a) Calculate the concentration of the sodium carbonate solution

Sodium carbonate is Na_2CO_3, MW = 2 × 22.99 + 12.01 + 3 × 16.00 = **105.99 g mol^{-1}** (5 sig. fig. – due to 2 decimal places)

Amount of Na_2CO_3 = 1.314 g / 105.99 g mol^{-1} = **0.01240 mol (4 significant figures)**

$[Na_2CO_3]$ = 0.01240 mol / 0.2500 L = **4.959×10^{-2} mol L^{-1}**

$$\text{Molarity} = \frac{\textit{Number of Moles } (n)}{\textit{Volume of Solution } (v)}$$

$$\text{no. moles} = \frac{\text{mass in g (that we have)}}{\text{MW (molecular weight)}}$$

Example of a Volumetric Acid–Base Analysis

- This sodium carbonate solution was used to determine the concentration of a solution of hydrochloric acid. Four 25.00 mL samples of the acid were titrated with the sodium carbonate solution. The average titration volume required to reach the end point was 23.45 mL.

(b) Write a balanced equation for the titration reaction

$$Na_2CO_3(aq) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + CO_2(g) + H_2O(l)$$

acid + carbonate $\longrightarrow$ salt + carbon dioxide + water

Make sure everything is in the same units and show units throughout

Example of a Volumetric Acid–Base Analysis

- This sodium carbonate solution was used to determine the concentration of a solution of hydrochloric acid. Four 25.00 mL samples of the acid were titrated with the sodium carbonate solution. The average titration volume required to reach the end point was 23.45 mL.

$$Na_2CO_3(aq) + 2\ HCl(aq) \rightarrow 2\ NaCl(aq) + CO_2(g) + H_2O(l)$$

(c) Calculate the concentration of the hydrochloric acid solution

Remember that we know the concentration of the sodium carbonate solution – can work out its moles from volume used in titration and can then work out moles of HCl and then finally [HCl]

Amount of Na_2CO_3 = $\mathbf{4.959\times10^{-2}\ mol\ L^{-1}}$ × $\mathbf{0.02345\ L}$ = $\mathbf{1.163\times10^{-3}\ mol}$

$$\text{molarity} = \frac{\text{no. moles}}{\text{volume (in L)}} \qquad \text{no. moles} = \text{molarity x volume (in L)}$$

moles of HCl = 2 × $\mathbf{1.163\times10^{-3}\ mol}$ = 2.326×10^{-3} mol

[HCl] = 2.326×10^{-3} mol / 0.02500 L = 9.303×10^{-2} mol L^{-1}

from the reaction stoichiometry, we need twice as many moles of HCl compared with Na_2CO_3

(Another) Example of a Volumetric Acid–Base Analyses

From 2001 HSC exam: A household cleaning agent contains a weak base of general formula NaX. 1.00 g of this compound was dissolved in 100.0 mL of water. A 20.0 mL sample of the solution was titrated with 0.1000 mol L^{-1} hydrochloric acid, and required 24.4 mL of the acid for neutralisation. What is the molar mass of this base?

Consider what have been given and what need to determine – you can determine moles of HCl and you know mass of base. Need stoichiometry of acid-base reaction to allow determination of moles of base necessary, and from mass of base can get molar mass

Step 1 *write a balanced equation*

Step 2 *calculate moles of HCl used for the titration*

Step 3 *calculate moles of NaX in original 100 mL and therefore 1.00 g*

Step 4: *calculate molar mass of NaX*

Step 1: write a balanced equation:

$$NaX(aq) + HCl(aq) \rightarrow NaCl(aq) + HX(aq)$$

1 HCl : 1 NaX

***Step 2: calculate moles of HCl used for the titration*:**

$$\text{molarity} = \frac{\text{no. moles}}{\text{volume (in L)}} \qquad \text{no. moles} = \text{molarity x volume (in L)}$$

= 0.1000 mol L^{-1} HCl × 24.4 × 10^{-3} L = 2.44 × 10^{-3} moles (*3 sig. figures*)

= number of moles NaX in the 20.0 mL sample titrated.

