d 8·2 Le Chatelier's Principle

Reactions at equilibrium oppose applied stresses

(If any of the factors influencing the rate of a reversible reaction is changed the system will react in such a way as to diminish the change.)

Effect (if any) on Equilibrium Position

Catalyst: Causes the reaction to reach equilibrium faster but does NOT change the position of equilibrium

(a) Temperature:- increasing the temperature will have the following results if the reaction is

Exothermic [ΔH negative] it will be driven backwards i.e. to the left

Endothermic [ΔH positive] it will be driven forwards i.e. to the right

Decreasing the temperature will have the opposite effect

Equilibrium Constant is Temperature Dependant

Change the temperature and the equilibrium constant changes

(b) Concentration:- Increasing the concentration of a reactant will **increase the rate of reaction towards the opposite side** and cause the concentration of the added substance to drop to as near its original concentration as possible.

Decreasing the concentration of a reactant (by removing it e.g. ammonia in the Haber Process) will **increase the rate of reaction towards the side from which the substance is removed** until it gets back as close to its original concentration as possible.

(c) Pressure: Increasing the pressure will **drive reaction to the side with fewer molecules** as fewer molecules will give less pressure.

Decreasing the pressure will **drive the reaction to the side with more molecules** as it tries to return the pressure to its original value by creating more molecules.

If the numbers of molecules on both sides of the equation are the same pressure does not affect the equilibrium position

e Industrial Application of Le Chatelier's Principle

Contact Process for the production of sulphuric acid

Catalytic oxidation of sulfur dioxide to sulfur trioxide

$SO_2 + \frac{1}{2} O_2 \rightleftharpoons SO_3$ **V_2O_5 is the catalyst (723 K)**

High pressure favours the forward reaction as there are fewer product molecules however a satisfactory yield is achieved at 1 atm.

Le Chatelier

Haber Process for the production of ammonia

$N_2 + 3 H_2 \rightleftharpoons 2 NH_3$

Pressure: Increasing improves yield by driving the reaction to the right as there are fewer molecules on the right. The higher the pressure the better but >200 atm. is too expensive to maintain.

Catalyst: Fe impregnated with alumina causes it to re-establish equilibrium faster

Temperature: The reaction is exothermic so increasing the temperature to 773 K will push the reaction to the left and reduce the yield. The relatively high temperture is a compromise which keeps the reaction going reasonably fast but does not push the equilibrium too far to the left.

Concentration: Concentration of reactants is kept up by recycling uncombined gases and replacing used gases.

Removal of ammonia: Removal by cooling and tapping off the ammonia also drives the reaction to the right.

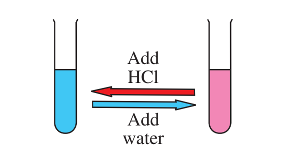
f

EXPERIMENT: To Illustrate Le Chatelier's Principle:

Concentration Changes in equilibrium mixture

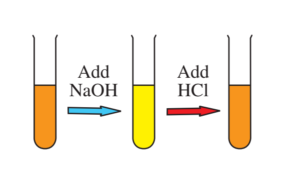
(i) $Co(H_2O)_6^{2+} + 4Cl^- \rightleftharpoons CoCl_4^{2-} + 6\,H_2O$
Pink — Blue

- Dissolve cobalt chloride in water. **Pink colour due to $Co(H_2O)_6^{2+}$**
- **Add conc. HCl** slowly – **goes** blue as **system reduces conc. of Cl^- by forming more $CoCl_4^{2-}$**
- **Add water** and it **goes pink** as system **reduces concentration of water by forming $Co(H_2O)_6^{2+}$**
- And so on



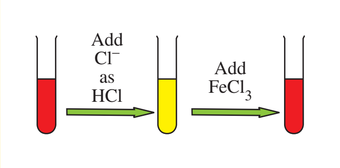
(ii) $Cr_2O_7^{2-} + H_2O \rightleftharpoons 2\,CrO_4^{2-} + 2H^+$
Orange — yellow

- Dissolve some potassium dichromate in water and it forms an orange solution
- **When NaOH is added the solution becomes yellow**. Because the OH^- reacts with the H^+ forming water and the system tries to replace H^+ by forming more H^+ but as it does this it also forms more chromate at the same time so this makes the solution yellow.
- When **HCl is added** the H^+ concentration increases. The system tries to lower it by reacting it with chromate **forming dichromate which is orange**.



(iii) $FeCl_3 + CNS^- \rightleftharpoons Fe(CNS)^{2+} + 3\,Cl^-$
yellow — red

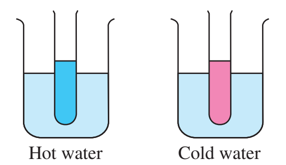
When we mix iron (III) chloride with potassium thiocyanate it forms $Fe(CNS)^{2+}$ which is red.
When we **add Cl^-** in the form of dilute hydrochloric acid the system tries to reduce its concentration by forming Fe^{3+} and CNS^-. The Fe^{3+} makes the solution yellow.
Adding more $FeCl_3$ to the mixture drives it to the right again as the system tries to use up the Fe^{3+} by forming $Fe(CNS)^{2+}$ so the solution goes red again



Temperature Changes

$$CoCl_4^{2-} + 6\,H_2O \underset{\text{Exothermic}}{\overset{\text{Endothermic}}{\rightleftharpoons}} Co(H_2O)_6^{2+} + 4Cl^-$$
Blue — Pink

- Dissolve cobalt chloride in water. **Pink colour due to $Co(H_2O)_6^{2+}$**
- Add conc. HCl slowly until just about to turn blue
- Place in a beaker of **hot water** and test tube goes **blue as $CoCl_4^{2-}$ is formed** when the system lowers the temperature by doing the **endothermic reaction**
- Place in a beaker of iced water and the test tube goes **pink as $Co(H_2O)_6^{2+}$ is formed,** as the system raises the temperature by doing the **exothermic reaction**
- Place back in hot water to reverse again.



It is essential that pupils know these equations from left to right and right to left i.e. know the colour associated with each compound.

Questions on this section from Past Exams Year by Year

2009	2008	2007	2006	2005	2004	2003	2002
11 a	7	10 a	11 b	9	9	11 a	4 g
							10 c

76-77 LE CHATELIER'S PRINCIPLE

a 9·1 pH Scale

Self-Ionisation of Water

Water reacts with itself according to the equation **$H_2O + H_2O = H_3O^+ + OH^-$**

Ionic Product *of water at 25ºC*

$K_w = [H_3O^+]\,[OH^-] = 10^{-14}$ [ ] = concentration in mol l^{-1}

(i) Define K_w, the ionic product of water.
(ii) Given that the value of K_w at 25 ºC is 1.0 x 10^{-14}. Show that the pH of pure water is 7.0 at 25 ºC.

(i) $K_w = [H_3O^+][OH^-]$

(ii) in pure water $[H_3O^+] = [OH^-]$ so $[H_3O^+]^2 = 1 \times 10^{-14}$

$=> [H_3O^+] = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7}$

pH = $-\log_{10} 1 \times 10^{-7}$ **= 7**

b Calculating pH

Strong acids dissociate completely in aqueous solution

$pH = -\log_{10} [H_3O^+]$ [ ] = concentration in mol l^{-1}

Concentration of $[H_3O^+]$ = concentration of the acid if it is **monobasic** e.g. HCl or HNO_3.
Dibasic acids e.g. H_2SO_4 the concentration of $[H_3O^+]$ = twice the acid concentration.

Calculate the pH of 0.1 M hydrochloric acid [HCl]

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

$= -\log_{10} [0.1]$

= 1

Calculate the pH of 0.1 M sulphuric acid [H_2SO_4]

Sulphuric acid is dibasic therefore concentration of H_3O^+ is 0.2 M

$pH = -\log_{10} [H_3O^+] = -\log_{10} [0.2]$

= 0.6989 **= 0.7**

Strong bases ionise completely in aqueous solution **$pOH = -\log_{10} [OH^-]$**

Monoprotic bases e.g. NaOH or KOH - concentration $[OH^-]$ = concentration of base.
Diprotic bases such as $Ca(OH)_2$ - the concentration of the $[OH^-]$ is twice concentration of base

pH of a base is worked out by subtracting the pOH from 14 **pH = 14 – pOH**

Calculate the pH of 0.1 M NaOH solution.

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

$= -\log_{10} [0.1]$

= 1

pH = 14 – pOH

= 14 – 1 **= 13**

Calculate the pH of a solution containing 2 g of NaOH in 250 cm³.

2 g in 250 cm^3 = 2 × 1000/250 per litre = 8 g l^{-1}

8 g l^{-1} = 8 / 40 mole l^{-1} = 0.2 M

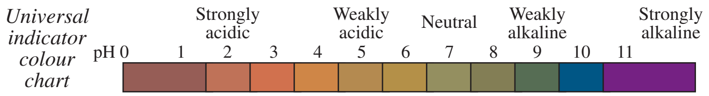
$pOH = -\log_{10} [OH^-] = -\log_{10} [0.2]$

= 0.06989 = 0.7

pH = 14 – pOH = 14 – 0.7 **= 13.3**

Universal Indicator Paper and Solution Colours

Universal indicator changes through a range of colours with pH.



PH SCALE 9

c Limitations of the pH Scale

Really only works well with **dilute aqueous solutions** and is temperature dependant.

pH of Weak Acids

$$pH = -\log_{10}\sqrt{(K_a \times [HA])}$$

Calculate the pH of 0.1 M solution of ethanoic acid given that K_a value for ethanoic acid is 1.8 x 10^{-5}.

pH $= -\log_{10}\sqrt{(K_a \times [HA])}$

pH $= -\log_{10}\sqrt{(1.8 \times 10^{-5} \text{ x } [0.1])}$

$= -\log_{10}\sqrt{1.8 \times 10^{-6}}$

$= -\log_{10} 0.001342$

= 2.8723

[HA] = acid concentration

Calculate the pH of a solution of methanoic acid containing 1.15g of methanoic acid in 250 cm^3, given that the K_a value for ethanoic acid is 1.6 x 10^{-4}.

