

## C.1 Diet

### C.1.1

Requirements of a Healthy Human Diet:

- Water: Necessary for life, biochemical activities within the body.
- Food groups:
  1. milk group : milk, cheese, yoghurt provides calcium, protein, vitamin A & D.
  2. meat group : meat, fish, poultry, eggs, legumes, nuts provides iron, vitamin B, energy.
  3. vegetable and fruit group provides vitamin A & C.
  4. bread and cereal group provides energy, vitamins, minerals, protein.
- Carbohydrates - Source of calories (energy), glucose important in energy-producing cycles within cells. RDA - ?.
- Proteins - Enzymes to catalyse the body's chemical reactions, hormones, muscle, connective tissue. RDA - 56g.
- Fats (& oils) - Concentrated source of energy. RDA - ?.
- Vitamins -
- Minerals:
  1. Calcium - Blood, cells, body fluids, bones (its absorption is enhanced by vitamin D).
  2. Magnesium - Maintains the electric potential across nerve-and-muscle-cell membranes.
  3. Phosphorus - Bones and teeth.
  4. Iodine - Essential for functioning of thyroid gland.
  5. Iron - Haemoglobin, enzymes.
  6. Zinc - Part of important enzymes in the body.

Importance of a Balanced Diet:

- Deficiency in caloric assumption results in deficiency diseases, starvation, or death.
- Over-nutrition results in obesity, high blood pressure, diabetes, heart attacks.
- Excess in saturated fat consumption leads to rise in blood cholesterol levels and possibly strokes.
- Deficiency in protein and minerals- anemia, edema, loss of pigment and hair, retarded growth.

### C.1.2

Calories and Enthalpy of Combustion:

- calories are the energy content of food.
- energy is stored in chem bonds that link atoms and molecules. Energy is captured by the body during biochemical reactions involving the combustion of nutrients. This energy is used to drive life processes of cells.

Proteins and Carbohydrates : 4kcal/g

Fat : 9kcal/g

Alcohol : 7kcal/g

For calculations, simply use  $DH = mc DT$ . Divide the change in heat by the number of grams of food burned, and the caloric value of the sample will be obtained.

## C.2 Proteins

### C.2.1

2-Amino Acids:

- There are 20 different 2-amino acids.
- They contain an amine group ( $NH_2$ ) on the central carbon atom ( $\alpha$ ), a carboxyl group and different R-groups.
- All amino acids are optically active (not needed, but good to know).

### C.2.2

Poly-peptides :

- Two amino acids join to form a dipeptide. The bond is called PEPTIDE BOND.
- Condensation reaction : A hydroxyl group is lost from one of the amino acids' carboxyl group, while the other amino acid loses a H from its amine group. (A diagram would be helpful here.)
- Amino acids join to form proteins.

### C.2.3

Chromatography :

- hydrolyze protein to release amino acids then place a sample spot on the paper. When solvent reaches solvent front, remove the paper, dry and spray with a locating agent such as ninhydrin.
- compare distance travelled aka RF with known values

$RF \text{ values} = \frac{\text{distance travelled by substance}}{\text{distance travelled by solvent}}$

Electrophoresis :

- R-groups of amino acids have different isoelectric points, (i.e. where the charge on the amino acid is zero). Similarly sized molecules can be separated by using the charge on the individual amino acids. Proteins are placed in a magnetic field and positive R-groups will be attracted to the negative pole of the magnet, while negative R-groups will tend to move towards the positive pole. The position where the individual amino acids stop is indicative of their charge. This reveals the isoelectric point, and consequently the R-group of the amino acid.
- pH can be used to separate proteins. They are placed in a pH gradient. Amino acids travel to where their net charge is zero. Given the position in which they stop, the amino acid can be identified.

### C.2.4

Protein structure :

**Primary** : Amino acids arranged in linear order.

**Secondary** :

- Alpha helix: coil of polypeptides, with hydrogen bonds between the amide hydrogen atom in one peptide and the carbonyl oxygen atom of another peptide, at a distance of three amino acids. Coil chains are held together by disulfide bonds between adjacent chains.
- Beta-pleated sheet: a folded sheet, stabilized by hydrogen bonds between the chains. There are no disulfide bonds in this structure.

**Tertiary** : Folded structure of chains of amino acids. 4 types of interactions :

1. Ionic bonds between R<sup>+</sup> and R<sup>-</sup>.
2. H-bonds between partial - and partial + R-groups.
3. Disulfide bonds.
4. Hydrophobic interactions - non polar R-groups tend to stay close together because repelled polar substances surrounding proteins.

**Quaternary** : More than one poly-peptide chain join to form a protein. Several folded chains joined by disulfide bonds (eg. haemoglobin).

## C.2.5

**Functions** :

- Structure, e.g. collagen (fibrous proteins).
- Biological catalysts e.g. enzymes.
- Transport e.g. haemoglobin.
- Energy source.

## C.3 Carbohydrates

### C.3.1

**Monosaccharides** :

- All sugars that contain a single carbohydrate unit, with an empirical formula: CH<sub>2</sub>O.
- Contain a carbonyl group (C=O), and at least two hydroxyl groups (-OH).
- e.g. -glucose, fructose, galactose.

### C.3.2

Glucose :

- C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>.
- A main source of energy.
- Contains six carbons with an aldehyde group (H-C=O) on the first and hydroxyl groups on each of the remaining carbons.
- In water, the 2nd C and the 6th C form a bond, forming a cyclic structure.
- A-glucose: Hydroxyl group on the sixth carbon is down.
- B-glucose: It is up.

