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# **Chapter 1:** Atomic Structure

### 1.1 About an Atom

### 1. Sub-atomic particles

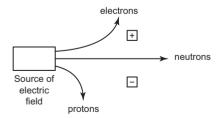
An atom consists of sub-atomic particles called protons, neutrons and electrons. The table below summarises the properties of theses sub-atomic particles.

Particle	Proton Neutron		Electron		
Location	Inside nucleus	Inside nucleus	Shells outside nucleus		
Mass (Unit mass)	1	1	<u>1</u> 1840		
Charge	+1	No charge	-1		

The nucleus is usually rather dense as most of the mass of the atom is found here. The nucleus of an atom is considered very small compared to the size of the atom. Most of the space taken up by an atom is by electrons, that orbit in shells around the nucleus.

### 2. Sub atomic particles exposed to an electric field

The diagram below shows how protons, neutrons and electrons deflect when subjected to an electric field.



From the diagram above, the **neutrons** move in a straight line as they have no charge.

The **protons**, being positively charged are deflected towards the negative terminal. These protons deflect lesser than the electrons as they have a greater mass than electrons.

The **electrons**, being negatively charged are deflected towards the positive terminal. These electrons deflect more than protons as electrons have a lower mass compared to protons.

For a charged particle, Angle of Deflection  $\sim$  Charge and Angle of Deflection  $\propto$  \_1\_\_\_

Mass

This technique is commonly used to separate isotopes or ions of different charges.

### 3. Representation of an atom

An atom is usually represented by the following symbol: <sup>A</sup><sub>7</sub>X

X: is the symbol of the Element

A: is the proton number (number of protons)

Z: is the mass number (number of protons + number of neutrons)

The number of neutrons = Z - A

### 4. Deducing the number of protons and Electrons

In a neutral atom, the number of protons and electrons are the same.

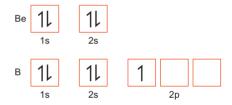
In a **negatively charged atom (anion)**, the number of protons is fewer than the number of electrons.

In a **positively charged atom (cation),** the number of protons is greater than the number of electrons.

- S Massive increase once electrons are removed from the next inner shell
  - Due to the ion being much smaller than the previous ion as a quantum shell is removed, resulting in an increase in attractive forces between the nucleus and electrons to be removed, thus the large jump in IE
- Slightly steeper increase from an electron subshell at a higher energy level to an electron subshell at a lower energy level
  - The electrons from the electron subshell at a lower energy level are closer to the nucleus than the electrons from the electron subshell at a higher energy level, thus the nucleus exerts a stronger attraction on them, which leads to a higher ionization energy.

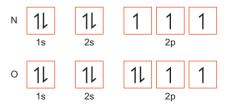
### 3. Abnormalities in Ionization Energies

### (i) DIP FROM GRP II TO GRP III (BERYLLIUM TO BORON)



As the 2p shell has a higher energy than 2s, and since there are weaker electrostatic forces of attraction between the nucleus and the outermost electron, less energy is needed to remove the electron in the 2p shell than in 2s shell

#### (ii) DIP IN IE OF NITROGEN TO OXYGEN (GRP V TO GRP VI)



Oxygen has an extra electron in the P shell which is paired.

This causes inter-electronic repulsion within that 3p orbital hence less energy is required to remove the paired electron from the 3p subshell in the atom in group VI. Hence lower first ionization energy is required.

#### The bond strength is affected by:

- (i) The greater the elctronegativity between the atoms involved in the covalent bond, the stronger the bond.
- (ii) The shorter the atomic radius, the shorter and stronger the bond.
- (iii) Triple bonds are stronger than double bonds, which are stronger than single bonds.

### 6. Bond and Shape of Molecules

Bonding pairs	Lone pairs	Shape and bond angles
2	0	linear
2	1	non-linear 120 – 2.5 = 117.5°
2	2	non-linear 109.5 – 2 × 2.5 = 104.5°
3	0	trig. Planer
3	1	pyramidal 109.5 – 2.5 = 107°
4	0	tetrahedral
4	2	square planar

Bonding pairs	Lone pairs	Shape and bond angles		
5	0	trig. bipyramidal	90° 17120°	
6	0	octahedral	90° 290°	

### 2.3 Induced Dipole and Hydrogen Bonding

Induced dipole are temporary polar bonds that last for a short period of time. For example in an oxygen atom, for a short period of time, the electrons will be towards one of the atoms, causing it to have a temporary negative charge. These bonds are very weak. Neural molecules and noble gases can also have induced dipole moments.

Hydrogen bonding involves the attraction between the hydrogen atom and an electronegative atom, like oxygen.