1.15 g in 250 cm^3 = 1.15 × 1000 / 250 = 4.6 g l^{-1}

4.6 g l^{-1} = 4.6 / 46 moles l^{-1} = 0.1 M

pH $= -\log_{10}\sqrt{(K_a \times [HA])}$

pH $= -\log_{10}\sqrt{(1.6 \times 10^{-4} \times [0.1])}$

$= -\log_{10}\sqrt{1.6 \times 10^{-5}}$

$= -\log_{10} 0.004$

= 2.3979

pH of Weak Bases

$$pH = 14 - pOH$$
$$pOH = -\log_{10}\sqrt{K_b \times [OH^-]}$$

Calculate the pH of 0.2 M solution of ammonia given that the K_b value for ammonia is 1.8 x 10^{-5}.

pOH $= -\log_{10}\sqrt{(K_b \times [OH^-])}$

pOH $= -\log_{10}\sqrt{(1.8 \times 10^{-5} \times [0.2])}$

$= -\log_{10}\sqrt{3.6 \times 10^{-6}}$

$= -\log_{10} 0.001897$

= 2.7219

pH = 14 – pOH = 14 – 2.7219

= 11.2781

Calculate the pH of a solution of ammonia containing 0.017 g in 100 cm^3, given that the K_b value for ammonia is 1.8 x 10^{-5}.

0.017 g in 100 cm^3 = $0.017 \text{ x } \frac{1000}{100}$

= 0.17 g l^{-1}

0.17 g l^{-1} = 0.17 / 17 moles l^{-1} = 0.01 M

pOH $= -\log_{10}\sqrt{(K_b \times [OH^-])}$

pOH $= -\log_{10}\sqrt{(1.8 \times 10^{-5} \times [0.01])}$

$= -\log_{10}\sqrt{1.8 \times 10^{-7}}$

$= -\log_{10} 0.0004244$

= 3.7324

pH = 14 – pOH = 14 – 3.7323 **= 10.6277**

d Theory of Acid-Base Indicators

Most indicators are weak acids so only dissociate slightly

Colour of the undissociated molecule must differ from anion it forms

Hin	⇋	H^+	+	In^-
Colour 1		Colourless		Colour 2

In acidic solution the H^+ concentration rises so the equilibrium moves to the left to reduce the H^+ concentration so Hin colour 1 shows.

In alkaline solution the H^+ drops when it reacts with OH^- to form water so the equilibrium moves right to replace the H^+ used up and In^- colour 2 shows.

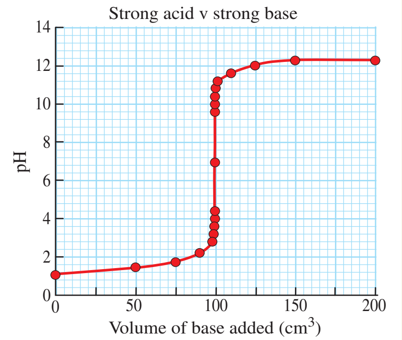
The intermediate colour shows until the concentration of one of the two species is ten times the other.

Choice of Indicator *(see also page 38)*

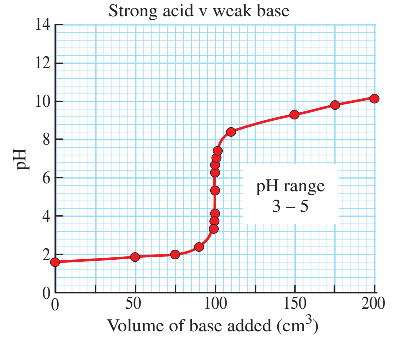
Indicator colour change should coincide with rapid change in pH of the reaction mixture

Indicator	Acid colour	Intermediate colour	Alkaline colour
Phenolphthalein	Colourless	Colourless	Purple or pink
Methyl Orange	Red	Orange	Yellow
Litmus	Red	Purple	Blue

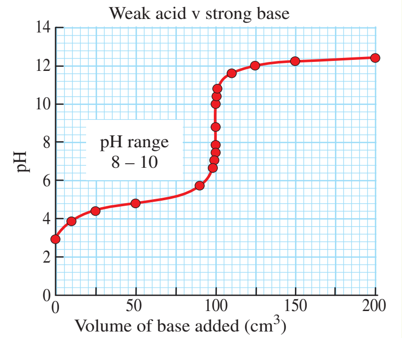
e Titration Curves



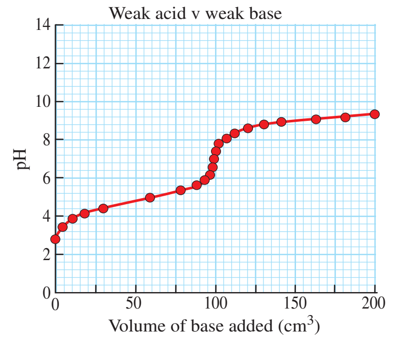
Any indicator suitable



Methyl Orange indicator



Phenolphthalein Indicator



No suitable indicator

Indicator should change colour at the vertical part of the graph

f 9·1 Hardness in Water

Hard Water is any water that forms a scum (Ca or Mg stearate) with soap.
Soft water forms lather with soap.

Types of Hardness

Temporary Hardness can be removed by boiling.

Permanent Hardness can't be removed by boiling

Causes of Hardness

Temporary	Permanent
$Ca(HCO_3)_2$	$CaCl_2$
$Mg(HCO_3)_2$	$MgCl_2$
	$CaSO_4$
	$MgSO_4$


Scum in hard water


Lather in soft water

Removal of Hardness

Limescale caused by temoprary hardness blocking a pipe

Temporary Hardness

can be removed by **boiling**

$$Ca(HCO_3)_{2(aq)} \overset{\text{Heat}}{=} CaCO_{3(s)} + CO_{2(g)} + H_2O_{(l)}$$

Problems caused by temporary hardness

– blocking of pipes with limescale, furring of kettles, scum in launderies

Permanent Hardness

Can be removed by **deionisation**

(i) Adding washing soda (sodium carbonate) removes the Ca^{2+} or Mg^{2+} ions by precipitation

$$Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} = CaCO_{3(s)}$$

(ii) Ion Exchange

Resins can carry out the following exchanges

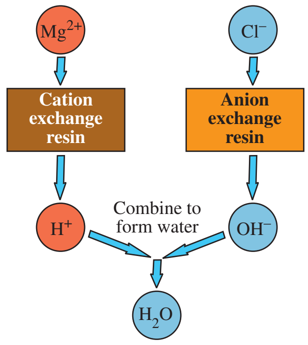
Cations [Metal ions] replaced by H^+

Anions [Non-Metal ions] replaced by OH^-

Then these ions react to form water

$$H^+ + OH^- = H_2O$$

Both above reactions remove temporary as well as permanent hardness



Relative Purity of Deionised and Distilled Water

- **Distilled** water is **completely pure**.
- **Deionised** water **contains no ions** but **can contain soluble covalent compounds** such as sucrose, ethanol and oxygen, as well as bacteria.

9·3 Water Treatment

To make water clean and safe to drink

Stages

1. **Sedimentation** - large particles are screened out and smaller particles left to settle to bottom
2. **Flocculation – Aluminium sulphate flocculating agent added**. This causes particles that were too small to sink to clump together and sink to the bottom as the water passes through a series of tanks where it moves really slowly giving the particles time to sink.
3. **Filtration** - water filtered through sand beds on top of gravel which removes the last of the suspended solids

4. (a) **Chlorination** - enough chlorine is added **to kill any pathogenic bacteria** present and keeps the water bacteria free till it reaches its destination.

4. (b) **Fluoridation** - fluoride is added **to strengthen teeth and prevent decay**

4. (c) **pH adjustment**- water which is
   – **too acid** may corrode pipes – adjusted by adding $Ca(OH)_2$
   – **too hard** may be softened by using Na_2CO_3 [this can make it too alkaline]
   – **too alkaline** - may be adjusted by adding sulphuric acid.

h

9·4 Sewage Treatment

Reduces water borne diseases e.g. typhoid or cholera, and can be used to remove the causes of eutrophication.

Stages

- **Primary** – minimum treatment - involves **screening then settlement** then periodic removal of sludge. Liquid passed on to next stage or into watercourse.
- **Secondary**, involves **biological oxidation** by **bacteria** and other micro-organisms; removes organic waste and pathogens from the liquid. Can be drip fed over gravel which gives a large surface area and ample oxygen or the active sludge process can also be used. Liquid either discharged to watercourse or passed to tertiary stage. Biologically safe now.
- **Tertiary**, involves the **reduction in levels of phosphates [PO_4^{3-}] and nitrates [NO_3^{1-}]**, and also heavy metals ions especially Pb^{2+}, Hg^{2+} and Cd^{2+} which are removed by precipitation before water is discharged into waterways.
  Tertiary treatment is expensive and is frequently not applied.

i

9·5 Pollution

- **PO_4^{3-} and NO_3^-** ions can be toxic and also cause **eutrophication [i.e. excess plant growth caused by excess nutrients**]. Result of excess application of fertilisers or application in wet conditions which can produce run off of these ions into water courses.
- **Pb^{2+}, Hg^{2+} and Cd^{2+}** usually come **from batteries that are not recycled**. There are EU limits to the amounts of all these ions that can occur in water.
  Two examples, e.g. nitrates 50 mg l^{-1}, Hg 1μg l^{-1}.
- **5 Day Biochemical Oxygen Demand [BOD] test for organic chemical pollutants** in water e.g. from sewage, industrial waste, silage or milk. Take sample of water and split it in two, test one sample immediately and keep the other **in dark [to prevent photosynthesis] at 20ºC for 5 days** and then retest. **Difference in Dissolved Oxygen values is BOD**.

j

9·6 Water Analysis

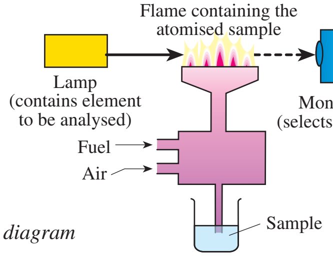
Instrumental Methods of Analysis:

Atomic Absorption Spectrometry [AAS]

Can be used to analyse water to identify the elements present

The degree of absorption enables us to estimate their concentration.