### C.3.3

Condensation/dehydration synthesis:

- Organic molecules join together by releasing water- a H is removed from one group, and an -OH group from another. A glycosidic bond is formed.
- Disaccharides - Formed by two monosaccharides.  
e.g. Lactose= glucose + galactose or sucrose= glucose + fructose
- Polysaccharides : A number of monosaccharides joined together.  
e.g. starch, a polymer of glucose, with formula  $(C_6H_{10}O_5)_n$ .  
e.g. glycogen, same molecular formula - gives glucose when hydrolysed, stored in liver and muscles as a reserve of carbohydrates. (This is not needed).

### C.3.4

Functions of polysaccharides :

- Basic energy sources for living organisms.
- Glycogen : An energy reserve, (stored in liver), can break down into glucose when it is needed.
- Precursors for other biologically important molecules : i.e. monosaccharides are used to make other molecules like glycerol and fatty acids and some amino acids.
- Cellulose : Structural material in plants (not in syllabus).

## C.4 Fats

### C.4.1

Composition of fats/oils:

- Fatty acids : Long chain of carbon and hydrogen atoms with a carbonyl group at the end ( $C=O$ ).
- Triglycerides : Molecules formed by the joining of three fatty acids to a molecule of glycerol (Propane 1,2,3-triol i.e.  $H_2COH-HCOH-H_2COH$ ). The latter loses the H atoms (from the hydroxyl group) and the fatty acids lose OH groups. Dehydration synthesis.
- Fats are solid at room temperature and oils are liquid at room temperature.
- Phospholipids : Similar to the above, but one or two of the fatty acids are replaced by a phosphate group, which links to an amine group of another molecule (I'm not sure you need this).
- All fats are hydrophobic, meaning they contain a high proportion of C-H bonds. The carbonyl end of the molecule is hydrophilic.

### C.4.2

**Saturated fats** : Fats with single bonds (no double bonds, not even one), C atoms can hold no more H atoms than they already have

**Unsaturated fats** : Fats with at least one double bond. The double bond causes fats (e.g. triglycerides) to have a lower boiling point. The double bond tends to keep the fat flat-linear meaning they are usually oils at room temp.

### C.4.3

Fat addition reaction :

The extent of unsaturation of a fat - tested by  $I_2$ . By calculating the number of moles that react with a fat, the number of double bonds will be discovered. This is because the double bonds between C atoms are broken, and I bonds itself to the C. One I will bond to each former double-bond location. Every molecule of  $I_2$  used indicates one double bond. Electrophillic addition  $R-C=C-R + I_2 \rightarrow R-I-C-C-I-R$ . When the reaction occurs, the iodine will become clear.

### C.4.4

Soap is made by the hydrolysis of fats. NaOH is added as a source of alkali.

3  $Na^+$  are required to saponify one fat molecule (generally a triglyceride). These will replace the glycerol, yielding three fatty acids with an  $Na^+$  tail. More info about soaps is given in the chemistry higher level section 21.6.

### C.4.5

Functions :

- Energy source (self-explanatory).
- Insulation (ditto).
- Cell membrane - made up of phospholipids.

## C.5 Vitamins

### C.5.1

Vitamins are any organic compounds required by the body in small amounts for metabolism. (they are micro-nutrients)

### C.5.2

**Water soluble** : Vitamins that contain many -OH groups making them polar and therefore water soluble. Examples including the eight B-group vitamins and vitamin C

**Fat soluble** : Vitamins that contain little or no -OH groups and are characterized by long hydrocarbon chains. Examples include vitamins A, D, E, F, and K.

### C.5.3

Structure and Functions: (structures listed in data-booklet)

**Vitamin A (Retinol)** : At night, light shining on the eye strikes a receptor, rodopsin which sends an impulse to the brain. Vitamin A is essential in the formation of rodopsin. Vitamin A deficiency and result in night-blindness and xerophthalmia (tear glands cease to function).

**Vitamin D (calciferol)** : Important in the production of a hormone involved in the metabolism of calcium. It is modified by the body (2OH groups are added) and it functions as a hormone which causes the intestines to absorb calcium from food. Vitamin D deficiency causes rickets (weak bones, low blood calcium level).

**Vitamin C (ascorbic acid)** : Essential in the formation of connective tissue-collagen. Works as a reducing agent to form one of the amino acids in the protein collagen. Vitamin C deficiency causes scurbutus ('scurvy'-connective tissue breaks down, hemorrhage).

#### C.5.4

Food processing :

- Most vitamins are destroyed or altered during cooking, especially water soluble vitamins, however fat soluble vitamins are relatively stable.
- Vitamin B is destroyed during milling processes.

### C.6 Hormones

#### C.6.1

Production/roles:

Organic molecules can be secreted by one part of the organism but have an effect on another. They are controlled by the pituitary gland, which is controlled by the hypothalamus. Secreted by endocrine glands.

**Adrenaline** : Synthesised from amino acid Tyrosine: When exercise is done, impulses are sent for adrenaline to be released into the blood stream. It causes blood to be sent into areas of more active circulation. Increase in volume of blood available. Increase in rate of heart beat, stimulated respiration. The breakdown of glycogen to glucose is stimulated which raises level of sugar in the blood stream.