Step 3: calculate moles of NaX in original 100 mL and therefore 1.00 g:

we only titrated 20 mL of the original 100 mL, *i.e.*, we only used 1/5 of the initial amount, therefore the number of moles in 1 g is 5 x our answer from above

= 100/20 (taking into account only analysed 20 mL) × 2.44 × 10^{-3} moles = 1.22 × 10^{-2} moles

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Step 4: calculate molar mass of NaX:

Remember moles = 1.22×10^{-2} moles = mass (1.00 g)/molar mass

molar mass = 1.00 g/1.22×10^{-2} moles = 82.0 g/mole (3 sig. figures)

$$\text{no. moles} = \frac{\text{mass in g}}{\text{MW}} \qquad \text{MW x no.moles} = \text{mass in g} \qquad \text{MW} = \frac{\text{mass in g}}{\text{no. moles}}$$

Similar questions seen for Q23 in 2003, Q24 in 2005, Q21 in the 2007, Q30 in 2014, Q26 in 2015 and Q29 in 2016 HSC exams. For full marks, show all steps; including providing a balanced equation, volumetric analyses questions ALWAYS are assessed!

Natural indicators

KNOWLEDGE BASED QUESTIONS

Red (Purple) Cabbage: Red cabbage contains a mixture of pigments used to indicate a wide pH range. Red onion also changes from pale red in an acidic solution to green in a basic solution

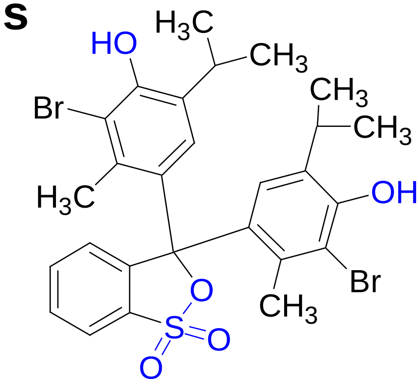
Tea: Tea is an acid-base indicator. Its colour changes from brown in basic solution to yellow-orange in acid. This is the reason why lemon juice is added to a cup of tea – not for the taste, but to reduce the intensity of the colour (called “brightening”)

Also **beetroots**, **cherries**, many **berries** and **grapes** contain pH sensitive pigments

Indicators for Acid–Base Titrations

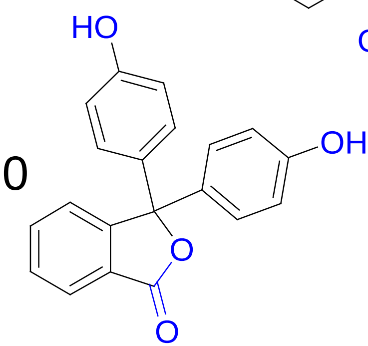
pH ~7 Bromothymol blue

– colour change pH 6.2–7.6



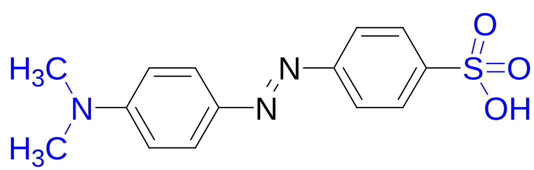
pH > 7 Phenolphthalein

– colour change pH 8.3–10



pH < 7 Methyl orange

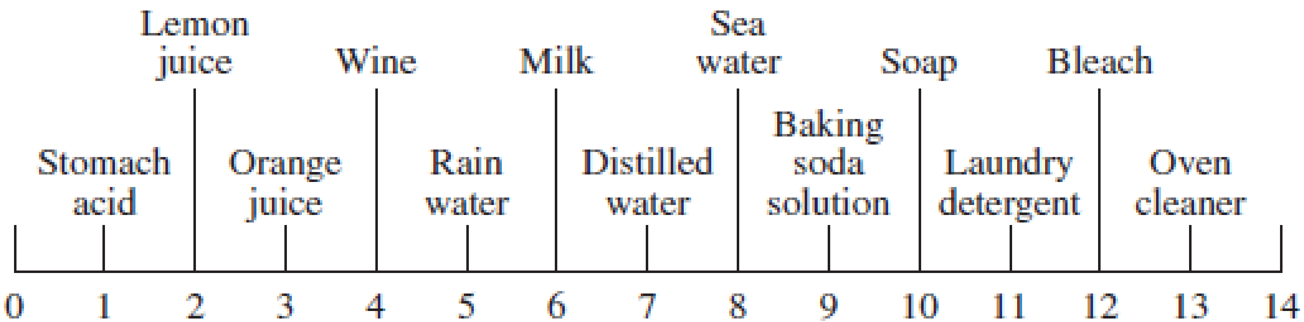
– colour change pH 3.1–4.4



Expect a question on indicators in the multiple choice section at least.

2014 *Question 12*

The diagram shows the pH values of some substances.