Examples include the **analysis of heavy metals in water, e.g. lead, mercury, cadmium and fertilisers such as nitrates**.



AAS diagram

k

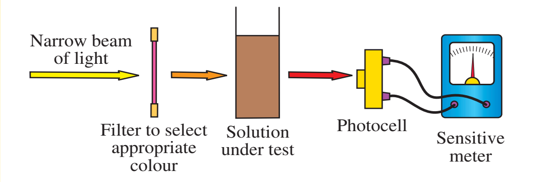
EXPERIMENT: Tests on Scale Deposits in a Kettle

Obtain scale deposits from kettle

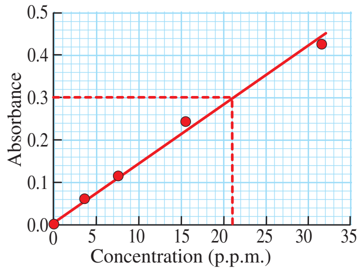
- Add dilute HCl
- Note effervescence and test gas produced with lime water
- Goes milky therefore CO_2 is gas produced which tells us scale deposit is a carbonate [*Hydrogencarbonate would be soluble in water*]

l EXPERIMENT: Estimate the Concentration of Free Chlorine in Swimming Pool Water. (Using a colorimeter)

- **HOCl is called free chlorine** is put in as calcium hypochlorite [$Ca(OCl)_2$]
- pH kept low to keep concentration of free chlorine at maximum
- Chlorine kills bacteria by oxidation – if concentration too high it can cause skin problems
- **Colorimeter** works on **principle that absorbance [colour] is proportional to concentration**
- Calibrate colorimeter transmission with I_2.
  0% = light switched off and 100% distilled water



- Select the wavelength of light for maximum absorbance
- Make up stock [standard] solutions 1, 2, 4, 8, 16 p.p.m. and run absorbance for each
- Draw graph of Absorbance vs. Concentration – this is called a **calibration curve**
- Take unknown solution add 2% KI and ethanoic acid
- Turns brown due to release of iodine [I_2] caused by free chlorine
- Take unknown solution and "Run" it.
- Read the value from the colorimeter (0.3) and then use the graph to find the corresponding concentration (21 p.p.m.).



m EXPERIMENT: In a Sample of Water Determine;
(a) total suspended solids (in p.p.m.)
(b) total dissolved solids (in p.p.m.)
(c) pH.

A. To Measure the Total Suspended Solids by Filtration

- Fill a 200 cm^3 volumetric flask to the mark with the sample of water.
- Find the mass of a dry filter paper. Let us say 10.56 g
- Filter the known quantity of water through the filter paper.
- Allow filter paper to dry or place in an oven at 100ºC for several hours
- Find new mass of filter paper. Let us say it is 10.59 g

Calculate the mass of suspended solids in sample [the change in mass of filter paper]
10.59 – 10.56 = **0.03g**
Calculate the mass of suspended solids in 1 litre
[mass of suspended solids in sample / volume of sample × 1,000]
0.03 / 200 × 1,000 = 0.15 g l^{-1}
Multiply by 1,000 to covert to mg l^{-1} [p.p.m.] = 0.15 × 1,000 = 150 p.p.m.

B. To Measure the Total Dissolved Solids by Evaporation

- Find the mass of a clean dry beaker. Let us say 150 g.
- Add a known quantity of filtered water from a graduated cylinder e.g. 250 cm^3.
- Evaporate the water to dryness
- Note solids remain in the beaker.
- Allow the beaker to cool and reweigh. = Let us say 150.15g

WORKED EXAMPLE

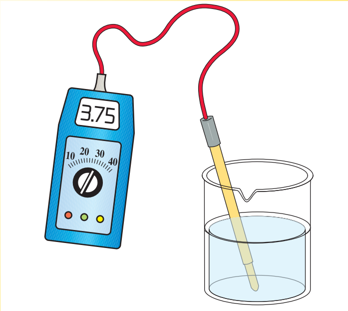
Dissolved solids = mass of beaker at end – mass of clean dry beaker

= 150.15 – 150 = 0.15 g

Mass in 1 Litre $= \frac{\text{mass of dissolved solids}}{\text{volume of sample}} \times 1{,}000 = \frac{0.15}{250} \times 1{,}000 = 0.6$ g

Multiply by 1,000 to get results in mg l^{-1} i.e. p.p.m. $0.6 \times 1{,}000 =$ **600 p.p.m**

C. To Measure the pH of a Sample of Tap or River Water

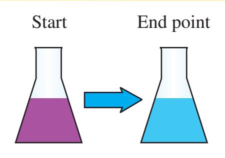


- Most accurate method is to **use a pH meter**.
- **Calibrate meter in buffer solution**
- **Wash with deionised water** then place electrode in the test sample
- Read the pH value.
  If a pH meter is not available use pH paper.

n

EXPERIMENT: Estimation of Total Hardness of Water using Ethylenediaminetetraacetic Acid

- Place 50 cm^3 of hard water in conical flask
- Add 1 cm^3 of **buffer solution** [pH 10] to **keep pH alkaline so indicator works properly**
- Add 5 drops of **Eriochrome Black** – gives **wine red colour**
- Add **0.01 M EDTA** from burette until solution turns blue
- Do 1 rough and 2 accurate titres - average 2 accurate
- For calculation assume the average titre = 6.9 cm^3



1 cm^3 of 0.01 M EDTA ≡ 1 mg $CaCO_3$ in the sample

Multiply average titre by 20 [assuming 50 cm^3 sample] to find mg l^{-1} [p.p.m.]

$6.9 \times 20 =$ **138 p.p.m**

Calculating Temporary and Permanent Hardness

- Take a sample of water
- Split it into two samples
- Measure hardness of one sample e.g. 65 p.p.m.
- **Boil other** sample then measure its hardness e.g. 24 p.p.m

Unboiled = permanent + temporary hardness = 65 p.p.m.

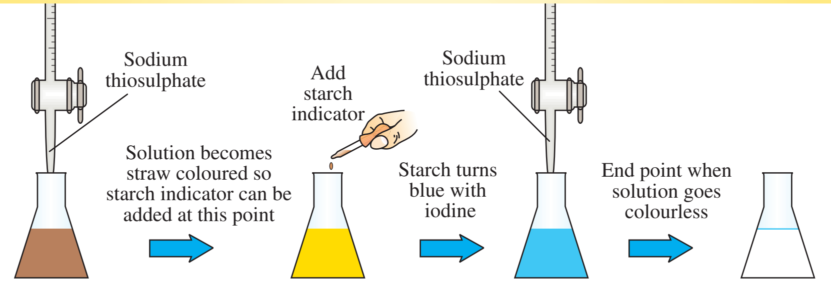
Boiled water = permanent hardness only = 24 p.p.m. [*temporary has been removed by boiling*]

Temporary Hardness = Unboiled value – Boiled value = 65 – 24 = **41 p.p.m.**

0

EXPERIMENT: To Measure the Amount of Dissolved Oxygen in a Water Sample by the Winkler Method.

- Rinse 500 cm^3 bottle with water [**stops bubbles forming on the sides** when filled]
- Fill and stopper it under water [*so no air is trapped*]
- Add **1cm^3 of conc. $MnSO_4$ and 1cm^3 of conc. alkaline KI** [*concentrated so not to upset volume*]
- **Brown precipitate** forms – **if white precipitate forms no oxygen present**.
- Add **conc. H_2SO_4**.
- **Brown Solution** due to the liberated iodine.
- Pipette 50 cm^3 of iodine solution into conical flask.
- Put 0.005 M **Sodium thiosulphate in burette** as standard solution
- Titrate until pale **straw coloured**
- Add a few drops of **starch indicator** and the **solution turns blue**



- Continue titrating until **colourless** [blue colour disappears]
- Do one rough and 2 accurate titres – average 2 accurate
- For the purposes of this experiment take the average titre to be 10.5 cm^3

Calculate the Concentration of O_2 in Water Expressing your Results in p.p.m.

Let dissolved oxygen = a and Let thiosulphate = b
Ratio of dissolved oxygen to thiosulphate = 1:4

therefore $n_a = 1$ and $n_b = 4$

Calculate molarity of the oxygen

$$M_a = \frac{V_b \times M_b \times n_a}{V_a \times n_b} = \frac{10.5 \times 0.005 \times 1}{50 \times 4} = \mathbf{0.0002625}$$

Convert to grams per litre

g l^{-1} = molarity x molar mass [*molar mass of O_2 = 16 x 2 = 32*]

= 0.0002625 × 32 = **0.0084**

Convert to milligrams per litre [p.p.m.]

Multiply by 1,000   0.0084 × 1,000 = **8.40 p.p.m.**

Questions on this Section from Past Exams Year by Year

2009	2008	2007	2006	2005	2004	2003	2002
4 f	1e, i, kA	7	3	1	1	4 e	4 d, h
7	8		4 e, h	4 kA	4 e, f	8	9
	10 a		8	8	11 b		

OPTION 1A – INDUSTRIAL CHEMISTRY

Higher Level must do either both Option 1's or both Option 2's.
Ordinary Level can do any one Option from A in even years and B in odd years.

a Process Types

Batch: Reactants added - reaction takes place - products removed - clean reaction vessel - start again. Used in medicine manufacture.

Continuous: Reactants fed in at one end - React - Products come out the other end - over a lengthy period of time. Used in lime production.

