

# FUELS AND HEATS OF REACTION

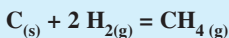
## Kilogram Calorific Value

The heat produced when 1 kg of a fuel is completely burned in excess oxygen.

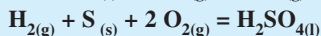
It is used to give a measure of the heat produced by fuels on an industrial scale.

## Heat of Formation

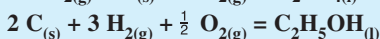
Heat change (in  $\text{kJ mol}^{-1}$ ) when one mole of a substance is formed from its elements in their standard states [i.e. as found in nature]



$$\Delta H = -74.9 \text{ kJ mol}^{-1}$$



$$\Delta H = -811 \text{ kJ mol}^{-1}$$



$$\Delta H = -235 \text{ kJ mol}^{-1}$$

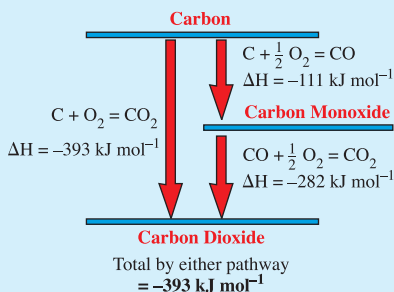
## Law of Conservation of Energy

Energy is neither created nor destroyed.  
It is simply changed from one form to another.

## Hess's Law (of Heat Summation)

The heat change for a reaction is the same whether it takes place in one step or many steps

Carbon dioxide can be made either directly or via carbon monoxide.  
The total heat change will be the same in both cases



## Calculations Involving Hess's Law

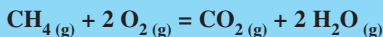
$$\Delta H_r = \Sigma \Delta H_f [\text{products}] - \Sigma \Delta H_f [\text{reactants}]$$

Heat change for the reaction is equal to the sum of heats of formation of the products minus the sum of the heats of formation of the reactants.

*You need to be able to do simple calculations of heat of reaction, using heats of formation of reactants and products – see across*

**Calculate the heat of combustion of methane gas given that the heat of formation of methane, carbon dioxide and water are -74.4 kJ mol<sup>-1</sup>, -393.5 kJ mol<sup>-1</sup> and -285.8 kJ mol<sup>-1</sup> respectively.**

The equation for the combustion of methane is



ΔH<sub>f</sub> of elements (e.g O<sub>2</sub> above) is 0.

$$\Delta H_c = \Sigma \Delta H_f [\text{products}] - \Sigma \Delta H_f [\text{reactants}]$$

$$\begin{aligned} \Delta H_c \text{ CH}_4 &= [\Delta H_f (\text{CO}_2) + 2\Delta H_f (\text{H}_2\text{O})] - [\Delta H_f (\text{CH}_4) + 2\Delta H_f (\text{O}_2)] \\ &= [-393.5 + 2(-285.8)] - [-74.4 + 2(0)] \\ &= [-393.5 - 571.6 + 74.4] \\ &= -890.7 \text{ kJ mol}^{-1} \end{aligned}$$

N.B.

- Heat change of products comes first
- ΔH<sub>f</sub> of elements = 0

# FUELS AND HEATS OF REACTION

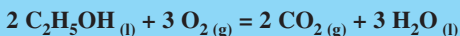
You need to be able to do simple calculations of heat of formation, using other heats of formation and one heat of reaction.

- N.B.** 1. Heat change of products comes first  
2.  $\Delta H_f$  of elements = 0

Given that the heat of combustion of ethanol is  $-1360 \text{ kJ mol}^{-1}$  and the heats of formation of liquid water and carbon dioxide are  $-285.8$  and  $-393.5 \text{ kJ mol}^{-1}$  respectively.

Calculate the heat of formation of ethanol.

The equation for the combustion of ethanol is



$$\Delta H_c = \Sigma \Delta H_f [\text{products}] - \Sigma \Delta H_f [\text{reactants}]$$

$$\begin{aligned} \Delta H_c (\text{C}_2\text{H}_5\text{OH}) &= [2 \times \Delta H_f (\text{CO}_2) + 3 \times \Delta H_f (\text{H}_2\text{O})] - [\Delta H_f (\text{C}_2\text{H}_5\text{OH}) + 3 \times \Delta H_f (\text{O}_2)] \\ -1360 &= [2 \times -393.5 + 3 \times -285.8] - [\Delta H_f (\text{C}_2\text{H}_5\text{OH}) + 3 \times 0] \\ -1360 &= [-787 + -857.4] - [\Delta H_f (\text{C}_2\text{H}_5\text{OH}) + 0] \\ -1360 &= -1644.4 - \Delta H_f (\text{C}_2\text{H}_5\text{OH}) \end{aligned}$$

$$\Delta H_f (\text{C}_2\text{H}_5\text{OH}) = -1644.4 + 1360 = -284.4 \text{ kJ mol}^{-1}$$

## 5.7 Oil Refining and its Products

Crude oil is a **mixture** of a variety of saturated hydrocarbons of different chain lengths.

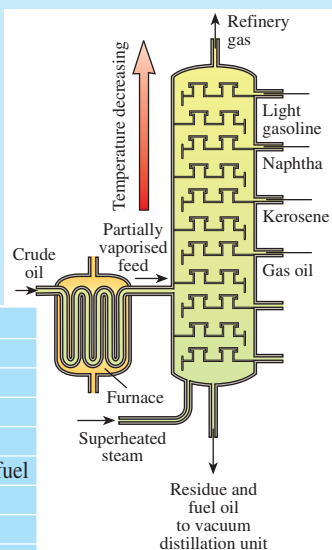
Boiling points of compounds tend to increase as molecular mass increases.

Their molecular mass increases as the number of carbons increases. Heated crude oil is added continuously near the base of a tall **fractionating column** and vaporised.

Vapour passes up the column and as it rises its temperature drops. At various levels the vapours pass through trays and the largest molecules in the vapour phase at that temperature condense and collect in the tray. They can then be tapped off. High boiling point compounds condense near base while low boiling point compounds condense near the top. Low boiling point gases exit at the top and have to be pressurised and cooled in order to be collected and distributed.

### Fractions, their Chain Lengths and Uses

Fraction	Carbons	Use
Refinery gas	1 – 4	Lighter fuel, bottled gas
Light gasoline	5 – 10	Petrol
Naphtha	7 – 10	Petrochemical industry
Kerosene	10 – 14	Jet and central heating fuel
Gas oil [Diesel]	14 – 19	Lorry fuel, heating system fuel
Lubricating oil	19 – 35	Gear oil
Fuel Oil	30 – 40	Power station fuel
Residue	>35	Making Tarmac for road surfacing



**Natural Gas** is mainly **methane** with some ethane. It is odourless and so **mercaptans** (sulphur compounds) are added to give it a smell in order that leaks can be detected easily.

**Liquid Petroleum Gas [LPG]** is a **mixture** of **ethane, propane and butane**.

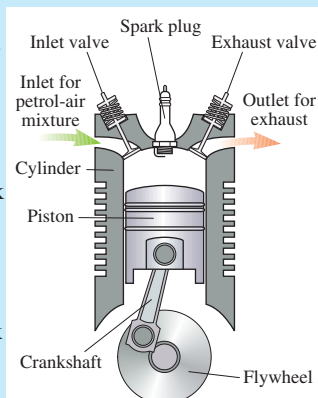
**Propane** is bottled gas. **Butane** is lighter fuel.

**Petrol:** a complex mixture of many compounds mainly branched chain hydrocarbons, some of which are aromatic (contain benzene rings).

# FUELS AND HEATS OF REACTION

## 4-Stroke Petrol Engine

- Induction** Petrol is vaporised and drawn with air into a cylinder as piston moves down.
- Compression** It is then compressed as the piston moves back up and this causes the temperature to rise.
- Ignition** Petrol/air mixture is ignited by a spark and the resulting explosion pushes the piston back down. This supplies the energy to propel the car.
- Exhaust** Finally the waste or exhaust gasses are pushed out as the piston rises back up the cylinder.



4-stroke petrol engine

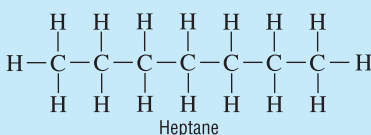
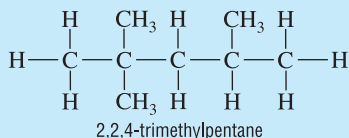
### Auto-ignition

If the petrol ignites before the spark it causes a large decrease in the efficiency of the engine. It is called **knocking**.

**Ignition Before the Spark is Produced**

### Octane Number

A measure of the tendency of a fuel to resist autoignition (or cause) knocking



### Octane Number Rating:

2,2,4 trimethylpentane = 100      Heptane = 0

High grade petrol has an octane number of 98 which means it behaves like a mixture containing 98% 2, 2, 4-trimethylpentane and 2% heptane.