**Thyroxin** : Iodated amino acid derivative, produced by the thyroid gland. Stimulates growth and development. Affects and regulates body's metabolic rate and cell respiration.

**Insulin** : Made up of 2 poly-peptide chains held together by disulphide bonds. Made in the pancreas by the Islet of Langerhorn. Regulates cellular intake of glucose from the blood. It is secreted in response to a rise in blood sugar or amino acid concentration. It also inhibits the breakdown of glycogen in the liver.

Sex hormones :

**Female** : Pituitary hormones (LH and FSH) are secreted at puberty, Estrogen: (produced by ovary) stimulates an increase in secretion of a hormone, which brings about the maturation of the follicle and the ovulation. Stimulates the development of female features: breasts, subcutaneous fat, menstrual cycle. Progesterone (corpus luteum of ovary) stimulate the endometrium (lining of the uterus) to thicken and to secrete a nourishing fluid in preparation for a fertilised egg.

**Male** : Testosterone hormones are secreted by the testes and the adrenal glands (above the kidneys). During puberty, the pituitary gland stimulates the release of a protein ABP, which has high affinity for testosterone. This stimulates development of male features: deepening of voice, development of male musculature, growth of hair on the face and other parts of the body.

#### C.6.2

Steroids: (see structure in data booklet)

- A type of lipid (hydrophobic)
- Structure: consist of four contiguous carbon rings (the common backbone)
- Different steroids have different functional groups attached to the backbone.

**Cholesterol** : Most common steroid. An essential component of cell tissue and brain and nervous tissue. It has a chain of alkanes on one ring, and a OH group on the last ring.

Some steroids act as hormones, which send chemical messages to different parts of the body, these hormones are synthesized from cholesterol in the ovaries, testes, and other glands that produce them.

**Progesterone** : Carbonyl group (ring=O) attached to a methyl group on the first ring, carbonyl group (ring=O) on the last ring.

**Testosterone** : OH group on the first, ring=O on the last.

Differences : Cholesterol is primarily hydrophobic, with only one carbonyl group, the sex hormones have carbonyl groups and hydroxyl groups which make the molecule partly hydrophilic on both ends.

### C.6.3

Oral Contraceptive:

The 'pill' consists of estrogen and progesterone hormones (synthetic). The excess of these hormones (at a given dosage) will prevent ovulation, thus avoiding pregnancy.

Negative feedback control : The increased levels of estrogen inhibit the levels of LH hormone released by the pituitary gland. The drop in LH and FSH levels stops the development of the endometrium lining. Without it the egg cannot implant and therefore no pregnancy will occur.

### C.6.4

Steroid Use and Abuse :

uses: -For the treatment of wasting illnesses or to gain muscle(when give to someone recoping from a serious illness to build up muscle) - For the treatment of eczema

Abuses: -Atheletes,footballers, weightlifters, wrestlers,ets are common abusers of steroids to increase their muscle mass, enhance their performance and increase their strength

**Option E - Chemical Industries (SL)**

**From kstructIB**

## E.1 Initial overview

### E.1.1

**Raw materials** : Natural substances which can be converted by chemical processes into useful products.

**By-Products** : Substances produced as a result of a chemical process, but not the major (or important) product.

**Waste products** : Substances produced that have no value/are dangerous and must be disposed of.

**Minerals** : Naturally occurring inorganic substances, such as metals and their ores.

**Air** : O<sub>2</sub>, N<sub>2</sub>, Ar

**Petroleum** : Coal, Oil etc...

### E.1.2

A number of factors influence positions for chemical industry establishment. Industry must comply with regulations (i.e. environmental restrictions), have good transport access to market and raw materials, availability and cost of labour, land, plant, equipment and energy source (electricity). Availability and cost of raw materials is also a major factor.

### E.1.3

**Speciality chemicals** : Drugs, Many organic substances (w/ specific uses).

**Bulk chemicals** : Sulphuric acid, Nitrogen, Oxygen, Ammonia, Sodium hydroxide, Chlorine.

## E.2 Principles of extraction and production

### E.2.1

Metals are rarely found free in nature, and have to be extracted and processed before they can be used. Gold is one prominent counter-example.

### E.2.2

Physical separation and purification from ores :

**Concentration of ores** : Froth, flotation etc.

**Separation** : Filtration, Centrifuge type stuff, magnetic properties, chromatography.

**Purification** : Zone refining (explained later).

### E.2.3

Chemical principles in the extraction of useful substance from raw materials ...

Changing into suitable form for oxidation, for example  $ZnS + O_2 \rightarrow ZnO + SO_2$ .

Reduction to metal, by electrolysis or chemical reaction (blast furnace).

Also consider : Reduction (Iron), electrolysis (Al<sub>2</sub>O<sub>3</sub>, Al ), equilibrium (Contact and Harber), energy requirements (electrolysis requires lots of energy and heat), catalysts (rate of reaction).

## E.3 Metals - iron and aluminum

### E.3.1

The main sources of iron are iron ores and scrap iron.

### E.3.2

Reactions which occur in a blast furnace (to produce iron)

$C(s) + O_{2(g)} \rightarrow CO_{2(g)}$  (carbon is partially oxidized to  $CO_2$ ).

$CO_{2(g)} + C(s) \rightarrow 2CO(g)$  (the carbon in  $CO_2$  is reduced to CO).

$3CO(s) + Fe_2O_{3(s)} \rightarrow 2Fe(s) + 3CO_{2(g)}$  (iron (III) oxide is reduced to Fe by the CO).