Semi-continuous: Combination of batch and continuous First stage involves batch process while second involves continuous. E.g. purifying the product (soft drinks) using feed from several batch reactors

b Characteristics of an effective and successful industrial chemical processes

- **Feedstock: Modified and purified Raw Materials**
- **Reaction Rate:**
- Overall rate **controlled by the slowest reaction**
- A catalyst can speed up the reaction in many cases
- **Product Yield:** Conditions can be modified to maximise product yield
- **Co-products:** Any other **substance formed along with the main product** being manufactured.
- **Waste disposal / Effluent Control:** Both of these need to be considered due to pollution issues and cost of disposal
- **Quality Control: Analysis of both reactants and products**
- **Safety: Personal protective equipment** used where required e.g. goggles, boots, helmets, earplugs, clothing [day-glow] and **Health and Safety Training**
- **Costs:**
  Fixed Independent of amount of product formed e.g. labour, loan repayments, plant depreciation
  Variable Depends on amount of product produced e.g. fuel for heat and pumping, raw materials
  Cost reduction Methods to reduce costs e.g. recycling and using waste heat to heat offices
- **Site Location: Infrastructure** e.g. road, rail, ports etc.
  Raw Material and Skilled Labour availability
- **Construction Materials: Suitable for conditions** e.g. stainless steel won't corrode, concrete won't react with lime etc.

Contributions of Chemistry to Society

Be aware that chemistry makes huge contributions to modern society by providing us with such things as

- Pure water, fuels, metals, medicines, detergents, enzymes, dyes, paints, semiconductors, liquid crystals and alternative materials, such as plastics and synthetic fibres;
- Increasing crop yields by the use of fertilisers, herbicides and pesticides;
- Food-processing e.g sterilising and packaging

A Case Study based on the Irish Chemical Industry

ONLY ONE of the three following Industrial Processes need be studied.

c

• Ammonia Manufacture [IFI Cobh, Co. Cork]

Produced by the Haber - Bosch process from natural gas, water vapour and air

Raw Materials	**Hydrogen** produced from Natural Gas by methane **reforming**. $CH_4 + H_2O = 3H_2 + CO$ then $CO + H_2O = CO_2 + H_2$ **CO_2 removed by reacting with K_2CO_3 to give $KHCO_3$** $CO_2 + H_2O + K_2CO_3 = 2\,KHCO_3$ **Nitrogen** from Air. Produced by burning unreacted CH_4 from above reaction leaving almost pure nitrogen. $N_2 + 3\,H_2 \overset{Fe}{=} 2\,NH_3$
Rate	Small Fe catalyst particles speed up reaction
Product yield	About 17%. Pressure 200 atm increases yield. 500ºC is a compromise – high enough to be fast but not too high to minimise pushing equilibrium too much to the left. Removal of NH_3 as formed drives reaction to the right.
Co-products	None. CO_2 produced in steam reforming (above) used for fizzy drinks and urea manufacture **Urea synthesis** $CO_2 + 2NH_3 = NH_2CONH_2 + H_2O$
Effluent Control	Emissions monitored for urea, dust and ammonia
Quality Control	Gas chromatography and IR spectroscopy. Sensors measure temps. and pressures etc. at various parts of the plant
Safety	Personal protective equipment used where required e.g. goggles, day-glow clothing. Health and Safety Training
Costs	**Fixed** Labour costs **Variable** Purchase of natural gas, water and electricity
Site Location	Good rail connections and near deep water harbour and natural gas supply. Good supply of skilled personnel
Plant Construction	Stainless steel used throughout to minimise corrosion

d

• Nitric Acid Manufacture [IFI Arklow, Co. Wicklow]

Raw Materials	Ammonia, Oxygen, Water **$4\,NH_3 + 5\,O_2 = 4\,NO + 6\,H_2O$ [Pt / Rh gauze is catalyst]** $2\,NO + O_2 = 2\,NO_2$ $4\,NO_2 + 2H_2O + O_2 = 4\,HNO_3$
Rate	Pt / Rh gauze catalyst is used to speed up reactions
Product yield	About 95%. Temperature around 900ºC
Co-products	None. Nitric acid used to make ammonium nitrate fertiliser $NH_3 + HNO_3 = NH_4NO_3$
Effluent Control	**Effluent** – automatically monitored for ammonia and nitrate levels. Recycling ensures minimum waste
Quality Control	Feedstock and products analysed for nitrogen content and to ensure particles flow properly
Safety	Personal protective equipment used where required e.g. day-glow clothing. Health and Safety Training
Costs	**Fixed** Labour costs **Variable** Purchase of natural gas, water and electricity
Site Location	Avoca river for fresh water for cooling Near harbour for export and near rail link
Plant Construction	Stainless steel used throughout plant to minimise corrosion

e (c) MgO [periclase] production by Premier Periclase [Drogheda, Co. Lough]

Periclase (MgO) is a refractory [high melting point] material used to line furnaces etc.

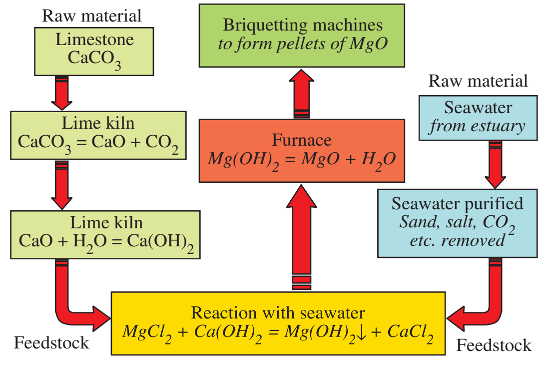
Raw Materials	**Raw materials** seawater and limestone **Feedstock** purified sea water and slaked lime Limestone turned to lime by heating $\mathbf{CaCO_3 = CaO + CO_2}$ Lime converted to slaked lime by adding water $\mathbf{CaO + H_2O = Ca(OH)_2}$ Slaked lime reacted with $MgCl_2$ in sea water $\mathbf{MgCl_2 + Ca(OH)_2 = Mg(OH)_{2(s)} + CaCl_2}$ Magnesium hydroxide converted to magnesium oxide by heat $\mathbf{Mg(OH)_2 = MgO + H_2O}$
Rate	Lime formation slow so controls overall rate
Product yield	1 litre seawater only gives 2 g so large quantities needed
Co-products	None
Effluent Control	Dust extracted by electrostatic precipitation Seawater pH adjusted before returning to sea Suspended solids monitored
Quality Control	Acid-base titrations used to check limestone quality and effluent pH. Emission spectroscopy used to check for **boron content** of periclase as this lowers its melting point
Safety	Personal protective equipment used as required e.g. helmets, day-glow clothing Health and Safety Training
Costs	**Fixed** – labour **Variable** – purchase of limestone, electricity Waste heat used to heat offices
Site Location	Close to good seawater and pure limestone supply. Good road and rail infrastructure Close to port for export
Plant Construction	Building made from steel with iron cladding

f Awareness of the range and scope of the Irish Chemical Industry

(You need to know two examples of chemical industry products other than those referred to in the case study chosen)

Use of

- **Urea as a fertiliser.**
- Ammonium nitrate as a fertiliser.
- Magnesium oxide as a heat-resistant material in the walls of furnaces.
- Nitric acid as an etching agent for copper



Summary of periclase production

Questions on this Section from Past Exams Year by Year

2009	2008	2007	2006	2005	2004	2003	2002
4 kB			11 cA				11 cA

OPTION 1B – ATMOSPHERIC CHEMISTRY

a Atmosphere

Composition of Atmosphere

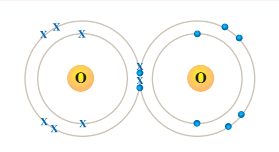
Atmosphere is about 100 km deep

Constituents of air	Approx %
O_2	21
N_2	78
CO_2	0.03
Noble Gases	1
Water	Variable
Pollutants	Variable

Mixture

Because components can be separated by fractional distillation of liquid air.
Air is filtered then compressed, cooled and released until temperature gets to -200ºC.
It is then allowed to warm up gradually in fractionating column.

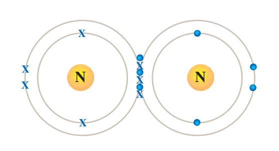
Oxygen (O_2)



Most reactive gas in air

Uses: Respiration, oxygen tents, steel making, combustion, oxyacetylene cutters, rocket fuel,

Nitrogen (N_2)



Unreactive

- Triple bond needs lots of energy to break
- Non-polar
- Colourless, odourless, tasteless

Uses

- Food packaging, stops crisps going rancid or getting crushed
- Fills storage tanks in ships and refineries to prevent explosions
- Making ammonia by Haber process
- Needed by plants to make proteins [from fixed N in compounds – not gas]
- **Liquid nitrogen** freezes pizzas, removing warts, preserving semen and ova

Nitrogen Fixation

Converting atmospheric nitrogen to compounds that can be used by plants

i) **Lightning** The high temperature around the lightning bolt causes nitrogen to react with oxygen.