### Factors Affecting Octane Number

Feature	Effect on Octane Number
Chain Length	shorter is higher
Degree of Branching	more branched is higher
Cyclic Structure	cyclic is higher than chain

### Lead in Petrol

**Tetraethyllead** used to be added to petrol to increase its octane number.

This was stopped in 2000 for environmental reasons – among other things it caused brain damage, especially in children.

### Improving Octane Number (Alternatives to Lead)

Method	What it does.
Isomerisation	causes branching
Dehydrocyclisation	converts chains into rings by removing 2 H
Catalytic Cracking	breaks long chains into shorter chains by heating in the absence of oxygen and the presence of a catalyst
Adding Oxygenates such as ethanol and MTBE	1. increases the octane number 2. reduces pollution by more complete combustion

Usually done in refineries because

- The raw materials are there in abundance
- the apparatus for separating them is also there.

# FUELS AND HEATS OF REACTION

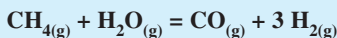
## 5.8 Other Chemical Fuels

### Hydrogen Manufacture

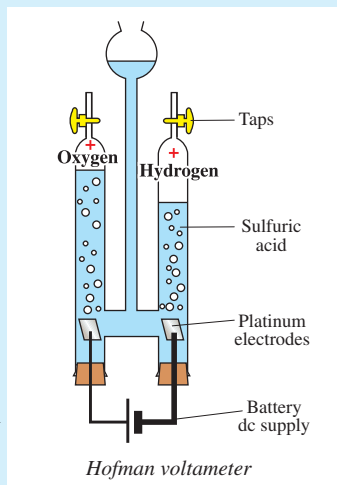
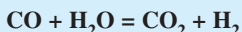
#### (i) Electrolysis of Water using the Hoffman Voltameter

- (Inert) **platinum** electrodes
- **dilute sulphuric acid** acts as a catalyst
- **Hydrogen** at cathode and **Oxygen** at anode
- **Ratio Hydrogen : Oxygen** is **2 : 1**
- **Oxygen** relights a glowing splint
- **Hydrogen** burns with a squeaky pop.

#### (ii) Steam Reforming of Natural Gas.

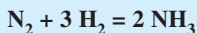


CO is poisonous so it oxidised by reaction with steam to give  $\text{CO}_2$  and more  $\text{H}_2$ .



### Industrial Uses of Hydrogen

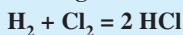
#### (i) Manufacture of Ammonia by Haber Process



#### (ii) Hydrogenation of Vegetable Oils

turns vegetable oils into saturated fats i.e. margarine

#### (iii) Making HCl



#### (iv) As a Fuel

**For**

- burns better than petrol
- non-polluting

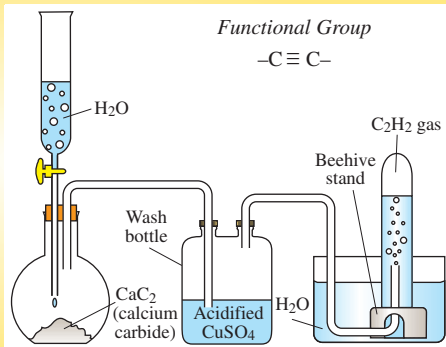
**Against**

- is expensive and difficult to store

## EXPERIMENT: Preparation of Ethyne

General Formula  $\text{C}_n\text{H}_{2n-2}$

- $\text{CaC}_2 + 2 \text{H}_2\text{O} = \text{Ca}(\text{OH})_2 + \text{C}_2\text{H}_2$
- $\text{CaC}_2$  is a **grey lumpy solid**
- Becomes a white powder with more volume
- Very **exothermic** reaction
- Acidified copper sulphate **removes impurities** e.g. **phosphine  $\text{PH}_3$** , produced by reaction of  $\text{H}_2\text{O}$  with  $\text{Ca}_3\text{P}_2$  and  $\text{H}_2\text{S}$  from  $\text{CaS}$
- **Ethyne** has a **sickly sweet smell**
- **Non-polar** so **insoluble in water**



### Combustion

- Yellow very smoky or sooty flame
- $\text{C}_2\text{H}_2 + 2 \frac{1}{2} \text{O}_2 = 2 \text{CO}_2 + \text{H}_2\text{O}$
- Very hot flame with excess oxygen so good fuel potential

### Unsaturated – shown by

1. Decolourises bromine water from red/orange to colourless when shaken with it
2. Decolourises acidified permanganate from pink/purple to colourless when shaken with it

### Uses • Oxyacetylene burner for cutting and welding steel

- Making monomers for addition polymerisation

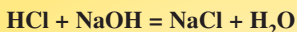


Oxy-acetylene torch

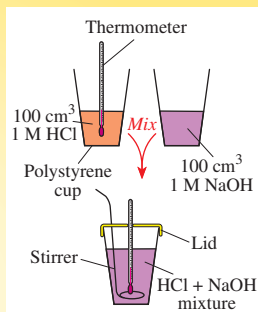
# FUELS AND HEATS OF REACTION

S

## EXPERIMENT: Heat of Reaction of Hydrochloric Acid with Sodium Hydroxide



- 100 cm<sup>3</sup> each of 1.0 M HCl and 1.0 M NaOH - gives 0.1 mole of each and forms 0.1 mole of water
- Take temperature of both and average = starting temp  
Let us assume that the average is 20.5°C for this experiment
- Mix the two solutions in a polystyrene cup [it has **negligible heat capacity** and also acts an insulator so no heat escapes]
- Stir mixture gently and record highest temperature
- Let us assume 27.3°C for this experiment



### Calculate heat change

$$H = mc\theta$$

m = Mass = **0.2 kg** [200 cm<sup>3</sup> dilute solutions which can be regarded as water]

C = **4.2 kJ kg<sup>-1</sup>** i.e. the specific heat capacity of water

θ = temp change = (final – initial temp) 27.3 – 20.5 = **6.8°C**

$$H = 0.2 \times 4.2 \times 6.8 = \mathbf{5.712 \text{ kJ}}$$

Heat change for 0.1 mole of water formed therefore multiply by 10 to get heat change for 1 mole.

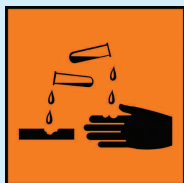
$$5.712 \times 10 = \mathbf{57.12 \text{ kJ mol}^{-1}}$$

If you are given a total heat capacity for the apparatus this = mc.

t

## 5-9 Hazard Symbols

You should be able to recognise and describe these symbols



Corrosive



Explosive



Flammable



Toxic



Oxidising



Harmful



Irritant



Environmental

Questions on this Section from Past Exams Year by Year

2009	2008	2007	2006	2005	2004	2003	2002
2	3	4 b, i	6	4 g	2	2	8
6	4 f	6		6	6	6	
	6					10 a	

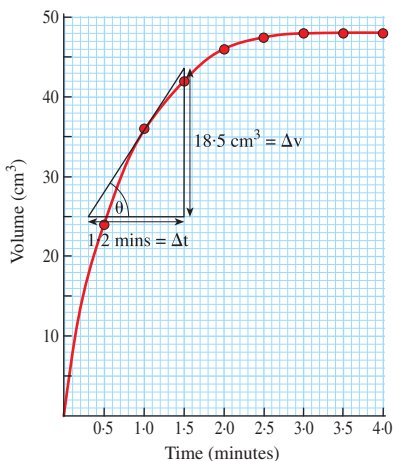
# REACTION RATES

## a 6.1 Rate of Reaction

Change in concentration of a reactant [or product] per unit time

### Plotting the Graph

- Time is on the horizontal [X] axis
- Amount of product is on the vertical [Y] axis
- **Label both axes and include the units of measurement**
- Mark your points carefully with a dot or cross and make sure it is on the exact spot
- Draw a line of best fit for the curve or straight line as the case may be.
- **Do not extrapolate the graph** unless it is justified



### Interpretation of Reaction Rate Graphs

- Reaction is finished when line becomes horizontal
- **Rate is proportional to the slope of the line** – the steeper the slope the faster the rate of the reaction
- Rate is normally fastest at start and then slows down because the concentration of the reactants drops as they are used up.