### Strength of bond

Induced Dipole – Induced Dipole > Induced Dipole – Polar Dipole > Polar Dipole – Polar Dipole > Hydrogen bonds

# **Chapter 3: The Gaseous State**

# 3.1 Ideal Gas Behavior and Deviation

### 1. What is an ideal gas?

A gas that follows the ideal gas law is called an ideal gas.

Ideal gases have negligible intermolecular forces of attraction between particles and have negligible volumes. The collision between ideal gases are termed "elastic".

### 2. What is a real gas?

Gases around us like oxygen are real gases. Real gases have mass, volume and forces of attraction between particles.

When the pressure of gases, both real and ideal increases, the greater the gas would deviate from the ideal behavior as the collisions are no longer elastic and the inter molecular forces of attraction between gases will not be negligible.

# 3. The conditions necessary for a gas to assume ideal gas behavior

Low Pressure: The lower the pressure, the further the gas particles are and the inter molecular forces of attraction between gases can be negligible.

Polar and Non-Polar molecules: Non-polar molecules have weaker forces of attraction between molecules are a closer to assume ideal gas behaviour.

High Temperature: The higher the temperature, particles have sufficient energy to overcome forces of attraction that are closer to ideal gas behaviour.

## 3.2 Gas Equation

### **1. General Gas Equation**

pV = nRT is the gas equation

*p* = pressure of gas in Pascal (Pa)

V = volume in m<sup>3</sup>

#### n = no. of moles

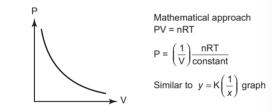
 $R = ideal gas constant = 8.314 JK^{-1}mol^{-1}$ 

#### From the equation,

- (i) Pressure is inversely proportional to volume
- (ii) Volume is proportion to temperature

# 2. Relationship between Pressure and Volume at constant temperature

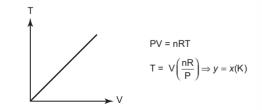
As volume increases, pressure decreases.



### 3. Relationship between temperature and volume

As temperature increases, volume also increases.

At constant pressure, volume is proportional to temperature.



The concentration of  $OH^-$  ions can be deduced from the concentration of  $H_3O^+$  ions and vice versa. The following table shows some examples:

[H₃O <sup>+</sup> ]	[OH <sup>-</sup> ]	Type of solution
0.1	$1 \times 10^{-13}$	Acidic
$1 \times 10^{-3}$	$1  imes 10^{-11}$	Acidic
1 × 10 <sup>-5</sup>	$1  imes 10^{-9}$	Acidic
1 × 10 <sup>-7</sup>	$1 \times 10^{-7}$	Neutral
1 × 10 <sup>-9</sup>	$1  imes 10^{-5}$	Alkaline
$1 \times 10^{-11}$	$1  imes 10^{-3}$	Alkaline
$1 \times 10^{-13}$	0.1	Alkaline

### 4.3 The pH Scale

### 1. Calculating pH

The acidity and alkalinity of a solution is often measured by its pH.

The pH of a solution is the negative logarithm to the base ten of the  $\rm H_3O^+$  concentration.

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

If  $[H_3O^+] = 1.0M$ , the pH of the solution is 0. If  $[H_3O^+] = 0.1M$ , the pH of the solution is 1. If  $[H_3O^+] = 0.01M$ , the pH of the solution is 2.

In alkaline solutions, the OH<sup>-</sup> concentration is known. The concentration of  $H_3O^+$  can be deduced from the ionic product of water:

$$[H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{dm}^6. \ [H_3O^+] = \frac{K_w}{\left[OH^-\right]} \ .$$

If  $[OH^-] = 1.0M$ ,  $[H_3O^+] = 1 \times 10^{-14}$  M and the pH of the solution is 14. If  $[OH^-] = 0.1M$ ,  $[H_3O^+] = 1 \times 10^{-13}$  M and the pH of the solution is 13. If  $[OH^-] = 0.01M$ ,  $[H_3O^+] = 1 \times 10^{-12}$  M and the pH of the solution is 12. Note that an increase in pH of one unit is equivalent to a tenfold fall in the  $H_3O^+$  concentration, and a decrease in pH of one unit is equivalent to a tenfold increase in the  $H_3O^+$  concentration.

### Calculating the pH of water:

In pure water,  $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$  M and the pH = 7.

It follows that the pH of acidic solutions is less than 7 and the pH of alkaline solutions is greater than 7.