$N_2 + O_2 = 2\ NO$

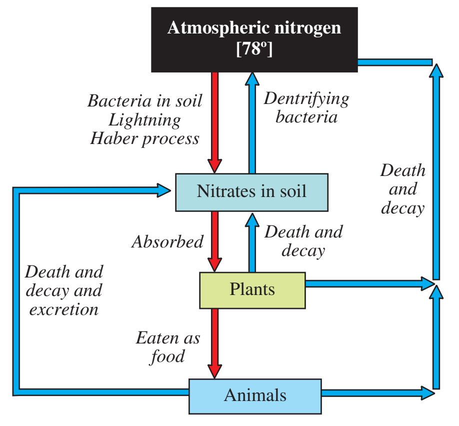
$2\ NO + O_2 = 2\ NO_2$

$2\ NO_2 + H_2O = HNO_2 + HNO_3$

Nitric acid falls in rain and forms nitrates in soil

ii) **Nitrogen fixing bacteria** [rhizobium] in root nodules of leguminous plants

iii) **Artificial Fixation by Haber-Bosch Process**



Nitrogen cycle

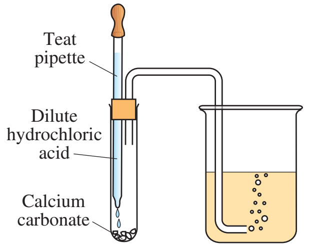
b Inorganic Carbon Compounds

Carbon Monoxide (CO)

- Formed by **incomplete combustion** in insufficient oxygen e.g. smouldering fire, **cigarettes and vehicle engines**

$$C + \tfrac{1}{2}O_2 = CO$$

- Colourless, odourless and tasteless
- It is a **cumulative poison**, it binds to haemoglobin where oxygen should go and stays there stopping the haemoglobin working
- **It is a Neutral oxide**
- **Insoluble** in water
- Does **not react with acids or bases**
- **It has no effect on Universal indicator** or litmus



Effect of CO_2 on Universal Indicator

Carbon Dioxide (CO_2)

- Formed by

(a) Combustion of **Carbon and Fossil fuels**

$$C + O_2 = CO_2$$

$$C_8H_{18} + 12\tfrac{1}{2}\ O_2 = 8\ CO_2 + 9H_2O$$

(b) Respiration in both plant and animal cells

$$C_6H_{12}O_6 + 6\ O_2 = 6\ CO_2 + 6\ H_2O + ATP$$

(c) Fermentation of glucose by zymase from yeast in anaerobic conditions

$$C_6H_{12}O_6 = 2\ C_2H_5OH + 2\ CO_2$$

- **It is an Acidic Oxide**
- **Soluble in water forming carbonic acid** which turns **universal indicator orange/yellow**

$$CO_2 + H_2O = H_2CO_3$$

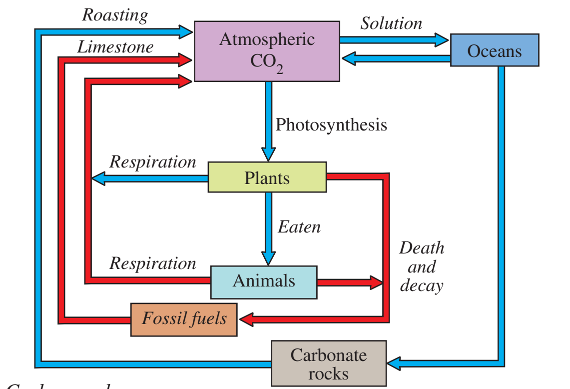
Carbonic acid dissociates in water to give both hydrogencarbonate (HCO_3^-) and carbonate ions (CO_3^{2-})

$$H_2CO_3 = HCO_3^- + H^+ = CO_3^{2-} + 2H^+$$

Uses

- **Photosynthesis** $6\ CO_2 + 6\ H_2O = C_6H_{12}O_6 + 6\ O_2$
- **Fizzy drinks** – sharp taste of acid and fizz of gas coming out of solution
- **Fire extinguishers** – heavier than air and does not support combustion
- **Dry ice** – solid CO_2 sublimes, forms stage mist with warm water

c Carbon cycle



Carbon cycle

Noble Gas Uses

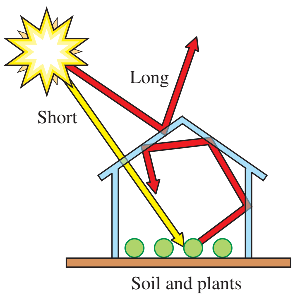
He - Super-cooling, Filling Airships, Deep-sea divers "air" *carrier for oxygen* - less chance of "*bends*"

Ar - Filling light bulbs

Ne - Neon lights.

OPTION 1B – ATMOSPHERIC CHEMISTRY

d Greenhouse Effect



How it works

- Sun produces both long and short wave radiation
- Long wave bounces off the atmosphere
- Short passes through
- Short wave radiation absorbed by soil and plants
- Radiation is released again as long wave radiation
- Thus is gets trapped in atmosphere
- Energy of the atmosphere rises with a result that the temperature rises

Effects

- Essential for life on earth as it keeps earth warm enough for life to exist.
- The problem is the **Enhanced Greenhouse Effect**
- Results are more **violent weather, melting ice-caps and raised sea levels** etc.
- CO_2 from **burning Fossil Fuels** and **CH_4 from rotting vegetation** and **ruminants** are main causes.
- **CFC's and N_2O more effective at producing Greenhouse Effect but not as important**
- **Residence Time** is how long a gas stays in atmosphere.
  CFCs and CO_2 = 100 yrs / CH_4 = 10 yrs
- CO_2 levels **decreased by solution in the sea**

e Atmospheric Pollution

Situation that exists when a constituent in the air is present to the extent that there is a significant risk to:- (a) present health (b) future health (c) the environment.

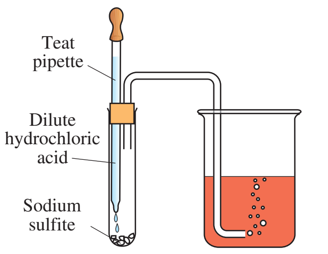
Pollution

The addition of any damaging substance to the environment

Acid Rain and its Causes

Rainwater normally contains CO_2 dissolved in it and is slightly acidic – **it is NOT acid rain.**

Acid rain has a pH of less than 4.5



SO_2 turns on Universal Indicator red

Sulphur Dioxide (SO_2)

Sources Volcanoes, fossil fuel combustion [about 85%] and Industry

Formation $S_{(s)} + O_{2(g)} = SO_{2(g)}$

$SO_{2\,(g)} + H_2O_{(l)} = H_2SO_{3(aq)}$ **[sulphurous acid]**

$H_2SO_{3(aq)} + \frac{1}{2}\,O_{2(g)} = H_2SO_{4(aq)}$ **[sulphuric acid]**

Nitrogen Dioxide (NO_2)

Sources N_2 is un-reactive and high temperature needed to make it react e.g. **Car engines, Industrial furnaces and lightning**

Formation $N_{2(g)} + O_{2(g)} = 2\,NO_{(g)}$ [*nitrogen monoxide – colourless*]

$NO(g) + \frac{1}{2}\,O_{2(g)} = NO_{2(g)}$ [*nitrogen dioxide - brown gas*]

$2\,NO_{2(g)} + H_2O_{(l)} = HNO_{2(aq)} + HNO_{3(aq)}$

Nitrous acid *Nitric acid*

Environmental Effects of Acid Rain

- **Corrosion** stonework particularly limestone marble, and metal
- **Health effects** (eyes and lungs damaged – most important in sick and elderly
- **Death of plants** -Trees in Black Forest by SO_2 exported from GB.
- **Leaching of metals** e.g. Al which can cause poisoning - Alzheimer's disease
- **Death of animals** - fish fry and eggs very sensitive to pH - salmon almost wiped out in Scandinavia.

Scrubbing of Waste Gases with Limestone

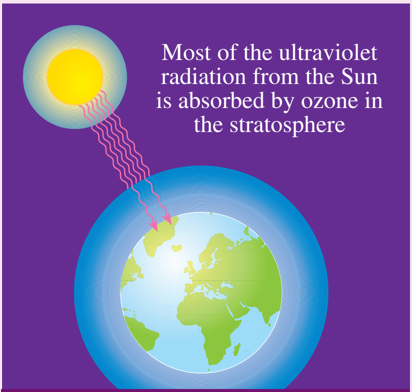
Limestone can be used in power stations to remove SO_2 from chimney gases.
This is called **scrubbing**

$$CaCO_3 + SO_2 = CaSO_3 + CO_2$$

f

Ozone Layer

- **Ozone has the molecular formula O_3**
- **UV radiation causes sunburn and ultimately skin cancer**
- **Ozone screens us from the harmful effect of UV radiation by absorbing the UV.**



Ozone Layer protects life on earth

Formation of Ozone

Photodissociation of oxygen
In the **stratosphere** which is 25 – 50 km up the concentration of ozone.

$$O_2 + UV = O^{\bullet} + O^{\bullet} \text{ [the UV light is absorbed]}$$

$$\text{then } O^{\bullet} + O_2 = O_3$$

The **absorption of UV protects us from its harmful effects**

Destruction of Ozone

Hole over Antarctic is cause for concern in that it indicates the ozone layer is becoming thinner and **providing less protection against the harmful effects of UV**

Ozone Breaks Down Naturally

Sunlight naturally breaks down ozone molecules as shown below but many of them immediately reform ozone.

$$O_3 + UV = O_2 + O^{\bullet}$$

The **absorption of UV by the above reaction also protects us from its effects**
However some oxygen atoms destroy ozone by reacting with it to form oxygen

$$O^{\bullet} + O_3 = 2\ O_2$$

Chlorofluorocarbons and Ozone Depletion

Chlorofluorocarbons [CFC's] used as **refrigerants** and **aerosol propellants** are the main culprits

Very unreactive at ground level and have a **long residence time** of many decades

In the **Stratosphere CFC's break down** and form **chlorine atoms** (radicals)

$CCl_3F + UV = CCl_2F + Cl^\bullet$ [*Chlorine radical*]

$O_3 + Cl^\bullet = O_2 + ClO^\bullet$ [*Chlorine oxide*]

$ClO^\bullet + O^\bullet = Cl^\bullet + O_2$

[Cl• radical free to destroy another ozone and can do this thousands of times]

Hydrochlorofluorocarbons [HCFC's] such as dichlorofluoroethane [CH_3CCl_2 F] are **not as damaging** and are **used as replacements** for CFC's

Fully hologenated hydrocarbons can be used as flame retardants and fire extinguishers. They are heavier than air and do not burn, or support combustion. Some of them are toxic and carcinogenic e.g. carbon tetrachloride (C Cl_4), others destroy ozone so their use in extinguishers is limited.