### Average Rate

The amount of product / period of time

- In the above example  $48 \text{ cm}^3$  is produced in 3 minutes
- rate is  $\frac{\text{volume}}{\text{time}} = \frac{48}{3} = 16 \text{ cm}^3 \text{ per minute}$

### Instantaneous Rate

- **is the rate at any moment** [instant in time]

### Calculation of Instantaneous Rate from Graphs

- To calculate this you need to draw a graph of the amount of product against time.
- You then pick the point on the slope directly above the time you want to find the rate at.
- You draw a tangent to the curve at this point
- Take a ruler and place it so that it crosses the curve at two points on either side of the selected point
- Adjust it so that there is the same length of curve between the ruler and the selected point on either side of the point
- Move it closer to the point but keep the length of curve on either side the same
- When you reach the point draw a line using a ruler – this is the tangent
- Find the slope by drawing a vertical and a horizontal to the tangent [as in diagram]
- **Slope =  $\tan \theta$  or Slope =  $\frac{\Delta v}{\Delta t} = \frac{18.5}{1.2} = 15.4 \text{ cm}^3 \text{ min}^{-1}$**

## 6.2 Factors Affecting Rates of Reaction

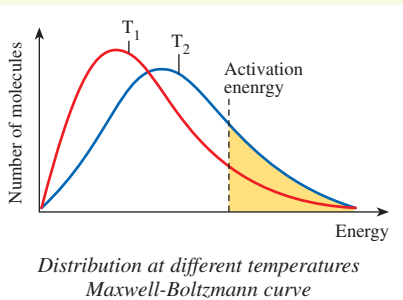
### Activation Energy

Minimum energy colliding particles must have in order to react

### Temperature

The higher the temperature the larger the proportion of particles that have **activation energy**, i.e. sufficient energy to react when they collide. As a guide a **10°C rise doubles the rate of a reaction.**

In the diagram (right) the higher the temperature ( $T_2$ ) the greater the proportion of the particles that have activation energy.



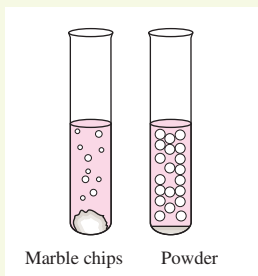
### Concentration

**Doubling the concentration of one reactant doubles the rate of the reaction.**

This gives a straight line graph going through the origin.

### Particle Size

Two test tubes containing dilute HCl  
Add powdered  $\text{CaCO}_3$  to one and marble chips to another.  
Note the different levels of effervescence [bubbling]  
**The smaller the particles – the faster the rate of reaction**  
due to the larger surface area.



### Nature of Reactants

**Ionic compounds react very quickly / Covalent compounds react slowly.**

### Catalyst

**A substance that alters the rate of a chemical reaction but is not used up at the end of the reaction**

## 6.3 Theories of Catalysis

Catalysts work by providing an **alternative reaction pathway with lower activation energy.**

### (i) Surface Adsorption

Reactants are **adsorbed onto the surface of the catalyst** and the product released when formed thus freeing active site again. E.g. nitrogen molecules onto iron catalyst in the Haber Process.

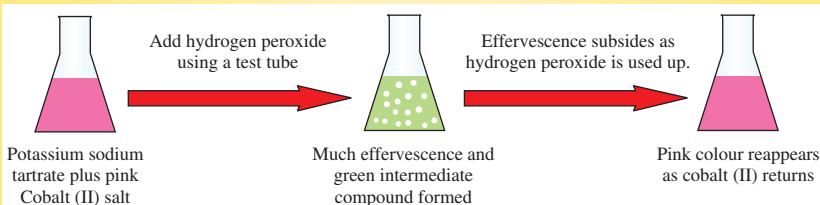
Occurs in heterogeneous catalysis.

### (ii) Intermediate Compound Formation

Catalyst forms unstable intermediate with reactants and decomposes readily releasing the products. Usually in homogeneous catalysis e.g. cobalt (II) chloride catalysing the reaction between  $\text{H}_2\text{O}_2$  and potassium sodium tartrate.

# REACTION RATES

## EXPERIMENT: The Oxidation of Potassium Sodium Tartrate by $\text{H}_2\text{O}_2$ , Catalysed by Cobalt (II) salts



This cycle of colour change repeats each time some fresh hydrogen peroxide is added because the catalyst has returned to its original state as the reaction was completed.

### Homogeneous Catalysts

Catalyst and reactants are in the same phase

e.g. Cobalt (II) chloride catalysing the reaction of potassium sodium tartrate and hydrogen peroxide.

### Heterogeneous Catalysts

Catalyst and reactants in different phases

e.g. Fe catalyses the reaction between  $\text{N}_2$  and  $\text{H}_2$  in the Haber Process for the production of Ammonia.

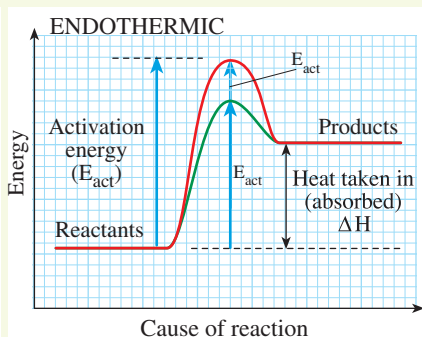
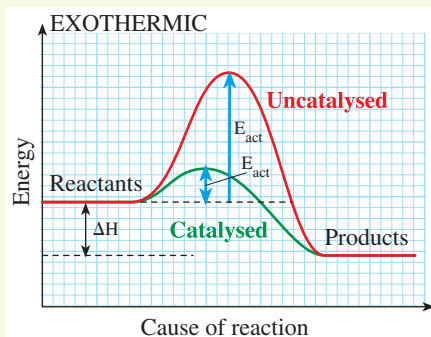
### Autocatalyst

One of the products of the reaction catalyses the reaction

$\text{Mn}^{2+}$  in permanganate titrations – the first few drops of  $\text{MnO}_4^-$  are slow to decolourise but once some  $\text{Mn}^{2+}$  has formed this catalyses the reaction and it decolourises quickly.

### Reaction Profile Diagrams

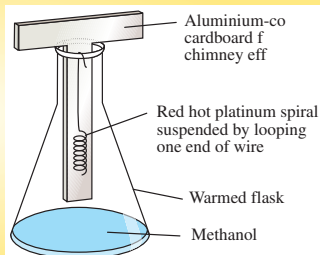
## d 6.4 Examples of Catalysis



## e EXPERIMENT: The Oxidation of Methanol using a Hot Platinum Catalyst

Place warm methanol in a conical flask and add some hot coiled platinum wire – the wire glows red hot and causes an explosion every few minutes by speeding up the oxidation of the methanol with oxygen in the air.

[If Pt .not available use thick copper electrical wire]





## Dust Explosions

A small explosion stirs up dust which has such a large surface area that it reacts quickly enough to cause a much bigger explosion.

*Lid being blown off a can containing a candle when lycopodium powder is puffed up in it.*



## f Enzymes are Biological Catalysts

Enzymes are **proteins** produced by living cells.

Yeast produces the enzyme **zymase** which turns glucose into ethanol and  $\text{CO}_2$ . This process is called **fermentation**

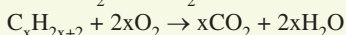
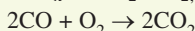
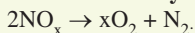


**Catalase** is an enzyme found in both liver and celery and it decomposes  $\text{H}_2\text{O}_2$  releasing oxygen

## Catalytic Converters on Car Exhausts:

(i) **Nature of Catalysts** Pt, Pd and Rh on a ceramic or metal honeycomb

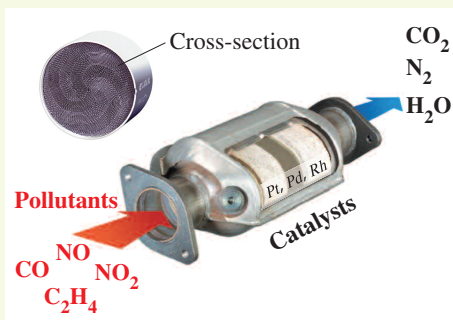
(ii) **Reactions Catalysed**



(iii) **Environmental Benefits**

Reduces Pollution

- less gasses that cause acid rain e.g. mainly  $\text{NO}_x$
- fewer unburned hydrocarbons
- less CO

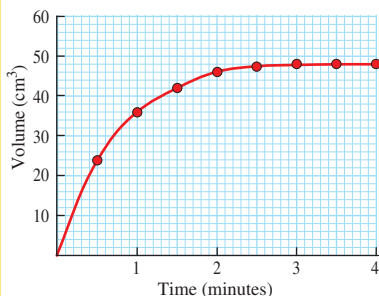


## Catalyst Poisons

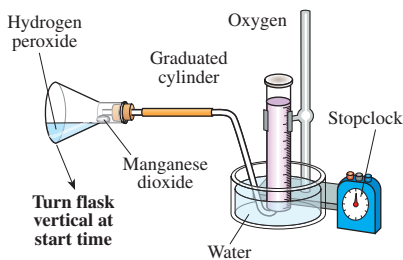
Lead: (Pb) in petrol is a catalytic poison and rapidly stops the catalyst working.