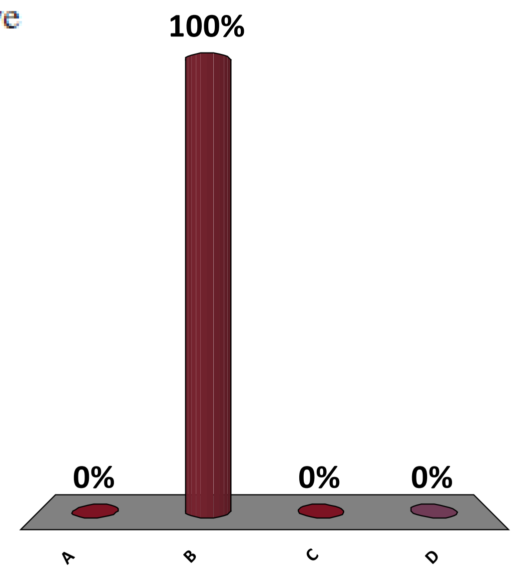
Based on the information provided, which of the following statements about the relative concentration of hydrogen ions is correct?

(A) It is 2 times higher in bleach than in milk.

(B) It is 10 times lower in stomach acid than in soap.

(C) It is 1000 times lower in distilled water than in wine.

(D) It is 100 times higher in laundry detergent than in baking soda solution.



2014 *Question 7*

This table contains information on three indicators.

Indicator	*pH range*	*Colour (lower pH – higher pH)*
Methyl orange	3.1 – 4.4	red – yellow
Methyl red	4.4 – 6.2	pink – yellow
Phenolphthalein	8.3 – 10.0	colourless – pink

A substance is tested with each of the indicators and the results are recorded below.

Indicator	*Colour*
Methyl orange	yellow
Methyl red	yellow
Phenolphthalein	colourless

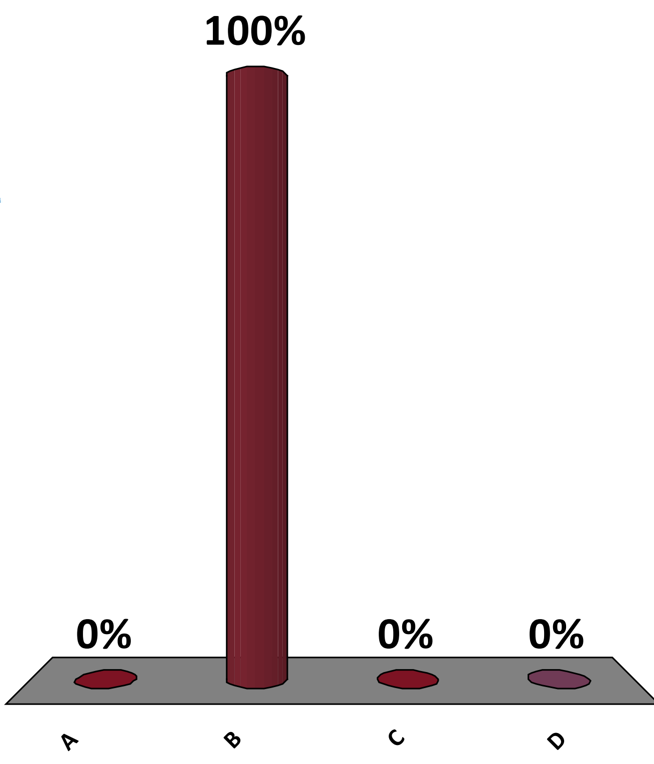
Which of the following substances will produce these results?

(A) Lemonade pH 2.9

(B) White wine pH 4.2

(C) Tap water pH 7.2

(D) Ammonia pH 11.2



2015

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Question 26 (continued)

(c) The sodium hydroxide solution was titrated against 25.0 mL samples of 0.100 mol L^{-1} citric acid ($C_6H_8O_7$). The average volume of sodium hydroxide used was 41.50 mL. Calculate the concentration of the sodium hydroxide solution. Note students were told citric acid is triprotic.

Step 1: Write and balance the chemical equation:

$$C_6H_8O_7 + 3NaOH \rightarrow C_6H_5O_7Na_3 + 3H_2O$$

Step 2: Convert concentration of citric acid to moles (n = cV)

Step 3: 3 moles NaOH to each 1 mole of citric acid. Find amount of moles of NaOH

Step 4: Find molarity of NaOH (moles/V)

A good answer also needed answer to 3 significant figures

The Acidic Environment
[The Basic Principles]