$CaCO_{3(s)} \rightarrow CaO(s) + CO_{2(g)}$  (this bit is about the production of slag, which is going to sit on top of the iron).

$CaO(s) + SiO_2 \rightarrow CaSiO_{3(l)}$  ( $CaSiO_3$  is the slag).

### E.3.3

Conversion of iron to steel in oxygen converter (steel is iron with a low proportion of carbon).

First, the converter is charged with about 25% scrap steel. In the bottom of the converter is also calcium oxide (lime) which reacts with impurities to form slag. Molten iron is then poured into the converter. In the converter there is also a tube blowing super heated oxygen into the molten iron. This will react with the carbon in the steel to produce  $CO_2$ , which then escapes. When the steel has been produced, the converter is tipped and the steel is tapped off through an outlet pipe.

### E.3.4

Different forms of iron :

**Cast iron** : Same as pig iron, high carbon content means it is relatively brittle, but also harder.

**Wrought iron** : More malleable (due to lower carbon content). Hammering/rolling removes impurities.

**Carbon steel** : Small ( >1% ) carbon content + Iron. It's very malleable, but not very hard.

**Alloy Steels** : The addition of other elements can change the physical properties of the alloy. For example, tool steels have to be strong, corrosion resistant and heat resistant. Stainless steel (18% chromium, 8% nickel) is resistant to corrosion, used in cutlery and surgical instruments.

### E.3.5

The principle uses of steel is in construction, and as reinforcement, as well as those given above (tools, cutlery, surgical instruments and so on).

### E.3.6

Production of Alumina from bauxite (aka Aluminium oxide,  $Al_2O_3$ ) :

$Al_2O_3$  will eventually be electrolysed, but first it must be purified.

$Al_2O_{3(s)} + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4(aq)$  (aluminium oxide produces sodium aluminate, and dissolves out any soluble impurities).

$NaAl(OH)_4(aq) \xrightarrow{\text{dilution}} Al(OH)_3(s) + NaOH(aq)$  (this occurs when the solution is diluted with water, producing aluminium hydroxide, which is a solid precipitate, and can be removed, leaving impurities behind).

$2Al(OH)_3(s) \xrightarrow{\text{heat}} Al_2O_{3(s)} + 3H_2O(g)$  (after heating, pure anhydrous aluminium oxide is produced).

### E.3.7

The aluminum oxide is then dissolved in molten cryolyte ( $\text{Na}_3\text{AlF}_6$ ) requiring the temperature to be kept above  $850^\circ\text{C}$ , and then electrolysed as follows.

Cathode :  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

Anode :  $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$  followed by  $\text{C} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})}$  because the anode is made of carbon.

The molten aluminum is then tapped off from the bottom of the container, since it is more dense than the cryolyte. Cryolyte is used because it greatly reduces the amount of energy to keep the aluminum oxide in a molten state.

The cell is generally produced as a large 'vat'. The cryolyte is in this, which is lined with carbon to be used as the cathode. Carbon anodes are dipped at intervals along it, and are slowly lowered as are eaten away (by the production of  $\text{CO}_2$ ).

### E.3.8

**Properties of aluminium** : Aluminium is resistant to corrosion (because it naturally forms a protective coating on  $\text{Al}_2\text{O}_3$ ). It is also very lightweight, and inexpensive compared to some alloys (stainless steel). It can not be made hard by the addition of carbon like iron.

### E.3.9

Aluminium is widely used due to its resistance to corrosion. Common uses are cans, construction (roofing, fences). Its lightweight nature also makes it useful in cars and airplanes.

Aluminium can not be made hard and so it is not very useful for tools, but doesn't corrode, making it useful in areas such as roofing, where steel would corrode, and stainless steel is too expensive.

### E.3.10

Environmental impacts of Aluminum production :

**Mining** : Destruction of land, which may require rehabilitation.

**Siting** : Some effluent and waste gases are inevitable, and so the plant would be best situated away from population centres.

**Recycling** : Avoids above problems, and may be less expensive than the production from bauxite. Also worth noting is that bauxite is a non renewable resource.

## E.4 Air

### E.4.1

Gases (oxygen, nitrogen and argon) are obtained by cooling air to below the boiling point of the desired gas

For example,  $\text{O}_2$  requires  $-183^\circ\text{C}$ ,  $\text{N}_2$  requires  $-196^\circ\text{C}$ , but I don't think these will be necessary.

### E.4.2

Uses :

**N<sub>2</sub>** : Producing NH<sub>3</sub>, HNO<sub>3</sub>, inert gas in incandescent light bulbs (and as an inert atmosphere in general). Also useful, as a liquid coolant for freezing food etc.

**O<sub>2</sub>** : Respiration (to air, eg oxygen rich air), production of steel, fuel (O<sub>2</sub> + C<sub>2</sub>H<sub>2</sub> or O<sub>2</sub> + H<sub>2</sub> for welding). Also used as an oxidizer in rocket propellant as liquid with reducer.

**Ar** : Inert gas used in fluorescent tubes, thermometers (above Hg), and in other cases where an inert gas is needed but N<sub>2</sub> can't be used.

## E.5 Equilibrium processes - The Harber and contact processes

### E.5.1

Many industrial processes depend on the manipulation of equilibria (because the valuable products are usually those which are hard to make). The ones we're going to see here are the harber and contact processes. First the harber process (this is sort of a recap from Topic 8).