## g EXPERIMENT: Monitoring the Rate of $\text{O}_2$ Production from $\text{H}_2\text{O}_2$ , using $\text{MnO}_2$ as a Catalyst

- Start reaction by turning flask vertical
- Record volume every 30 seconds
- Table the results
- Draw graph of volume against time
- Average rate = volume / time



Volume of  $\text{O}_2$  produced against time



# REACTION RATES

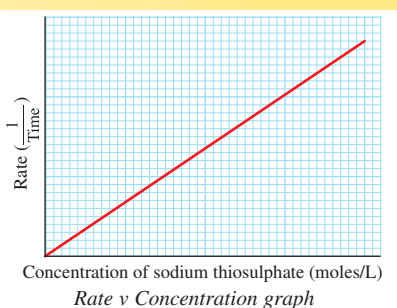
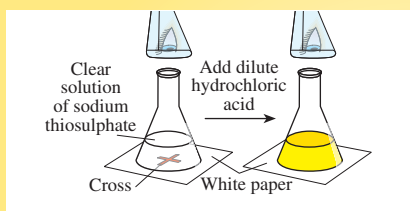
## EXPERIMENT: (continued)

### Instantaneous Rate

- mark point
  - draw tangent
  - draw both a vertical and a horizontal to the tangent
  - rate = rise/run [volume / time] of the tangent line
- See plotting the Graph p. 61.

h

## EXPERIMENT: Factors Affecting the Reaction Rate of Sodium Thiosulfate Solution with Hydrochloric Acid.

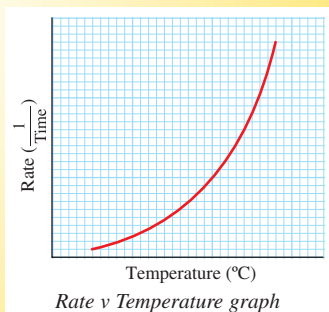


### (a) Concentration

- Pour 50 cm<sup>3</sup> sodium thiosulfate solution of known concentration into conical flask on top of a cross
- Add 10 cm<sup>3</sup> dilute HCl
- Note time taken for cross to disappear
- Rinse out and repeat at different concentrations
- Draw a graph of rate [1/time] against concentration

### (b) Temperature

- Pour 50 cm<sup>3</sup> sodium thiosulfate solution into conical flask
- Use a water bath to bring it [and HCl] to a set temperature 20, 30, 40, 50 or 60°C
- Dry flask and place it on top of the cross
- Add 10 cm<sup>3</sup> dilute HCl at the same temperature
- Note time taken for cross to disappear
- Rinse out and repeat at different temperatures
- Draw a graph of rate [1/time] against temperature

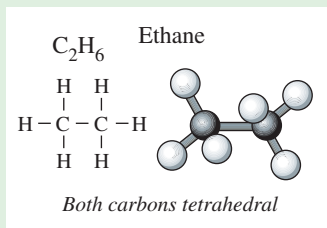


## Questions on this section from Past Exams Year by Year

2009	2008	2007	2006	2005	2004	2003	2002
9	3	4 d	7	3	8	4 j	3
	4 h	9				7	

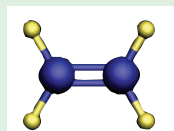
## a 7.1 Tetrahedral Carbon

- Has only single bonds
- **Tetrahedral in shape** i.e. three dimensional
- Molecules can rotate around single bonds / this allows different shapes
- Alkanes, chloroalkanes and alcohols are examples of tetrahedral compounds.
- They are used as fuels and solvents



## b 7.2 Planar Carbon

- Has double or triple bond
- **Two dimensional**
- Single bonds allow free rotation.
- Alkenes, alkynes etc. Are typical examples



Both carbons planar

Molecules can have planar parts and tetrahedral parts

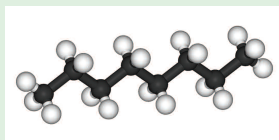
## Hydrocarbon

Contains C and H only

### Saturated

Only have single carbon to carbon covalent bonds

e.g. alkanes, chloroalkanes, alcohols



Octane - a typical hydrocarbon

### Unsaturated

Contains at least one double or triple carbon to carbon bond

e.g. alkenes, alkynes

### Test for Unsaturation

Turns Bromine water from red to colourless or decolourises acidified  $KMnO_4$  from purple to colourless

## c Solubility of Organic Compounds

### (a) Caused by the Polar OH group

This can lead to hydrogen bonding

**Soluble in polar** solvents [water] – **insoluble in non-polar** solvents [cyclohexane and benzene]

Boiling point and melting point higher than expected for Molecular Mass due to increased intermolecular attraction caused by the polar group

### (b) Caused by the Polar C = O group

Does not lead to hydrogen bonding

**Soluble in polar** solvents [water] – **insoluble in non-polar** solvents [cyclohexane and benzene]

Boiling point and melting point higher than expected for Molecular Mass due to increased intermolecular attraction caused by the polar group

# ORGANIC CHEMISTRY

**d** You need to know the names and structures of each homologous series up to the  $C_4$  member ( $C_5$  for alkanes).

## Production and Uses of each Homologous Series

Name	Production	Uses
Alkanes	Crude petroleum / natural gas / decomposing organic matter	Fuel
Alkenes	$C_2H_5OH = C_2H_4 + H_2O$ [ $Al_2O_3$ (Catalyst), heat]	Making plastics
Alkynes	$CaC_2 + 2H_2O = C_2H_2 + Ca(OH)_2$	Fuel
Alcohols	$C_6H_{12}O_6 = 2C_2H_5OH + 2CO_2$ [zymase yeast]	Beverage, solvent, fuel
Aldehydes	$3C_2H_5OH + Cr_2O_7^{2-} + 8H^+ = 3CH_3CHO + 2Cr^{3+} + 7H_2O$ Primary Alcohol in excess / remove immediately	Making plastics, fuels
Ketones	$3CH_3CH(OH)CH_3 \rightarrow 2Cr_2O_7^{2-} + 22H^+ = 3CH_3COCH_3 + 4Cr^{3+} + 14H_2O$ Propan-2-ol [secondary alcohol]	Solvents
Carboxylic Acids	$3C_2H_5OH + 2Cr_2O_7^{2-} + 16H^+ = 3CH_3COOH + 4Cr^{3+} + 11H_2O$ Dichromate in excess / reflux / then distil	Condiment, solvent, cellulose acetate, food preservatives
Esters	$C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O$	Solvents, flavours

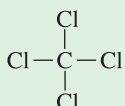
**e** **Alkanes** (see earlier in Fuels page 45)

- These are **saturated hydrocarbons** (only single covalent bonds – made of C and H only)
- They are **aliphatic** i.e. consist of chains
- They are **non-polar** and so are **insoluble in water**
- Sources include crude petroleum, natural gas and decomposing animal and plant matter
- They are separated by **fractional distillation** – This is possible because they have different boiling points due to different relative molecular masses.
- They are our **main source of fuels**

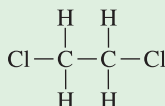
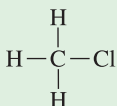
## Chloroalkanes

Used as solvents and also flame retardants when fully halogenated e.g.  $CCl_4$  and CFCs.

Chloromethane

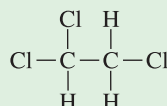
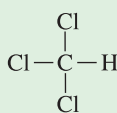


tetrachloromethane



1,2-dichloroethane

Trichloromethane  
chloroform



1,1,2-trichloroethane

**f** **Alkenes**

General Formula  $C_nH_{2n}$

Name	Formula	Structure
Ethene	$C_2H_4$	$\begin{array}{c} \text{H} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$
Propene	$C_3H_6$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
Butene	$C_4H_8$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}=\text{C}-\text{C}-\text{C}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$

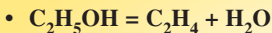


Alkene Functional  
Group

They contain a non-polar double bond so are insoluble in water

## EXPERIMENT: Production and Properties of Ethene

- Dehydration of ethanol - **Elimination reaction**



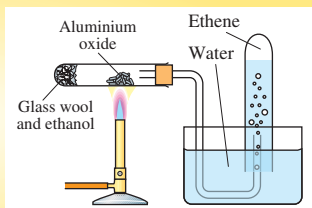
- Aluminium oxide [white powder] is a dehydrating agent**

- Glass wool holds ethanol in place**

- Heat evaporates ethanol

- Safety precautions**

- Remove tube before you stop heating to prevent suck back and possible explosion
- Wear safety glasses and heat proof gloves



### Combustion



Combustion can be explosive

[you need to be able to write balanced equations for combustion of alkenes up to butene]

### Unsaturated

- Shake with bromine water - Decolourises it from red-brown to colourless
- Shake with acidified  $\text{KMnO}_4$  - Decolourises it from purple to colourless

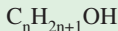
### Solubility

Insoluble in water as water is polar and ethene is not.

Soluble in cyclohexane as both are non-polar.