Nitrogen Monoxide and the Ozone Layer

Nitrogen monoxide also destroys ozone

$$O_3 + NO = O_2 + NO_2$$

Methane Removes Chlorine Atoms

It reacts with the chlorine atoms to form a methyl radical and hydrogen chloride

$$CH_4 + Cl^\bullet = CH_3^\bullet + HCl$$

This stops the chlorine atoms damaging ozone molecules

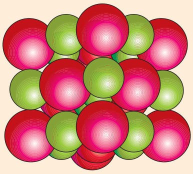
Questions on this section from Past Exams Year by Year

2009	2008	2007	2006	2005	2004	2003	2002
11 cB	11 cA	4 kA	4 kA	11 cB	4 kA	4k A	4 kA
		11 cA			11 cB	11 cA	

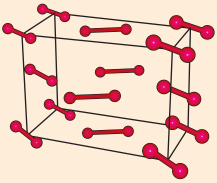
OPTION 2A – MATERIALS

a Crystals

Ionic e.g. NaCl, KI, MgO
Lattice points occupied by ions
Binding force is electrostatic attraction between + and –

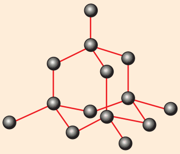


Ionic



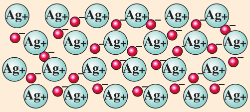
Molecular

Molecular, e.g. I_2, CO_2, S_8, H_2O
Lattice points occupied by molecules
Binding force is weak van der Waals forces
Iodine molecules held together by van der Waals forces
In polar molecules such as HCl the binding forces are dipole-dipole
In water the binding forces are hydrogen bonds



Macromolecular

Covalent Macromolecular e.g. diamond, quartz [SiO_2]
Lattice points occupied by atoms
Binding force is covalent bonds



Metallic

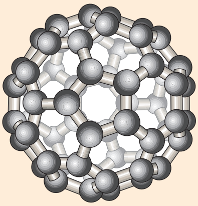
Metallic e.g. Fe, Cu, Ag
Lattice points occupied by positive metal ions
Binding force is electrostatic attraction caused by a sea of electrons

X-Rays and Crystal Structure

Crystal Type	Melting Point	Hardness Conductivity	Electrical	Solubility
Ionic	High e.g. NaCl 801ºC	Hard and brittle	Only when melted or in solution	Soluble in polar solvents such as water
Molecular	Low e.g. I_2 114 ºC	Quite soft	Non-conductors	Polar molecules e.g. HCl dissolve in water Non-polar e.g. I_2 are insoluble in water but soluble in hexane
Macromolecular	High	Very hard	Non-conductors	Insoluble
Metallic	Vary greatly -39 to 3,410ºC	Very variable	Good conductors	Insoluble but some react with water

Father and son **William and Lawrence Bragg** received the Nobel Prize for Physics in 1915 for using **X-ray scattering to determine the internal arrangement of particles in crystals**.

Dorothy Hodgkin took this further and used it to determine the crystal structure of complex organic molecules, e.g. **vitamin B12 and penicillin**.
Buckminsterfullerenes are groups of carbon molecules which look like footballs. They were discovered in 1985 and named after an architect who was famous for building structures of similar shape.



Buckminsterfullerene

b Addition Polymers

Polymer — **A molecule made up of large numbers of repeating units.**

The repeating units are called **monomers**. If these monomers are based on ethene then they are joined by an addition reaction and so they are called **addition polymers**

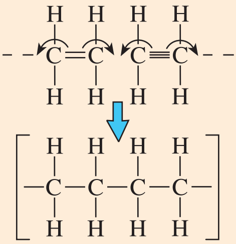
Poly(ethene) or Polyethene

Discovered (1933) by **Eric Fawcett** and **Reg Gibson** while checking the effects of high pressure and temperature on certain reactions. A white waxy material formed which had good electrical insulating properties. First used 1939 to insulate underwater cables. This was **low-density polythene** because chains were branched and had lots of empty space between them.

Uses: cling film, plastic bags, milk bottles

1935 **Karl Zeigler** used catalysts such as $Al(C_2H_5)_3$ and produced a high-density polythene. This has little branching and is harder and stiffer than low-density polythene. It has a high melting point as well.

Uses: washing up basins, buckets, bottle crates etc.



Ethene - Polyethene

Poly(chloroethene) or Polyvinylchloride or PVC

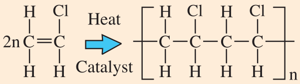
Polarisation of the C – Cl bond increases the attraction between chains making it strong and rigid.

Uses: uPVC - windows and drainpipes. **u** = unplasticised.

Adding a plasticiser makes it softer and more flexible.

This form is called pPVC, p = plasticised.

Uses: pPVC - colourful raincoats and shower curtains.



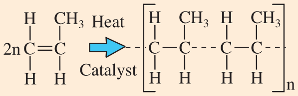
PVC Polyvinylchloride

Poly(propene) or Polypropylene

Similar structure to PVC except that the Cl has been replaced by a CH_3 (methyl) group.

Closely packed chains make it similar to high-density polythene. **Uses: chairs, cases and water pipes**.

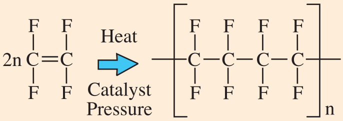
It can be turned into fibres and used to make rot proof **ropes and carpets and fishing nets**.



Poly(propene) Polypropylene

Poly(tetrafluoroethene), or Teflon or PTFE

Discovered by accident in 1938 by **Roy Plunkett**. He was researching refrigerants when he opened a bottle of tetrafluoroethene and nothing came out. He cut the cylinder open and found that it had polymerised. The PTFE was chemically unreactive, insoluble in most solvents and very slippy.



Teflon [PTFE]

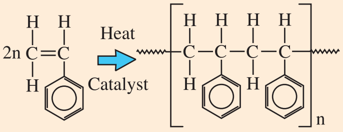
Uses: non-stick frying pans, lubricant in space and making body implants because it is so inert it is not rejected by the body.

Poly(Phenylethene) or Polystyrene

Discovered 1839 by **Eduard Simon** from Liquidambar tree resin.

Three forms

Expanded polystyrene foam used as a packing and thermal insulating material



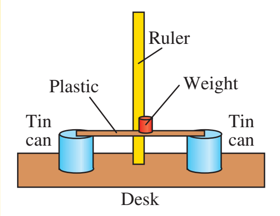
Poly(phenylethene) Polystyrene

Extruded polystyrene foam or “Styrofoam” is easy to cut and used to make architectural models and thermal insulation

Extruded polystyrene is hard and used in model aeroplane kits and plastic cutlery

EXPERIMENT: Demonstration of Density, Flexibility and Hardness.

Flexibility
Set up apparatus as in diagram
Note the height of the plastic strip
Add a known mass to the centre
Note the drop in height of the plastic
Repeat for each material in turn
Arrange samples in order of flexibility



Flexibility testing

Hardness
Use a nail to scratch the surface of each sample
Try to tear each sample
Try to cut each sample with a scissors
Arrange samples in order of hardness

Density
Using thick samples of each substance
Find the mass and volume of each
Calculate density = mass/ volume
Arrange in order of density

Recycling Plastics e.g. Polystyrene
About 60% of plastics in Ireland are now recycled

Stage	Description
Sorting	Separated from other plastics by hand.
Shredding	Granulated by machine
Washing	Washed with steam and detergent to remove impurities
Drying	Warm air removes excess water
Extrusion	It is melted in an extruder and then remoulded into the required item

Metals

Comparison with Non-Metals

Metal	Non-Metal
Hard – most solids at room temperature	**Soft** – most liquid or gas at room temperature
Lustre [metallic shine]	**Dull**
Ductile [can be pulled into wire]	**Can't be drawn into wires**
Malleable [can be hammered into sheets]	**Brittle**
Good conductor of heat	Poor conductor of heat
Good conductors of electricity	Insulators [carbon is exception]

Alloys
Mixture of two metals [steel is an exception as it is a mixture of Fe and C]
Properties are not intermediate between two constituents

Alloy	Constituents	Property change
Brass	Copper and Zinc	Different colour and harder
Bronze	Copper and Tin	Harder than either
Steel	Iron and Carbon [0.15%]	Harder and tougher under tension

Questions on this Section from Past Exams Year by Year

2009	2008	2007	2006	2005	2004	2003	2002
4 kA		11 cB			11 cA	11 cB	

OPTION 2B – ADDITIONAL ELECTRO-CHEMISTRY & EXTRACTION OF METALS

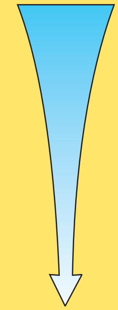
a Electrochemical Series

Different combinations of metals produce different voltages. Each voltage is measured relative to a standard hydrogen electrode.
A list is made in order of their tendency to lose electrons and is called the **electrochemical series**.

Those at the top tend to be more reactive.
They also tend to corrode more easily.

Note that Ca and Na are in the opposite order to Activity Series

K
Ca
Na
Mg
Al
Zn
Fe
Pb
H
Cu
Hg
Ag
Au



Important Contributors to Early Studies

Luigi Galvani showed that electricity is generated whenever two different metals are placed in a conducting solution.
Alessandro Volta was the first to construct a battery using copper and zinc plates separated by leather moistened with salt solution. This was called a voltaic pile.
This invention allowed **Michael Faraday** to experiment with electrolysis and he gave us most of the vocabulary to do with electrolysis,
Humphrey Davy used it to isolate many reactive elements.

b Electrolysis

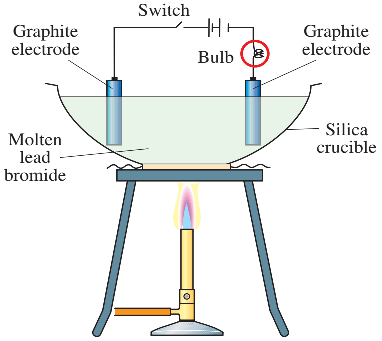
Is a chemical reaction caused by an electric current passing through a liquid called the electrolyte

EXPERIMENT: Demonstration Electrolysis of Lead Bromide.

The bulb does not light while the lead bromide is solid showing that no current flows. However **when it melts the bulb lights as a current begins to flow**. At the same time red bromine gas is produced at the anode and molten lead accumulates below the cathode.
These are formed as in the equations below.

Anode reaction $2\,Br^- = Br_{2\,(g)} + 2e^-$

Cathode reaction $Pb^{2+} + 2\,e^- = Pb$



Electrolysis of Molten Lead Bromide

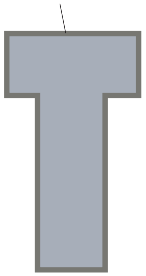
c Corrosion

In general metals high on the electrochemical series corrode easily

is any undesired process where a metal is converted to one of its compounds.