Considerations : LCP predicts that the best yield will occur with low temperature and high pressure, but rate requires a high temperature for fast reaction. Equipment to maintain high pressure is expensive.

Generally we use 450°C, 250 atm and a catalyst (finely divided iron) which produces about 30% yield. NH<sub>3</sub> is separated by liquifying (NH<sub>3</sub> melts at about 20°C) other gases are returned to the reaction.

### E.5.2

Uses of ammonia :

- Essential nutrient for healthy plant growth - problem (nitrogen fixation) . It is difficult to use N<sub>2(g)</sub> from the atmosphere, thus nitrogen based fertilizers are used.
- Used to make nitric acid (HNO<sub>3</sub>), for the nitration of benzene.
- Used for production of TNT (tir-nitro toluene, which is methyl benzene with 3 substituted NO<sub>2</sub> groups at 2,4,6).
- Used to make dyes.

### E.5.3

*Contact process (this is the production of H<sub>2</sub>SO<sub>4</sub>).*



LCP suggests low temperature and high pressure (other considerations as above).

We generally use 450°C, 1 atm and vanadium (v) oxide catalyst. This produces about a 97% yield, so a higher pressure is not really necessary.

SO<sub>3(g)</sub> + H<sub>2</sub>SO<sub>4</sub> -> H<sub>2</sub>S<sub>2</sub>O<sub>7</sub>. When this is diluted in H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub> will be produced.

### E.5.4

Uses of sulphuric acid :

- Making fertilizers, explosives, dyes, production of other acids, detergents
- Catalyst for making esters
- Producing nitrating mixture
- As a dehydrating mixture.

Sulphuric acid is the most important industrial acid, and apparently you need to understand that.

## E.6 The oil industry

### E.6.1

Importance of oil as a chemical feed-stock :

About 90% of the crude oil products from fractional distillation are used in transport, heating fuels and electricity production. The other 10% is used as a feed-stock for the production of other organic chemicals, but it is still the most significant source of organic chemicals.

### E.6.2

There are three types of cracking; catalytic cracking, thermal cracking and hydrocracking.

**Catalytic cracking** : Superior to thermal cracking. Occurs at a lower temp (250°C) 1 atm pressure and a catalyst. Produces high quality gasoline with less CH<sub>4</sub> and more useful C<sub>3</sub> and C<sub>4</sub> molecules and many alkenes rather than alkanes.

**Thermal cracking** : 500°C, 50 atm pressure (older and possibly out of date).

**Hydrocracking** : Variation of thermal cracking using sodium aluminosilicate where some Na<sup>+</sup> is replaced by Pt. Performed in the presence of H<sub>2</sub>, so products are saturated (alkanes not alkenes).

### E.6.3

Reforming comes in a number of different types.

**Catalytic reforming** : Produces branched carbon chains, which have a higher octane number. This is done at 500°C in an atmosphere of hydrogen.

**Aromatisation** : The production of aromatic molecules (benzene rings) (usually 500°C and H<sub>2</sub> atmosphere like catalytic).

**Cyclisation** : The production of cyclic molecules, again at 500°C and in atmosphere of H<sub>2</sub>.

**Alyklation** : The reaction of alkanes and alkenes to form branched alkanes.

In all of these, hydrogen will be produced, which is commonly then used as an input to the harber process.

### E.6.4

Removal of sulphur from crude oil:

S in crude oil, when heated or burned forms  $\text{SO}_2$  (and some  $\text{SO}_3$ ), which can dissolve in water and form acid rain, so it's a good idea to remove it first.

$\text{SO}_2$  formed in fractional distillation can be removed by reaction with  $\text{MgO}$  or  $\text{NaOH}$ , both of which react with  $\text{SO}_2/\text{SO}_3$  to form a salt and water. The  $\text{SO}_2/\text{SO}_3$  can then be used in the production of  $\text{H}_2\text{SO}_4$ .

### E.6.5

Refinery products as feed-stock :

Can produce from spare fractions of crude oil : solvents, plastics, pesticides, food additives, pharmaceuticals, detergents, cosmetics, dyes.

### E.6.6

Properties and uses of polymers :

**Polythene** : Long branched molecules produce a soft, malleable substance, useful in packaging.

**Polyvinyl Chloride** : Considerably more rigid, and this stronger due to polar C-Cl bonds. Useful for glue and as a sealant.

**Nylon** : Strong, long fibres, commonly used in tights or stockings, but also to as strength to other fibres (i.e. carpets are a combination of wool and nylon).

**Polyester** : Long chain fabrics with great strength which do not rot. Commonly used in sails, ropes and other fibres which must be strong and not rot.

### E.6.7

These polymers will not break down naturally and can not be burnt without the production of toxic gases. They are also produced from oil non-renewable resource (but can sometimes come from agricultural products).

## E.7 Other chemical industries

### E.7.1

Other chemical industries include the production of alloys, cement, ceramics, glasses, paper, silicones and natural products.

### E.7.2

Biotechnology is also an important source of some chemicals, such as ethanol, insulin and biopolymers (such as starch, rubber, proteins, wool, cotton, paper).

## H.1 Stereoisomerism

### H.1.1

Geometric isomers occur because the  $\text{C}=\text{C}$  bond is not able to rotate. Thus, cis and trans isomers are created when there are different compounds possible (if the 'top' and 'bottom' branches are swapped on either side). For things like 1,2-dichloroethane, the cis isomer is when the two chlorines are both top (or bottom) where as the trans is where they are opposite (cis means on the same side, and trans means on opposite sides).