## Alcohols

General formula



You need to know structure and names up to C4

Name	Formula	Structure
Methanol	$\text{CH}_3\text{OH}$	$\begin{array}{c} \text{H} \\   \\ \text{H}-\text{C}-\text{O}-\text{H} \\   \\ \text{H} \end{array}$
Ethanol	$\text{C}_2\text{H}_5\text{OH}$	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}-\text{O}-\text{H} \\   \quad   \\ \text{H} \quad \text{H} \end{array}$
Propanol	$\text{C}_3\text{H}_7\text{OH}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$
Butanol	$\text{C}_4\text{H}_9\text{OH}$	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C}-\text{O}-\text{H} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$

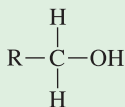
### Primary Alcohol

The C to which OH is attached has 1 other C attached directly to it [form aldehydes]

### Secondary Alcohol

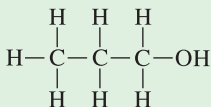
The C to which OH is attached has 2 other C attached directly to it [form ketones]

Primary alcohol



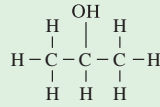
Methanol

Primary alcohol



Propan-1-ol

Secondary alcohol



Propan-2-ol

# ORGANIC CHEMISTRY

## Production

### (a) Naturally by Fermentation

$C_6H_{12}O_6 = 2 C_2H_5OH + 2 CO_2$  zymase from yeast is catalyst

### (b) Chemically

Hydration of ethene  $C_2H_4 + H_2O = C_2H_5OH$

## Combustion

$C_2H_5OH + 3 O_2 = 2 CO_2 + 3 H_2O + \text{energy}$

Flame slightly luminous

[most organic compounds burn to give  $CO_2$  and  $H_2O$ ]

## Solubility

**Short chain alcohols are soluble in water** due to polar OH group but are insoluble in non-polar solvents such as cyclohexane and benzene

**Long chain alcohols are insoluble in water but soluble in cyclohexane**

Boiling and melting points are higher than expected for their Relative Molecular Mass due to polar nature of the OH group.

## Reaction with Na

$Na + C_2H_5OH = C_2H_5ONa + \frac{1}{2} H_2$

*sodium ethoxide*

This reaction is used for safe disposal of Na leftovers

## Uses

**Solvent** for perfumes etc

**Beverage** Beer 4%, Wine 13%, (Made by **Brewing**) Spirits 40% concentrated by **distillation**

**Methanol to denature ethanol i.e. make it unfit to drink – methylated spirits**

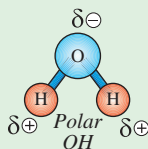
**Fuel** Spirit or Tilley lamp and Gasohol [80% petrol:20%alcohol]



Fermentation



Spirit burner



## Aldehydes

### Structure and Name

Name	Formula	Structure
Methanal	HCHO	$\begin{array}{c} \text{O} \\ \parallel \\ \text{H}-\text{C} \\   \\ \text{H} \end{array}$
Ethanal	CH <sub>3</sub> CHO	$\begin{array}{c} \text{H} \quad \text{H} \\   \quad   \\ \text{H}-\text{C}-\text{C}=\text{O} \\   \\ \text{H} \end{array}$
Propanal	C <sub>2</sub> H <sub>5</sub> CHO	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{O} \\   \quad   \quad \parallel \\ \text{H}-\text{C}-\text{C}-\text{C} \\   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \end{array}$
Butanal	C <sub>3</sub> H <sub>7</sub> CHO	$\begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \\   \quad   \quad   \quad \parallel \\ \text{H}-\text{C}-\text{C}-\text{C}-\text{C} \\   \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \end{array}$

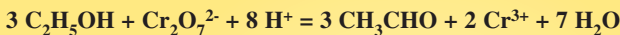
Functional Group -CHO

[C=O is polar]

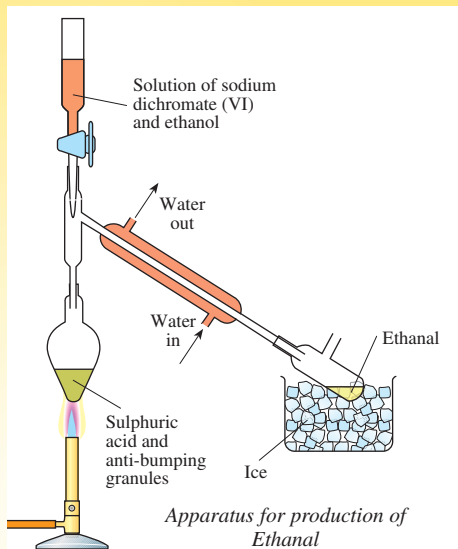


- Methanal gas at room conditions
- Short chains liquids and longer chains solids

## EXPERIMENT: Production and Properties of Ethanal

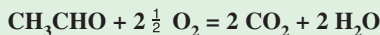


- Made from a **Primary Alcohol**
- Make sure **alcohol is in excess** [or that  $\text{Cr}_2\text{O}_7^{2-}$  is the limiting reactant]
- Put dil.  $\text{H}_2\text{SO}_4$  into the pear shaped flask.
- When diluting, add acid to water, mix constantly and cool as the acid reacts very exothermically with water.
- Add **anti-bumping granules**. [Stops **bumping** (large bubbles) which may damage apparatus by forming lots of small bubbles]
- Put a mixture of dichromate and **excess** ethanol into a dropping funnel.
- Heat acid to boiling and stop heating then add mixture from funnel

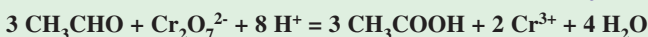


- Add alcohol/dichromate mixture at a rate such that
  - (i) the acid keeps boiling [**exothermic reaction**] and
  - (ii) the rate of addition of the mixture equals the rate of production of ethanal.
- Solution of ethanol/dichromate is amber due to dichromate  $\text{Cr}_2\text{O}_7^{2-}$  ( $\text{Cr} + 6$ )
- As reaction proceeds it goes **green** as  $\text{Cr}^{3+}$  is formed as dichromate is **reduced**
- **Remove ethanal as it is formed** so it can't react further into carboxylic acid.
- Condense and collect ethanal in **ice bath** - it is **volatile** [BP  $20.8^\circ\text{C}$ ] - **ice bath stops it evaporating**.
- **Always show water in at base and out at top** of condenser in your diagram
- Distillate contains small amounts of **impurities** - **water and ethanol** boiled over with the ethanal.
- Remove  $\text{H}_2\text{O}$  [shake with **anhydrous sodium sulphate**  $[\text{Na}_2\text{SO}_4]$  for 10 min. - filter off hydrated crystals]
- **Re-distil** and collect **fraction** boiling at 20 and  $23^\circ\text{C}$ . This leaves the alcohol behind.
- Ethanal reduces **Fehling's Solution** from **blue to red precipitate** when heated.
- Produces silver mirror on clean test tube when heated with Tollen's Reagent - **ammoniacal silver nitrate**
- Short chain aldehydes soluble in water due to polar carbonyl group  $[\text{C}=\text{O}]$  insoluble in Cyclohexane. Longer chains soluble in cyclohexane but not in water.

## Combustion

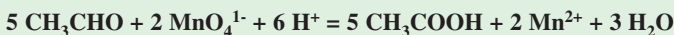


## Reaction with Acidified Dichromate – Oxidised to Carboxylic Acid



$\text{Cr}_2\text{O}_7^{2-}$  goes from orange to green as it is reduced to  $\text{Cr}^{3+}$

## Reaction with Acidified Permanganate – Oxidised to Carboxylic Acid



$\text{MnO}_4^{1-}$  goes from purple to colourless as it is reduced to  $\text{Mn}^{2+}$

# ORGANIC CHEMISTRY

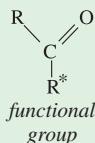
## Uses

- Solvents
- **Made in body as alcohol is metabolised** – [smell on breath morning after heavy nights drinking]
- **Benzaldehyde found in almond kernels**
- Solution of methanal in water is called formalin - preserves biological specimens – Embalming
- Aldehydes are reduced to primary alcohols by heating with  $H_2$  and Ni catalyst

## k Ketones

Functional group  $R - CO - R'$

Name	Formula	Structure
Propanone	$CH_3COCH_3$	<pre>      H   H             H - C - C - H                        H   O   H</pre>
Butanone	$CH_3COC_2H_5$	<pre>      H   O   H   H                     H - C - C - C - C - H                           H   H   H   H</pre>



- Made from **secondary alcohols** using dichromate and acid and heat
- Reflux for 30 minutes
- **They do NOT oxidise further to carboxylic acids**
- Distil off the ketone
- Ketones are reduced to secondary alcohols by heating with  $H_2$  and Ni catalyst

## Impurities

**Water** – remove using anhydrous sodium sulphate – shake for 10 min – filter off crystals

**Alcohol** – remove by fractional distillation

**State** – first 2 [propanone and butanone] are liquids

## Solubility

Short chain ketones are soluble in water due to polar carbonyl group  $[C=O]$

Longer chains insoluble in water, soluble in cyclohexane.