Apparent Exception

Aluminium which is high on the list
It does corrode quickly but it forms a layer of **unreactive aluminium oxide which sticks** to the fresh aluminium and prevents further attack by air.
This and its lightness and strength make it an excellent material for building



Aluminium rivet covered in oxide layer

Prevention of Corrosion

Corrosion **requires air and water** and is made **worse if an electrolyte such as sodium chloride** is present.

A surface layer of oil, grease or paint prevents corrosion by excluding air and water.

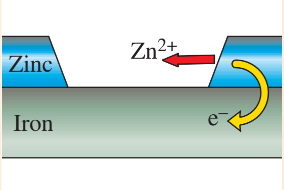


Diagram.

- **Galvanising:** Iron can also be covered by a layer of Zn. The zinc forms a layer of unreactive oxide on its surface which prevents further corrosion and if this is punctured the **zinc will corrode in preference to the iron as it is higher in the electrochemical series**.
- **Tin Plating:** – tin is unreactive and a layer of it can be applied to protect iron as in tin cans. **Once broken the iron corrodes faster because it is higher in the electrochemical series than tin**.

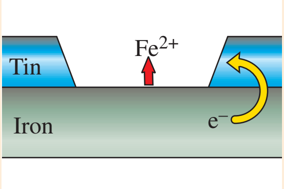


Diagram.

- **Anodising:** The layer of **unreactive oxide on Al** can be thickened by making the aluminium the anode in a solution of sulphuric acid – this is called anodising
- **Chromium Plating:** Chromium is a very unreactive metal is used as a protective layer on steel e.g. on car bumpers and taps to prevent corrosion and make them look good.

Sacrificial Anodes

This is similar in some respects to galvanising. The iron is attached to a metal higher in the electrochemical series e.g. zinc or magnesium. This reacts in preference to the iron and so the magnesium or zinc is sacrificed to save the iron of the ship. This is also called **cathodic protection** as the iron is being made a cathode to protect it from corrosion.


Sacrificial Anode on Hull of Ship

Alloying can also prevent corrosion.

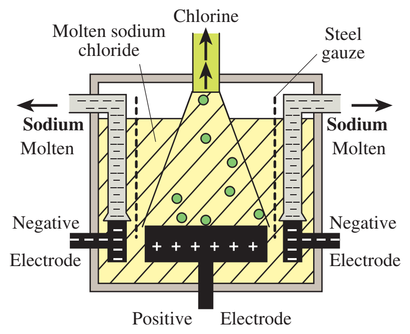
Stainless Steel does not rust because iron is alloyed with carbon and chromium.

d Strongly Electropositive Metals (Na and Al)

Need to be extracted by electrolysis as they are too reactive to extract by smelting.

Sodium Extraction

Sodium is used in orange street lamps and as a coolant in nuclear reactors.
It is extracted from molten sodium chloride in a **Downs Cell**. Sodium chloride is mixed with calcium chloride to lower the melting point and a large current is passed through it. The sodium is 99% pure and chlorine gas is a useful by-product. The steel gauze stops the Na and Cl_2 meeting and reacting



Downs Cell

Anode reaction

$$2\ Cl^- = Cl_{2(g)} + 2e^-$$

Cathode reaction

$$2\ Na^+ + 2\ e^- = 2\ Na_{(l)}$$

e

Aluminium Extraction

Aluminium is extracted from the ore **bauxite**

Stage 1 Purification of bauxite to give **Alumina [Al_2O_3]**

- **Crushing and Mixing** - with hot NaOH solution
- **Digestion** - Aluminium oxide reacts with NaOH to form sodium aluminate. Insoluble impurities mainly oxides of iron sink to the bottom

$$Al_2O_3.3H_2O + 2\ NaOH = 2\ NaAlO_2 + 4\ H_2O$$

- **Clarification** - Impurities precipitate out as “red mud.”
- **Precipitation** – solution is pumped to clean tanks and seed crystals of $Al_2O_3.3H_2O$ are added to speed up crystal formation.

$$2NaAlO_2 + 4\ H_2O = Al_2O_3.3H_2O + 2\ NaOH$$

- **Removal of Water of Crystallisation** the crystals are roasted in a rotary kiln to drive off the water of crystallisation and leave pure alumina as a white powder.

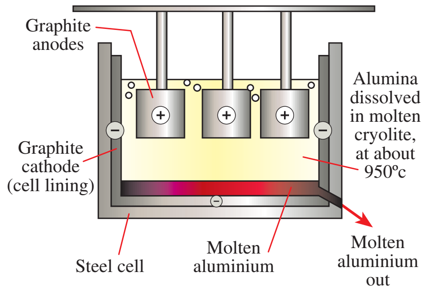
$$Al_2O_3.3H_2O = Al_2O_3 + 3\ H_2O$$

Stage 2 Extraction of Aluminium Metal from the Alumina

Alumina is mixed with **cryolite [Na_3AlF_6]** to **lower the melting point**
Electrolysed at 950ºC.
Al is tapped off periodically.

Anode reaction $2\ O^{2-} = O_{2(g)} + 4\ e^-$

Cathode reaction $Al^{3+} + 3\ e^- = Al_{(l)}$



Aluminium smelter

Environmental Aspects

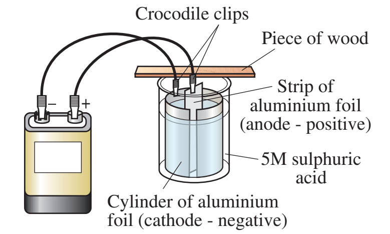
Smelting and electrolysis use huge amounts of electricity so it occurs where there are supplies of cheap electricity; often **near hydroelectric power stations**.

Recycling

Lots of CO_2 produced so recycle as much Al as possible. Recycling is also far cheaper.

Anodised Aluminium

Uses: For windows and doors when it has had its **oxide coat thickened** by making it the **anode in dilute H_2SO_4** this increases its resistance to further oxidation. It is also used to make cutlery and engine blocks because it is light, strong and resistant to corrosion.



Annodising bath

Oxide layer is **porous** which **makes it easy to colour using dye**.

Anode reaction $2\ Al + 3\ H_2O = Al_2O_3 + 6\ H^+ + 6e^-$

Cathode reaction $2\ H^+ + 2e^- = H_2$

f

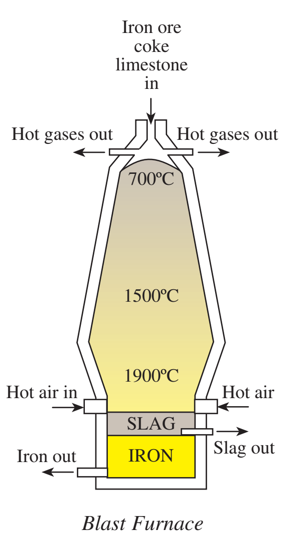
D-Block Metals

Transition elements have three main properties

- They have **variable valencies** e.g. copper(I), copper (II) or iron (II) and iron (III)
- They and their compounds have **catalytic properties** e.g. Fe in the Haber Process for making ammonia and V_2O_5 in the Contact Process for making sulphuric acid
- **Coloured ions** e.g. Cu^{2+} blue, MnO_4^{1-} purple, Fe^{3+} brown, Fe^{2+} green.

Iron Extraction

Haematite Fe_2O_3 - main ore of iron. It is **reduced** by carbon in the **blast furnace**.
A mixture of **iron ore, coke and limestone** added through the top.
Hot air is blown in at the bottom to fan the flames
At around **1500°C**. $\mathbf{Fe_2O_3 + 3\ CO = 2\ Fe + 3\ CO_2}$
This is an endothermic reaction so heat needed
Coke (i) supplies the **CO to reduce the iron oxide**
(ii) fuel providing heat for the reaction
(iii) Supports the materials allowing movement.
The **limestone removes impurities** of SiO_2 [sand] as **slag**
$\mathbf{CaCO_3 = CaO + CO_2}$ then $\mathbf{CaO + SiO_2 = CaSO_3}$ [Slag]



Blast Furnace

Both the iron and slag sink to the bottom but the slag floats on top of the iron. Slag is **tapped off** first and discarded followed by the iron into large containers called "pigs".
Uses: Some is used as cast iron **for manhole covers and engine blocks** but most is converted into steel.

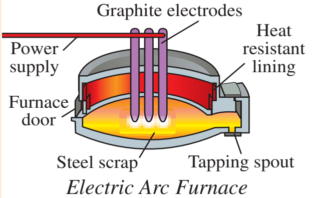
Steel Manufacture

Stages

- **Oxygen** is blown through the molten iron which **removes impurities e.g. C and S as CO_2 and SO_2**.
- Measured amounts of various elements are added to give it particular properties e.g. Tungsten for hardness and chromium for resistance to corrosion.

Electric Arc Process

- **Charging** Steel and iron scrap "charge" placed in furnace
- **Melting** Huge current passed between electrodes close to scrap. The temperature reaches 3,500°C which melts the scrap.
- **Sampling and refining** samples analysed for various elements using emission line spectra. Oxygen blown through lance to remove C as CO_2. Si oxidised to SiO_2 and lime is added to form $CaSiO_3$ slag which floats on top and can be scraped off.
- **Tapping** molten steel transferred to ladle and various elements are added to alloy with the iron and give it particular properties.
- **Casting** the steel is poured into a machine which forms a slab. This is then cut into suitable sizes



Electric Arc Furnace

Uses of Iron and Steel

Iron is the most important metal in daily life for thousands of years
Iron used for tools, manhole covers and wrought iron gates.
Steel used in car bodies, stainless steel used in motor cycle exhausts, building frames

Environmental Aspects

Open cast mining can devastate large areas but these now have to be reinstated
Air pollution by dust during smelting is controlled by electrostatic removal
SO_2 produced during steel making is removed by "scrubbing" i.e. neutralising it by passing it through limestone

Questions on this Section from Past Exams Year by Year

2009	2008	2007	2006	2005	2004	2003	2002
11 c A	1 k B	4 k B	4 k B	4 k B	4 k B	4 k B	4 k B
	11 c B		11 c B				11 c B

CHEMICAL FORMULAE USING TABLE OF ELECTROVALENCIES

Predict simple chemical formulae of the first 36 elements (excluding d-block elements) of hydroxides, carbonates, nitrates, hydrogencarbonates, sulfites and sulfates of these elements (where such exist).