### H.1.2

It is possible for one of the cis or trans isomers to be polar while the other is not, and this allows them to have different boiling points. In 1,2-dichloroethane, the cis-isomer is polar, and so its boiling point is 60 as opposed to 47 for the trans isomer.

In terms of chemical properties, when cis-but-2-ene-1,4-dioic acid is heated, H<sub>2</sub>O is eliminated and the two carbons at either end of the chain are linked across the remaining central oxygen, giving 2-butene-1,4-dioic anhydride (though I don't think we need to know the name). The trans isomer will not react, because the alkanolic acid sections are on opposite sides rather than together.

### H.1.3

Rotation can also be made impossible by the carbon atoms in question being linked together as part of a loop (a cyclo alkane). For example, 1,2-dichloro cyclobutane has both cis and trans isomers because the ring stops the bond between the carbons with the Cl molecules attached from rotating. The same goes for cyclopropane. [\[edit\]](#)

### H.1.4

Plane polarised light is light which only travels in one plane (see physics waves & optics sections for more info). Enantiomers (aka optical isomers) can be determined by their effects on such light. There are, for an optically active compound, two different enantiomers, which will rotate plane polarised light passing through them in opposite directions. The direction of rotation can be determined using an analyzer, or a polaroid.

### H.1.5

Enantiomers occur due to the fact that carbon atoms form four bonds. If the carbon is bonded to 4 different groups, then there will be two possible arrangements of them which are non-superimposable. You can demonstrate this with models, but for the time being we'll just assume you trust me. The two enantiomers are generally denoted L and D-enantiomers, we do not need to identify which is which. These are known as optical isomers because one is the mirror image of the other.

### H.1.6

A racemic mixture is a substance which contains equal percentages of both enantiomers, and so has no effect on plane polarise light. Enantiomers usually exist as racemic mixtures, though in many biological systems, one is favored over the other.

### H.1.7

Physical properties are effectively identical for both enantiomers, as are the chemical properties, except in the presence of other optically active compounds. This is particularly common in biological systems, for example, the tastes sweet and sour are optical isomers of the same compound.

## H.2 Free radical substitution reactions

### H.2.1

Free radicals are molecules with one (or more) unpaired electrons, and are very reactive. I'll be representing them as  $\text{Cl}^\bullet$  (with a bullet point).

**Alkanes with halogens** : In the presence of UV light,  $\text{Cl}_2 \rightarrow 2\text{Cl}^\bullet$ , because the light provides sufficient energy to split the bonds (this is initiation). The  $\text{Cl}^\bullet$  then reacts with  $\text{CH}_4$  as follows. By the way, everything here is in the gas state, so I won't write it each time.



The  $\text{CH}_3^\bullet$  then reacts with  $\text{Cl}_2$ , as follows.



This, and the previous step, are the propagation steps. This can be repeated to form  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$  and eventually  $\text{CCl}_4$ .

Termination occurs when two free radicals react.  $\text{Cl}^\bullet + \text{Cl}^\bullet \rightarrow \text{Cl}_2$ ,  $\text{Cl}^\bullet + \text{CH}_3^\bullet \rightarrow \text{CH}_3\text{Cl}$ ,  $\text{CH}_3^\bullet + \text{CH}_3^\bullet \rightarrow \text{C}_2\text{H}_6$ .

**Methylbenzene with halogens** : The halogen substitutes preferentially into the side chain (the methyl bit), with the same mechanism as above.

## H.2.2

The effect of  $\text{RCl}$  on  $\text{O}_3$  : As above, in UV light, the  $\text{RCl}$  bond breaks homolytically, forming  $\text{CH}_3^\bullet$  and  $\text{Cl}^\bullet$  (this is the initiation).



Followed by,  $2\text{ClO}^\bullet + \text{O}_2 \rightarrow 2\text{Cl}^\bullet + 2\text{O}_2$ . This produces more chlorine, thus producing a chain reaction.

Termination :  $\text{ClO}^\bullet + \text{ClO}^\bullet \rightarrow \text{Cl}_2\text{O}_2$ ,  $\text{Cl}^\bullet + \text{Cl}^\bullet \rightarrow \text{Cl}_2$ .

## H.3 Electrophilic addition reactions

### H.3.1

The reaction mechanism for electrophilic addition really needs a picture, but I'll try to describe it. This example is hydrogen chloride adding to ethene, but could apply to anything.

The reaction can be drawn with curly arrows. The  $\pi$  electrons from the ethene double bond move on to the less electronegative element in the electrophile (in this case hydrogen). This causes the electrons from the  $\text{H-Cl}$  bond to be moved onto the  $\text{Cl}$  atom. This creates  $\text{CH}_3\text{C}^+\text{H}_2$  and  $\text{Cl}^-$ , followed by which, the  $\text{Cl}^-$  is attracted to the carbocation and forms a dative covalent bond with the carbon. The movement of electrons should be drawn with curly arrows

### H.3.2

Markovnikov's rule is basically that the less electronegative atom in a molecule adds to the atom carbon atom on the double bond with the most hydrogens already on it. This can be explained by the stability of the carbocation intermediate. Either way, after the first atom adds on, there will be a carbocation, but if there are more electron donating (i.e. not hydrogen) groups around it, it will be more stable. It is the less electronegative atom which bonds first because it is attracted to the electron rich  $\pi$  electron area, and because the carbon will be stronger electron donating (of course, this only applies to the major product, some of the other will still be produced).