## Uses

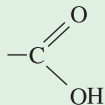
**Solvents** – propanone as nail varnish remover



Nail varnish remover

## I Carboxylic Acids

Functional Group -  $COOH$

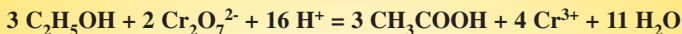


Name	Formula	Structure
Methanoic Acid	$HCOOH$	<pre>      O          H - C               O - H</pre>
Ethanoic Acid	$CH_3COOH$	<pre>      H   O              H - C - C                   H   O - H</pre>
Propanoic Acid	$C_2H_5COOH$	<pre>      H   H   O                  H - C - C - C                       H   H   O - H</pre>
Butanoic Acid	$C_3H_7COOH$	<pre>      H   H   H   O                      H - C - C - C - C                           H   H   H   O - H</pre>

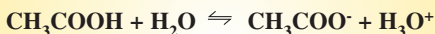


## EXPERIMENT: Production and Properties of Ethanoic Acid

- Heat Ethanol with **acidified dichromate** in **reflux** apparatus for **30 minutes**.
- Make sure that the **oxidising agent** ( $\text{Cr}_2\text{O}_7^{2-}$ ) is in **excess**.

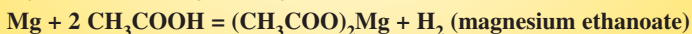


- Reflux stops volatile components escaping and ensures complete oxidation.**
- Alcohol is converted first to aldehyde and then onto a carboxylic acid.
- Orange dichromate** ( $\text{Cr}_2\text{O}_7^{2-}$ ) **reduced to green chromium (III)** ( $\text{Cr}^{3+}$ ).
- Weak acid pH 3-4** [only partly dissociates in aqueous solution]



- Turns **Universal Indicator orange/yellow** and **litmus blue to red**
- Conc. sulphuric acid acts as a **catalyst**.
- Ethanoic acid removed by fitting condenser sideways and collecting distillate.
- Replace water bath with sand bath. [Boiling Pt. of acid  $119^\circ\text{C}$ ]

### Reactions of ethanoic acid



- Ethyl ethanoate has the **fruity** smell of an ester

### Impurities -

**water** removed by shaking with anhydrous sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) and filtering off crystals.

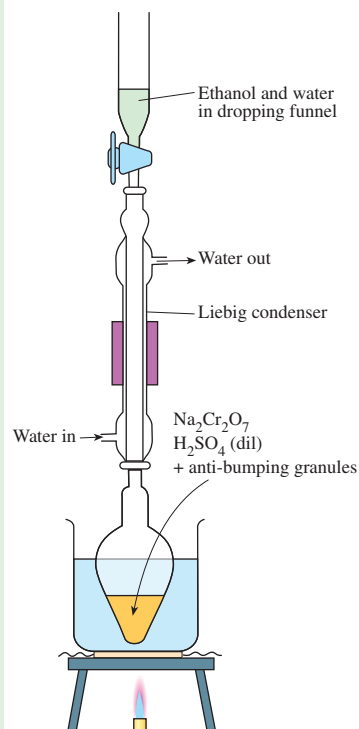
**ethanol** discard fraction boiling at  $80^\circ\text{C}$ .

### Solubility

- Quite soluble in Cyclohexane
- Lower members soluble in water due to Hydrogen bond formation**

### Uses of carboxylic acids

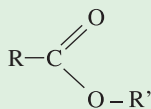
- Condiment** - vinegar
- Methanoic acid** - nettle and ant stings
- Preservatives** Ethanoic acid (vinegar) in pickles  
Propanoic and benzoic acids and their salts also used as preservatives
- Making esters** - e.g. cellulose acetate film



Making ethanoic acid under reflux

# ORGANIC CHEMISTRY

## Esters



Functional Group

Name	Formula	Structure
Methylmethanoate	$\text{HCOOCH}_3$	
Methylethanoate	$\text{CH}_3\text{COOCH}_3$	
Methylpropanoate	$\text{CH}_3\text{CH}_2\text{COOCH}_3$	
Ethylmethanoate	$\text{HCOOC}_2\text{H}_5$	
Ethylethanoate	$\text{CH}_3\text{COOC}_2\text{H}_5$	

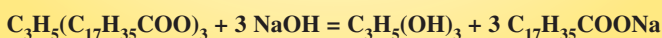
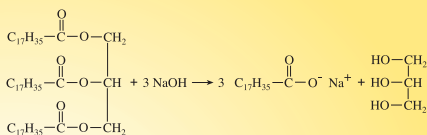
- $\text{HCOOH} + \text{C}_2\text{H}_5\text{OH} = \text{HCOOC}_2\text{H}_5 + \text{H}_2\text{O}$   
Methanoic Acid + Ethanol = Ethyl Methanoate + Water
- **Reflux for 30 min**
- To give reaction time and **prevent volatile components escaping**
- **Conc.  $\text{H}_2\text{SO}_4$**  as **dehydrating agent** to speed up reaction
- Fats are natural tri-esters
- Ethyl ethanoate used as a solvent
- Fruity smells and flavours are caused by esters - pentylethanoate smells of pears/bananas
- Reaction can be called **substitution** or **condensation**

## Solubility

- **Soluble in cyclohexane**
- **Lower members soluble in water due to Hydrogen bonds with water**

## EXPERIMENT: Preparation of Soap

- Reaction is called **Saponification [alkaline hydrolysis]**
- Into pear shaped flask pour **sunflower oil** [or any fat or oil]
- Add 3 g of **NaOH** pellets [**caution – very caustic** (burns skin)]
- Add 30 cm<sup>3</sup> **ethanol** to dissolve fat
- Add **anti-bumping granules**
- Boil under **reflux for 30 min.** as reaction is slow
- Reflux **prevents loss of volatile components** (vapour) during boiling
- Swirl flask to remove substances stuck to side of flask [*Na salts of fatty acids and un-hydrolysed fat*]
- Cool and rearrange apparatus for distillation
- Distil off most of the ethanol [about 20ml] to make it easier to isolate the soap
- Pour contents of flask into **concentrated NaCl solution (Brine)**
- Soap does not dissolve in salt solution so it **precipitates** out [called **salting out**]
- Filter off the soap residue and wash with salt solution
- Excess NaOH stays in solution as does glycerol and alcohol. These pass through the filter in the filtrate

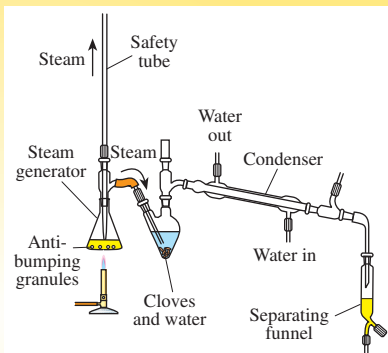


- Soap **lathers with deionised [soft] water** / forms **scum [calcium stearate]** with **hard water**. This is a test for hard/soft water

## P Organic Natural Products

### EXPERIMENT: Extraction of Clove Oil

- **Have a safety opening to the atmosphere** – prevents explosion
- **Steam distillation** used because some components of clove oil have high boiling points and this temp would damage molecules in the oil
- Some organic compounds are immiscible with water. Usually these compounds have a low vapour pressure. After mixing them with steam, however, the mixture will distil when the sum of the two vapour pressures reaches atmospheric pressure. It follows that this must happen below the boiling point of water.



This process is known as **steam distillation**.

- Cover cloves with a little warm water (about 5 cm<sup>3</sup>)
- Use **anti-bumping granules** in the steam generator.
- If the level of the boiling water in the steam generator falls too low, the system will not work smoothly. Refill with hot water.
- Reconnect everything and heat again.
- After **30 mins disconnect** steam generator to avoid **suck-back** then turn off the heat.
- Collect 40 - 50 cm<sup>3</sup> of the **pale milky distillate** [emulsion]. Note the smell
- Oil separated by **solvent action** i.e. it is first added to an organic solvent (cyclohexane) and placed in a **separating funnel**.
- Collect organic solvent fraction and then **evaporate solvent**.
- **Solvents** can also be used to extract natural products
- **Used for flavouring** (e.g. clove rock), **painkiller** (clove oil on sore teeth)



Clove Rock

## Q Reaction Types

You are required to be able to write balanced equations for the reactions, using **structural formulas** [Unless otherwise indicated.]

### 1 Addition [Ionic Addition – Heterolytic Fission] of ethene with

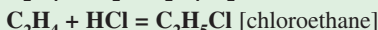
Chlorine, [Mechanism required]



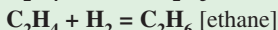
Bromine [Mechanism required]



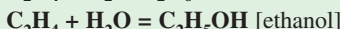
Hydrogen chloride, [Mechanism reqd.]