At higher temperatures, the ionic product of water is greater and  $[H_3O^+]$  is greater than  $1\times 10^{-7}$  M. The pH of pure water is thus slightly less than 7 at higher temperatures. The solution is still neutral, since the concentrations of  $H_3O^+$  and  $OH^-$  are still the same. The pH of a neutral solution is just lower at higher temperatures.

### 4.4 Strong and Weak Acids

Acids can be classified as one of two types; strong acids and weak acids. Each must be considered separately:

### 1. Strong acids

A strong acid is one which dissociates completely in water into  $H_3O^+$  and  $A^-$ . A strong acid must therefore be a better proton donor than  $H_3O^+$ . Examples of strong acids are HC/, HNO<sub>3</sub> and  $H_2SO_4$ .

### Calculating the pH of strong acids:

Since strong acids dissociate fully, the concentration of  $H_3O^+$  will be the same as the concentration of the acid (ignoring the auto-ionisation of water).

A 1.0 M solution of HC/ will therefore be 1.0 M with respect to both  $H_3O^+$  and  $C/^-$  ions if the  $H_3O^+$  present due to the auto-ionisation of water (which will be small in comparison) is ignored:

$$\label{eq:HClarger} \begin{split} HCl(aq) + H_2O(I) \rightarrow H_3O^{+}(aq) + C\varGamma(aq) \\ 1.0M \qquad 1.0M \end{split}$$

To prepare a buffer solution of a given pH, it is necessary to have the acid and base concentrations in a suitable ratio.

**EXAMPLE:** To prepare an 
$$\frac{NH_3}{NH_4C/}$$
 buffer of pH = 10.

$$\frac{\left[H_{3}O^{+}\right]}{K_{a}} = \frac{[acid]}{[base]} \qquad \text{so } \frac{\left[NH_{4}^{+}\right]}{\left[NH_{3}\right]} = \frac{1 \times 10^{-10}}{5.6 \times 10^{-10}} = \frac{1}{5.6}$$

So 5.6 moles of NH<sub>3</sub> are required for every 1 mole of NH<sub>4</sub>C/

Given equimolar solutions of both, 100 cm<sup>3</sup> of this buffer could be made by taking 10 cm<sup>3</sup> of NH<sub>4</sub>C*l*, adding 56 cm<sup>3</sup> of ammonia and the total volume made up to 100 cm<sup>3</sup>.

It is possible to express the pH directly in terms of the concentrations of the reactants:

### 6. Showing how buffer solutions limit changes in pH.

It is possible to show quantitatively the ability of buffer solutions to limit changes in pH:

### Example

A mixture of 0.6M HC/O (K  $_{a}$  = 3.7  $\times$  10  $^{-8}$  M) and 0.2M NaC/O has a pH of 7.0.

If 0.01 moles of HC/ are added to 100 cm<sup>3</sup> of the buffer:

	C/O⁻(aq)	$+ H_3O^+(aq)$	$\rightarrow$ HC/O(aq) +	H <sub>2</sub> O(I)
Initially:	0.02	0.01	0.06	
Finally:	0.01	-	0.07	

So the 
$$\left(\frac{\text{[base]}}{\text{[acid]}}\right)$$
 ratio is  $\frac{0.01}{0.07}$ 

$$pH = pK_a + log_{10} \left( \frac{[base]}{[acid]} \right) = 6.58$$
 (a change of 0.4 units)

If 0.01 moles of HC/ were added to  $100 \text{ cm}^3$  of pure water, the pH of the resulting solution would be 1.0 (a change of 6 units)

If 0.01 moles of NaOH are added to the buffer:

	HC/O(aq) +	OH⁻(aq)	$\rightarrow$	C/O⁻(aq)	+	$H_2O(I)$
Initially:	0.06	0.01		0.02		
Finally:	0.05	-		0.03		

So the 
$$\left(\frac{\text{[base]}}{\text{[acid]}}\right)$$
 ratio is  $\frac{0.03}{0.05}$ 

$$pH = pK_a + log_{10} \left( \frac{[base]}{[acid]} \right) = 7.21$$
 (a change of 0.2 units)

If 0.01 moles of NaOH were added to 100  $\rm cm^3$  of pure water, the pH of the resulting solution would be 13.0.

So buffer solutions do not change their pH much on adding small quantities of acid or alkali.

NB it is possible to exceed the buffering capacity of a buffer solution by adding too much acid or alkali; in such cases the buffer will be unable to maintain the pH and the pH will change dramatically. This would be the case of more than 0.02 moles of HC/ or more than 0.06 moles of NaOH were added to the above mixture.

It can be shown that buffer solutions are most efficient at resisting changes in pH when the concentrations of acid and alkali are the same.