+1	+2	+3	-1	-2	-3
Na^{1+} Sodium	Mg^{2+} Magnesium	Al^{3+} Aluminium	F^{1-} Fluoride	O^{2-} Oxide	N^{3-} Nitride
K^{1+} potassium	Ca^{2+} Calcium	Cr^{3+} Chromium	Cl^{1-} Chloride	CO_3^{2-} carbonate	P^{3-} Phosphide
Ag^{1+} Silver	Fe^{2+} Iron(II)	Fe^{3+} Iron(III)	Br^{1-} Bromide	CrO_4^{2-} Chromate	PO_4^{3-} Phosphate
Cu^{1+} Copper(I)	Cu^{2+} Copper(II)		I^{1-} Iodide	$Cr_2O_7^{2-}$ Dichromate	
NH_4^{1+} Ammonium	Zn^{2+} Zinc		OH^{1-} Hydroxide	SO_4^{2-} Sulphate	
H^{1+} Hydrogen	Ba^{2+} Barium		NO_3^{1-} Nitrate	SO_3^{2-} Sulphite	
Li^{1+} Lithium	Pb^{2+} Lead		NO_2^{1-} Nitrite	S^{2-} Sulphide	
	Mn^{2+} Manganese		MnO_4^{1-} Permanganate	$S_2O_3^{2-}$ Thiosulphate	
	Co^{2+} Cobalt		OCl^{1-} Hypochlorite	O_2^{2-} Peroxide	
	Hg^{2+} Mercury		HCO_3^{1-} Hydrogencarbonate		
			CH_3COO^{1-} Ethanoate		

Using the rules below this table can be used to work out the formula of most of the compounds one is likely to encounter in Leaving Certificate Chemistry.

- Positive radical or ion comes first
- Multiply each radical or ion so that the total number of pluses and minuses are the same. *[bring the charge on the ion down to subscript level and apply it to the other ion]*
- If the charges are the same ignore them *[see magnesium sulphide]*
- Enclose radicals (complex ions) in brackets if there is more than one of them e.g. $Al(SO_4)_3$

Write the formulae of the following compounds

Calcium chloride	Ca^{2+}	Cl_{1-}	$CaCl_2$
Magnesium Sulphide	Mg^{2+}	S^{2-}	MgS *[not Mg_2S_2]*
Ammonium sulphate	NH_4^{1+}	SO_4^{2-}	$(NH_4)_2SO_4$
Barium Nitrate	Ba^{2+}	NO_3^{1-}	$Ba(NO_3)_2$
Aluminium carbonate	Al^{3+}	CO_3^{2-}	$Al_2(CO_3)_3$

Try the following

Iron(II)nitrate	Ammonium Sulphide	Sodium nitrite	Iron(II) phosphide
Chromium nitride	Lead Chloride	Calcium phosphate	Copper(I)oxide
Mercury chloride	Copper(II) dichromate	Magnesium hypochlorite	Potassium dichromate
Barium nitrate	Hydrogen sulphide	Iron(III) thiosulphate	Zinc permanganate
Silver carbonate	Tin hydrogensulphate	Aluminium sulphate	Magnesium iodide
Lead phosphide	Manganese peroxide	Zinc phosphate	Cobalt carbonate

Answers on bottom of next page

FORMULAE FOR REVISION

Relative Atomic Mass(Ar)

$$Ar = \frac{(A\,X \times \%) + (A\,Y \times \%)}{100}$$

Combined Gas Law

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

Equation of State (ideal gas)

$$PV = nRT$$

Empirical Formula

$$\frac{\text{Mass } X}{A_r\, X} : \frac{\text{mass } Y}{A_r\, Y}$$

OR

$$\frac{\%\, X}{A_r\, X} : \frac{\%\, Y}{A_r\, Y}$$

Percentage Yield

$$= \frac{\text{Actual Yield}}{\text{Theoretical Yield}} \times 100$$

Molarity

$$= \frac{\text{Grams per Litre}}{\text{Molar Mass}}$$

Concentration in g l^{-1}

$$= \text{Molar mass} \times \text{molarity}$$

Number of Moles

$$= \frac{\text{Volume}}{1000} \times \text{molarity}$$

Effect of dilution

$$V_{dil} \times M_{dil} = V_{conc} \times M_{conc}$$

Temperature conversion

$$K = {}^{\circ}C + 273$$

Titration

$$\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$$

OR

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_r}{n_r}$$

Hess's law

$$\Delta Hr = \Sigma \Delta H_{f\,[prod]} - \Sigma \Delta H_f\,[react]$$

Heat Produced

$$H = mc\theta$$

Heat Capacity

$$= mc$$

Equilibrium Constant for
y A + z B = r C + s D

$$K_c = \frac{[C]^r\,[D]^s}{[A]^y\,[B]^z}$$

pH Strong Acid

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

pOH Strong Base

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

pH Strong Base

$$pH = 14 - pOH$$

Ph weak Acid

$$pH = -\log_{10}\sqrt{(K_a \times [HA])}$$

pH Weak Base

$$pOH = -\log_{10}\sqrt{(K_b \times [OH-])}$$

The Periodic Table of Elements

Atomic Number = Number of Protons = Number of Electrons
Chemical Symbol
Chemical Name
Mass Number = Number of Protons + Number of Neutrons*

Example: 6 C CARBON 12

METALS / NON-METALS

1 H HYDROGEN 1																	2 He HELIUM 4
3 Li LITHIUM 7	4 Be BERYLLIUM 9											5 B BORON 11	6 C CARBON 12	7 N NITROGEN 14	8 O OXYGEN 16	9 F FLUORINE 19	10 Ne NEON 20
11 Na SODIUM 23	12 Mg MAGNESIUM 24											13 Al ALUMINUM 27	14 Si SILICON 28	15 P PHOSPHORUS 31	16 S SULFUR 32	17 Cl CHLORINE 35	18 Ar ARGON 40
19 K POTASSIUM 39	20 Ca CALCIUM 40	21 Sc SCANDIUM 45	22 Ti TITANIUM 48	23 V VANADIUM 51	24 Cr CHROMIUM 52	25 Mn MANGANESE 55	26 Fe IRON 56	27 Co COBALT 59	28 Ni NICKEL 59	29 Cu COPPER 64	30 Zn ZINC 65	31 Ga GALLIUM 70	32 Ge GERMANIUM 73	33 As ARSENIC 75	34 Se SELENIUM 79	35 Br BROMINE 80	36 Kr KRYPTON 84
37 Rb RUBIDIUM 85	38 Sr STRONTIUM 88	39 Y YTTRIUM 89	40 Zr ZIRCONIUM 91	41 Nb NIOBIUM 93	42 Mo MOLYBDENUM 96	43 Tc TECHNETIUM 98	44 Ru RUTHENIUM 101	45 Rh RHODIUM 103	46 Pd PALLADIUM 106	47 Ag SILVER 108	48 Cd CADMIUM 112	49 In INDIUM 115	50 Sn TIN 119	51 Sb ANTIMONY 122	52 Te TELLURIUM 128	53 I IODINE 127	54 Xe XENON 131
55 Cs CESIUM 133	56 Ba BARIUM 137		72 Hf HAFNIUM 178	73 Ta TANTALUM 181	74 W TUNGSTEN 184	75 Re RHENIUM 186	76 Os OSMIUM 190	77 Ir IRIDIUM 192	78 Pt PLATINUM 195	79 Au GOLD 197	80 Hg MERCURY 201	81 Tl THALLIUM 204	82 Pb LEAD 207	83 Bi BISMUTH 209	84 Po POLONIUM 209	85 At ASTATINE 210	86 Rn RADON 222
87 Fr FRANCIUM 223	88 Ra RADIUM 226		104 Rf RUTHERFORDIUM 267	105 Db DUBNIUM 268	106 Sg SEABORGIUM 271	107 Bh BOHRIUM 272	108 Hs HASSIUM 277	109 Mt MEITNERIUM 276	110 Ds DARMSTADTIUM 281	111 Rg ROENTGENIUM 280	112 Uub UNUNBIUM 285	113 Uut UNUNTRIUM 284	114 Uuq UNUNQUADIUM 289	115 Uup UNUNPENTIUM 288	116 Uuh UNUNHEXIUM 291	117 Uus UNUNSEPTIUM NOT YET OBSERVED	118 Uuo UNUNOCTIUM 294

57 La LANTHANUM 139	58 Ce CERIUM 140	59 Pr PRASEODYMIUM 141	60 Nd NEODYMIUM 144	61 Pm PROMETHIUM 145	62 Sm SAMARIUM 150	63 Eu EUROPIUM 152	64 Gd GADOLINIUM 157	65 Tb TERBIUM 159	66 Dy DYSPROSIUM 163	67 Ho HOLMIUM 165	68 Er ERBIUM 167	69 Tm THULIUM 169	70 Yb YTTERBIUM 173	71 Lu LUTETIUM 175
89 Ac ACTINIUM 227	90 Th THORIUM 232	91 Pa PROTACTINIUM 231	92 U URANIUM 238	93 Np NEPTUNIUM 237	94 Pu PLUTONIUM 244	95 Am AMERICIUM 243	96 Cm CURIUM 247	97 Bk BERKELIUM 247	98 Cf CALIFORNIUM 251	99 Es EINSTEINIUM 252	100 Fm FERMIUM 257	101 Md MENDELEVIUM 258	102 No NOBELIUM 259	103 Lr LAWRENCIUM 262

KEY
- = **Solid** at room temperature
- = **Liquid** at room temperature
- = **Gas** at room temperature
- = **Radioactive**
- = **Artificially Made**