Hydrogen,



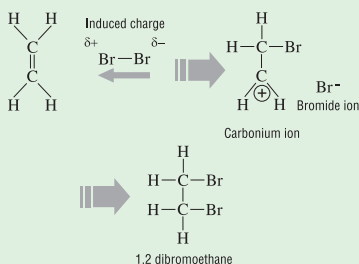
Water



Polymerisation



**Mechanism of Reaction with Bromine** [or other Halogen] - decolourises quickly – this is a test for unsaturation



You need to be able to draw these diagrams using

- $\text{H}-\text{Cl}$   
HCl approaches double bond and H attaches first followed by Cl.
- $\text{Cl}-\text{Cl}$
- $\text{H}-\text{OH}$  ( $\text{H}_2\text{O}$ )

# ORGANIC CHEMISTRY

## Proof of Mechanism

If this is done in the presence of aqueous chloride ions then some **1-bromo, 2-chloroethane and 2 bromoethanol and 1,2 dibromoethane** will be formed.  
Shows presence of positive **carbonium ion** intermediate

## Polymerisation

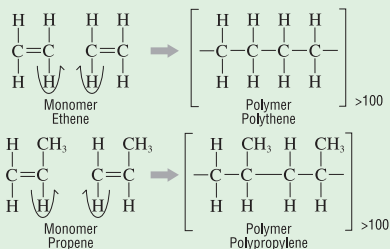
Ethene + ethene = polyethene

Propene + propene = polypropylene

**Alkenes are raw materials for plastics** e.g. chloroethene

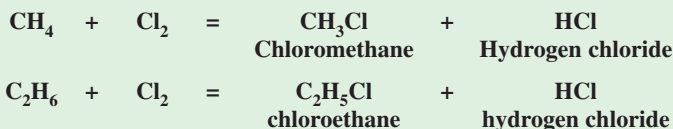
**Hydrogenation of vegetable oils**

When oils are hydrogenated using catalysts they turn to fats i.e. they turn from liquids to solid



## 2 Substitution Reaction [Homolytic Fission]

**Reaction of Alkanes with halogens [monochlorination of methane and ethane with chlorine]**



**Mechanism of Free Radical Substitution – Homolytic Fission**

### Initiation

$\text{Cl}_2 = \text{Cl}^\bullet + \text{Cl}^\bullet$  [in presence of Ultra Violet light]

### Propagation

$\text{Cl}^\bullet + \text{CH}_4 = \text{CH}_3^\bullet + \text{HCl}$  then

$\text{CH}_3^\bullet + \text{Cl}_2 = \text{CH}_3\text{Cl} + \text{Cl}^\bullet$  [ $\text{Cl}^\bullet$  free to react with another  $\text{CH}_4$  etc etc.]

### Termination

$\text{Cl}^\bullet + \text{Cl}^\bullet = \text{Cl}_2$

$\text{CH}_3^\bullet + \text{Cl}^\bullet = \text{CH}_3\text{Cl}$

$\text{CH}_3^\bullet + \text{CH}_3^\bullet = \text{C}_2\text{H}_6$

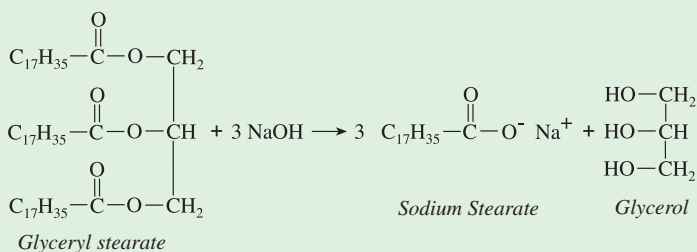
Learn same using ethane

### Proof of the mechanism

- Formation of ethane [or butane with ethane]
- UV speeds up reaction
- tetra ethyl lead and other sources of free radicals also speed up reaction.

**Learn both these mechanisms as one is almost certain to come up**

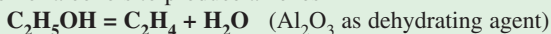
## Esterification



## 3 Elimination Reactions

Removal of water or some other small molecule with the formation of a double bond in the larger molecule

e.g. Dehydration of alcohols to produce alkenes



t

## 4 Redox Reactions – Involve both Reduction and Oxidation

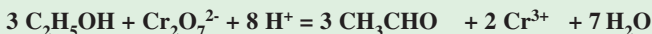
### Oxidation

$\text{Na}_2\text{Cr}_2\text{O}_7$  and  $\text{KMnO}_4$  turning alcohols to aldehydes, ketones or carboxylic acids

#### Ethanal production

Alcohol in excess / remove ethanal as soon as it is formed

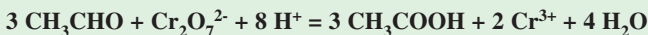
Orange  $\text{Cr}_2\text{O}_7^{2-}$  reduced to green  $\text{Cr}^{3+}$  / ethanol oxidised to ethanal



Ethanal is a product of the metabolism of ethanol in the body and causes the characteristic smell from someone who has been drinking heavily the previous night.

#### Ethanoic Acid

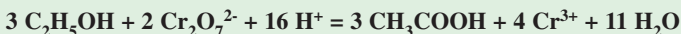
Ethanal can be oxidised to ethanoic acid with either hot acidified dichromate or manganate (VII)



Orange  $\text{Cr}_2\text{O}_7^{2-}$  reduced to green  $\text{Cr}^{3+}$  / ethanal oxidised to ethanoic acid

Ethanol can be oxidised to ethanoic acid with either hot acidified dichromate or manganate (VII)

Dichromate in excess / reflux for 30 minutes

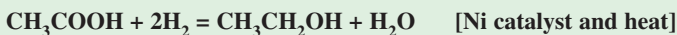


Orange  $\text{Cr}_2\text{O}_7^{2-}$  reduced to green  $\text{Cr}^{3+}$  / ethanol oxidised to ethanal then to ethanoic acid

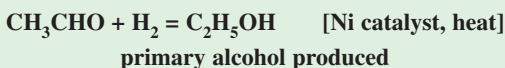
Ketones are not easily oxidised

### Reduction

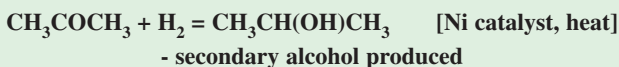
#### Ethanoic acid to ethanol



#### Ethanal to ethanol



#### Propanone to propan-2-ol



## 5 Reactions as Acids – carboxylic acids with $\text{H}_2\text{O}$ , $\text{Mg}$ , $\text{NaOH}$ and $\text{Na}_2\text{CO}_3$

- ## V Organic Synthesis

*You can be asked to work out reaction schemes of up to three conversions, recalling familiar reactions. Below is a summary of the main conversions and the conditions required for each conversion. Learn diagram section by section dividing it into three sections, as shown below.*

[illegible]

You need to know to know **2 examples** of compounds that are synthesised  
e.g. **Aspirin, Paracetamol** (structures are not required)

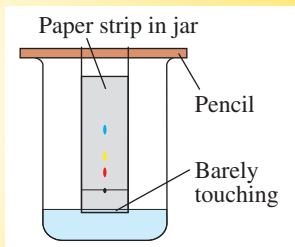
## W Chromatography and Instrumentation

### EXPERIMENT: Separation of a mixture of indicators using Paper Chromatography

#### Chromatography

A separation technique in which a **mobile phase** [*water + alcohol*] carrying a **mixture** [*of indicators or dyes from fibres*] is caused to **move in contact** with a **selectively absorbent stationary phase** [*paper*] and this separates the components of the mixture.

- Set up chromatography tank
  - Place 1 cm depth of solvent in tank
  - Draw pencil line 2 cm from bottom of paper and one near top
  - Spot line with individual indicators and the mixture of indicators several times allowing to dry between spotting
  - Place end of chromatogram in solvent **making sure spots are above solvent**
  - Cover tank and allow to run till solvent front reaches line near top
  - Remove and dry
  - Calculate and record  $R_f$  values [ $R_f = \text{distance moved by substance} / \text{distance moved by solvent front}$ ] of each substance
- Ammonia vapour can be used to locate [develop] phenolphthalein spot which will turn pink.
- Uses separating dyes from fibres



## X Gas Chromatography [GC]

More advanced form.