### H.3.3

Carbocations are more stable the more electron donating group they have around them, so the more CH<sub>3</sub> groups replace the carbons around a carbocation, the more stable it will be. Ph<sup>+</sup> (which is a carbocation in a benzene ring) is more unstable than any alkane carbo-cations due to the loss of the delocalized Pi electron system.

## H.4 Electrophilic substitution reaction

### H.4.1

The nitration of benzene, i.e. adding NO<sub>2</sub> to C<sub>6</sub>H<sub>6</sub> :

First a nitrating mixture is used to produce NO<sub>2</sub><sup>+</sup>. H<sub>2</sub>SO<sub>4</sub> is added to HNO<sub>3</sub> and since H<sub>2</sub>SO<sub>4</sub> is the stronger acid, it donates a proton to the HNO<sub>3</sub>, producing H<sub>2</sub>O<sup>+</sup>-NO<sub>2</sub>.

This compound then decomposes to form H<sub>2</sub>O + O=N<sup>+</sup>=O. This NO<sub>2</sub><sup>+</sup> is then attracted to the delocalized Pi electron system of the benzene ring. The benzene ring donates an electron pair to form a dative covalent bond with the NO<sub>2</sub>, but since there is already a hydrogen connected to the carbon, a carbocation is produced. Since this is unstable, the hydrogen will break off (and conveniently go back to reform the H<sub>2</sub>SO<sub>4</sub>, making it a catalyst) leaving Nitrobenzene.

### H.4.2

The production of methylbenzene with a Friedel-Crafts catalyst :

The catalysts are FeCl<sub>3</sub> or AlCl<sub>3</sub>, and these are used to polarise the electrophile. The reaction begins with a Haloalkane as follows.

Cl-R + AlCl<sub>3</sub> -> R<sup>+</sup> + Al<sup>-</sup>Cl<sub>4</sub>. First the R-Cl bond is broken heterolytically with both electrons going to the chlorine, which then joins to the catalyst as above.

The R<sup>+</sup> is then attracted to the delocalised Pi system, forming an intermediate where both the R and H are bonded to a carbocation, and then the H<sup>+</sup> breaks off, and reacts with the Chlorine we left on the catalyst to form HCl, and we're left with alkylbenzene. It should be noted that the two steps happen sort of simultaneously, as the chlorine is pulled off by the catalyst the R forms a dative covalent bond with the benzene, so the mechanism should be drawn in one step.

[edit]

### H.4.3

**Electron donating groups** : Increase in delocalised electron density results in faster electrophilic substitution. These groups are also generally 2,4,6 directing. Examples include CH<sub>3</sub> and OH<sup>-</sup>.

**Electron withdrawing groups** : Decrease electron density resulting in slower electrophilic substitutions, and tend to be 3,5 directing.

The following table explains the examples which are required.

<b>-OH</b>	Strongly activating (fast)	2,4,6 directing
<b>-CH<sub>3</sub></b>	Activating (fast)	2,4,6 directing
<b>-Cl</b>	Deactivating (slower)	2,4,6 directing
<b>-C(=O)-O-CH<sub>3</sub></b>	Strongly deactivating (slower)	3,5 directing
<b>-NO<sub>2</sub></b>	Very strongly deactivating	3,5 directing

As you can see, -Cl is deactivating, but 2,4,6 directing (that's why they're only general principles)

The directing type means that means that subsequent electrophilic substitutions will tent towards these positions if we take the given group as being in position 1 on the carbon atom.

For example,  $C_6H_5OH + 3Cl_2 \rightarrow C_6Cl_3H_2OH + 3HCl$  (with the chlorines in the 2,4 and 6 positions)

## H.5 Nucleophilic addition reactions

### H.5.1

HCN first breaks to form  $H^+ + CN^-$ . The  $CN^-$  molecule then attacks the central carbon atom in an alkanone (the one with the double bond to the oxygen. Note that alkanals can also be used). This then forms  $N\equiv C-C(R)(R/H)-O^- + H^+$ . The  $H^+$  being the one broke off at the start, which then forms  $N\equiv C-C(R)(R/H)-OH$ . This is then reacted as follows.

$N\equiv C-C(R)(R/H)-OH + 2H_2O + H^+ \rightarrow HOOC-C(R)(R/H)-OH + NH_4^+$ , which is forming carboxillic acid.

The rates may be relevant. Alkanals are faster than alkanones because there are fewer electron donating groups in alkanals, resulting in a larger  $\delta^+$  charge, and so the  $CN^-$  nucleophile is more attracted. If one of the R groups is benzene, this is even slower as the  $\delta^+$  becomes delocalised.

## H.6 Nucleophilic Substitution reactions

### H.6.1

The rate of nucleophilic substitution is affected by the polarity of the nucleophile and the polarity of the charge on the  $\delta^+$  atom which is being attacked. For example, substitutions with  $OH^-$  will be faster than those with  $H_2O$ , because of the greater polarity of the oxygen atom in  $OH^-$ .

The rate of substitution of  $CH_3NH_2$  will be faster than  $NH_3$  due to the electron donating effect of the  $CH_3$  group creating a larger  $\delta^-$  charge on the N atom (which is the nucleophile).