Gas is mobile phase

Stationary phase liquid on a solid support

Uses:- **Drug tests on athletes;**  
**Blood alcohol tests.**

### High Performance Liquid Chromatography [HPLC]

Liquid mobile phase – under pressure

Solid stationary phase compacted

Uses:- (i) **examining growth-promoters in meat**  
(ii) **Vitamins in foods.**

### Atomic Absorption Spectrometry

#### (1) Infra-red Absorption Spectrometry [IR]

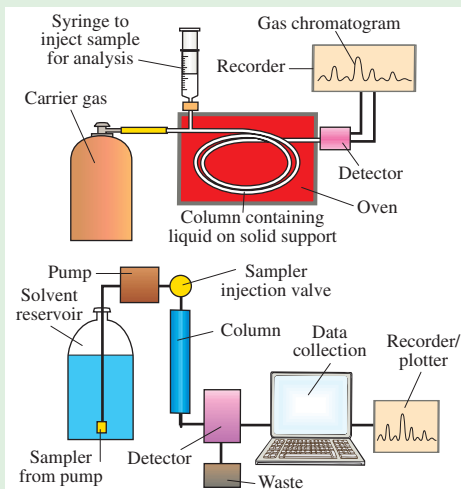
A 'fingerprinting' technique involving **absorption of infra-red radiation**  
Tells us the **chemical groups** present by **identifying bonds**

Uses: **Identification of organic compounds, e.g. plastics and drugs**

#### (2) Ultraviolet Absorption Spectrometry [UV]

A **quantitative** technique involving the **absorption of ultraviolet light**

Uses:- **Quantitative determination of organic compounds (e.g. drug metabolites, plant pigments)**



# ORGANIC CHEMISTRY

**Y**

## EXPERIMENT: Recrystallisation of Benzoic Acid and Melting Point Determination

### [a] Recrystallising

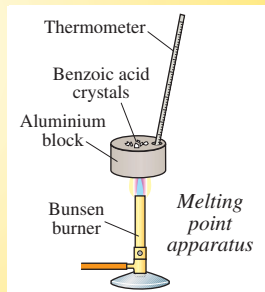
- Dissolve impure benzoic acid in minimum hot solvent [water]
- Filter using a hot apparatus to remove any insoluble impurities
- Cool filtrate to recrystallise
- Filter to retrieve crystals and remove soluble impurities as they pass through into filtrate
- Wash crystals with cold solvent  
[wash away last traces of impurity with minimum solution of crystals]
- Dry crystals in a desiccator



*Buchner filter*

### [b] Melting point determination

- Take a very small amount of benzoic acid
- Heat slowly on aluminium block with thermometer in it
- Place mineral oil in hole with the thermometer [to ensure good thermal contact]
- Note the temperature at which the sample starts to melt.
- Note the temperature at which **all** of the sample is melted.



**Melts over several degrees = impure**

**Melts sharply = pure**

### Questions on this Section from Past Exams year by Year

2009	2008	2007	2006	2005	2004	2003	2002
4 h, i	1 d, i	2	2	2	3	4 c, h	2
8	2	4 g, j	4 g, f	4 i, j	7	6	4 j
	9	8	9	7		9	6
	11 a	11 b	10 c	10 c			7 a, b, d



## a 8.1 Chemical Equilibrium

**Reversible Reaction**      Reaction that can, and does, go in both directions

**Equilibrium** - When rate of forward = rate of reverse the reaction

### Dynamic Equilibrium

Reaction appears to have stopped but it is continuing in both directions

At equilibrium, **the rate of the forward reaction equals the rate of the reverse reaction** so there is no change in concentration.

For the reaction  $yA + zB \rightleftharpoons rC + sD$

**Equilibrium Constant Expression** in terms of concentration

$$K_c = \frac{[C]^r [D]^s}{[A]^y [B]^z} \quad \text{Note that the multiplication sign is usually omitted}$$

This relationship is also called the **Equilibrium Law**

E.g.  $N_2 + 3H_2 \rightleftharpoons 2NH_3$        $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$       [ ] = concentration in mol l<sup>-1</sup>

## b Calculations involving Equilibrium Constant ( $K_c$ )

(i) Given number of moles of reactants and products at equilibrium

In a reaction at 293K between sulfur dioxide and oxygen producing sulfur trioxide it was found that the equilibrium concentrations of SO<sub>2</sub>, O<sub>2</sub> and SO<sub>3</sub> were 0.14 mol l<sup>-1</sup>, 0.07 mol l<sup>-1</sup> and 0.06 mol l<sup>-1</sup> respectively.

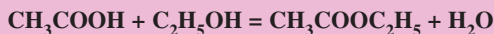
Given that the equation for the reaction is  $2SO_2 + O_2 \rightleftharpoons 2SO_3$   
Calculate the equilibrium constant for the reaction.

$$K_c = \frac{[SO_3]^2}{[SO_2]^2[O_2]} = \frac{[0.06]^2}{[0.14]^2 [0.07]} = 2.62 \text{ mol l}^{-1}$$

(ii) Given masses and volumes of reactants and/or products

When 30g of ethanoic acid and 23g of ethanol were placed in a conical flask and a few drops of concentrated sulfuric acid added, an equilibrium was set up with the formation of ethylethanoate and water.

The equilibrium is represented by the following equation.



When the equilibrium mixture was analysed it was found to contain 10 g of ethanoic acid. Calculate the value of the equilibrium constant,  $K_c$ .

Values given

Start       $CH_3COOH = 30/60 = 0.5 \text{ mol}$ ;  $C_2H_5OH = 23/46 = 0.5 \text{ mol}$ ;

Equilibrium  $CH_3COOH = 10/60 = 0.16^* \text{ mol}$



Start      0.5 mol      0.5 mol      0      0

Used      0.33\*      0.33\*

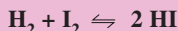
Equilibrium 0.16\* mol      0.16\* mol      0.33\* mol      0.33\* mol

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{0.33^* \text{ mol} \times 0.33^* \text{ mol}}{0.16^* \text{ mol} \times 0.16^* \text{ mol}} = 4$$

# EQUILIBRIUM

C

2,240 cm<sup>3</sup> of hydrogen (measured at s.t.p.) were placed in 4 litre flask with 25.4g of iodine. The flask was sealed and an equilibrium was allowed to establish. The mass of hydrogen iodide formed was found to be 20.48g. Calculate the equilibrium constant for the reaction at this temperature. The equilibrium is represented by the following equation.



Values given

Start  $\text{H}_2 = 2,240 / 22,400 = 0.1 \text{ mol}$ ;  $\text{I}_2 = 25.4 = 0.1 \text{ mol}$ ;  
Equilibrium  $\text{HI} = 20.48 / 128 = 0.16 \text{ mol}$

$$\text{Moles} = \frac{\text{Mass}}{M_r}$$

Concentrations in moles per litre [divide by 4 since it is a 4 litre flask]

Start  $\text{H}_2 = 0.1 / 4 = 0.025 \text{ mol l}^{-1}$ ;  $\text{I}_2 = 0.1 / 4 = 0.025 \text{ mol l}^{-1}$ ;  
Equilibrium  $\text{HI} = 0.16 / 4 = 0.04 \text{ mol l}^{-1}$

$$\text{Moles} = \frac{\text{volume}}{22,400}$$

	$\text{H}_2$	+	$\text{I}_2$	=	$2 \text{HI}$
Start	0.025 mol		0.025 mol		0
<i>It takes 0.02 moles of <math>\text{H}_2</math> to produce 0.04 moles of HI</i>					
Used	0.02		0.02		
Equilibrium	0.005 mol l <sup>-1</sup>		0.005 mol l <sup>-1</sup>		0.04 mol l <sup>-1</sup>

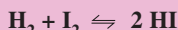
$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{[0.04]^2}{[0.005] \times [0.005]} = 64$$

If the total number of moles on each side of the equation is the same then the volume of container need not be taken into account.

(iii) Given the equilibrium constant and working out the equilibrium values

Always ask can I square root both sides of equation to get the answer easily

A gaseous mixture of hydrogen, iodine and hydrogen iodide form an equilibrium according to the following equation.



The value of the equilibrium constant,  $K_c$ , for this reaction is 50 at 721 K.

If 2 moles of hydrogen iodide gas were introduced into a sealed vessel at this temperature calculate the amount of hydrogen iodide gas present when equilibrium is reached.

Values given

$K_c = 50$   $\text{HI} = 2 \text{ moles at start}$

	$\text{H}_2$	+	$\text{I}_2$	=	$2 \text{HI}$
Start	0 mole		0 mole		2 mole
<i>If x moles of HI is used then it follows that x/2 moles of <math>\text{H}_2</math> and <math>\text{I}_2</math> are formed</i>					
Used					x
Equilibrium	$\frac{1}{2} x \text{ mole}$		$\frac{1}{2} x \text{ mole}$		2 - x

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \Rightarrow 50 = \frac{[2 - x]^2}{[\frac{1}{2} x]^2} \quad \text{Square root both sides of the equation.}$$

$$\Rightarrow 7.07 = \frac{2 - x}{\frac{1}{2} x} \quad \text{solving this equation} \Rightarrow x = 0.44$$

$$[\text{HI}] = 2 - x = 2 - 0.44 = 1.56$$