### H.6.2

**Inductive effects** : If an electron withdrawing group (such as a halogen) is connected to the  $\delta^+$  carbon being attacked, then the  $\delta^+$  charge will be increased, resulting in a greater rate of nucleophilic substitution. Conversely, if an electron donating group (such as  $CH_3$ ) is attached, then the  $\delta^+$  charge will be decreased, resulting in a slower rate.

**Steric effects** : This refers to the incoming nucleophiles being blocked by other groups surrounding the carbon atom being attacked. For example,  $R_3-C-X < R_2-CH-X < R-CH_2 < CH_3-X$ . Beyond the inductive effects, the bulky alkyl groups block the attack, making it difficult for the nucleophile to get to the  $\delta^+$  C atom, and so on up the list.

Note, SN<sub>1</sub> and SN<sub>2</sub> mechanisms apply here, and substitution rate into CH<sub>3</sub>F < CH<sub>3</sub>Cl < CH<sub>3</sub>Br < CH<sub>3</sub>I. It is like this because the C-I bond has the lowest bond energy, and so on up, and this outweighs the increased electronegativity (meaning we get a more δ<sup>+</sup> C with fluorine etc.).

### H.6.3

Benzene-X (a halogenated benzene ring) is unreactive to nucleophilic substitution reactions under normal conditions. The lone pairs on the halogen atom interact with the delocalized Pi system, which strengthens the C-X covalent bond. The high electronegativity of the ring also tends to repel any approaching nucleophiles. The reactions are possible, however, at high temp and pressure (possibly with a catalyst)

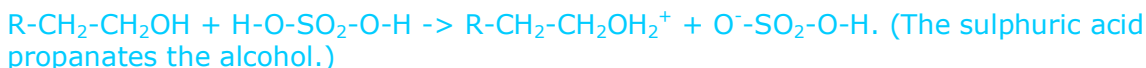


[edit]

## H.7 Elimination reactions

### H.7.1

Elimination of water from alkanols (dehydration) : The object here, is to produce an alkene from an alkanol, eliminating water in the process. This can be done in acidic conditions and high temperature, as follows.



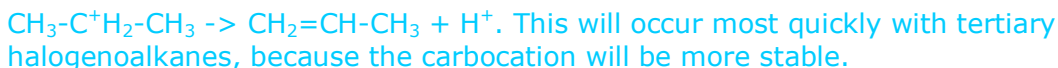
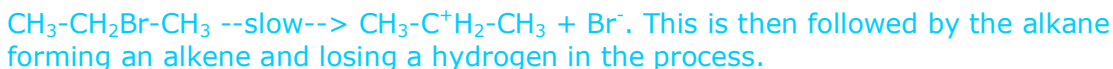
The more alkyl groups which surround the carbon atom, the faster this will occur, because the carbocation will be more stable. Tertiary alkanols are therefore faster than secondary which are faster than primary.

### H.7.2

The elimination of HBr from a bromoalkane can occur via two different mechanisms, one of which involves a nucleophilic attack.

#### Mechanism 1

The C-Br bond breaks spontaneously, and heterolytically (with Br getting both electrons as follows.



#### Mechanism 2

An OH<sup>-</sup> nucleophile forms a dative covalent bond with one of the hydrogen atoms. This causes the hydrogen to be removed, leaving the carbon with a spare pair of electrons, which then forms a double bond with an adjacent carbon (which conveniently has a Br atom on it). This double bond formation causes the C-Br bond

to break heterolytically with the Br getting both electrons. This all occurs in one step, but should be represented with curly arrows.

$\text{CH}_3\text{-CH}_2\text{Br-CH}_3 + \text{OH}^- \rightarrow \text{CH}_2=\text{CH-CH}_3 + \text{H}_2\text{O} + \text{Br}^-$ , which is again eliminating HBr.

## H.8 Addition-elimination reactions

### H.8.1

Reaction of 2,4-dinitro phenylhydrazine (  $\text{H}_2\text{N-NH-Benzene-(NO}_2\text{)(NO}_2\text{)}$  ) with alkanals and alkanones.

$(\text{R})(\text{R})\text{-C=O} + \text{H}_2\text{N-NH-Benzene-(NO}_2\text{)(NO}_2\text{)} \rightarrow (\text{R})(\text{R})(\text{OH})\text{-C-NH-NH-Benzene-(NO}_2\text{)(NO}_2\text{)}$

Then water is eliminated as follows.

$(\text{R})(\text{R})(\text{OH})\text{-C-NH-NH-Benzene-(NO}_2\text{)(NO}_2\text{)} \rightarrow (\text{R})(\text{R})\text{-C=N-NH-Benzene-(NO}_2\text{)(NO}_2\text{)} + \text{H}_2\text{O}$

This product is a yellow/orange precipitate with a characteristic melting point, often used to determine the alkanol/alkanone we started with.

## H.9 Acid-base reactions

### H.9.1

Phenol (a benzene ring with an OH on it) is acidic due to the stability of the Benzene- $\text{O}^-$  ion (formed when it donates a proton). This is unlike alkanols which are not significantly acidic. The acidity of phenols is due to the fact that the spare electrons around the  $\text{O}^-$  ion become involved in the delocalised Pi electron system, which makes the charge delocalized rather than concentrated on the O atom, which is energetically favourable and more stable. Phenols are still not strong acids though (weaker than RCOOH). They do not react with  $\text{Na}_2\text{CO}_3(\text{aq})$ , but do react with NaCl. Their  $K_a$  is about  $10^{-10}$ .

If phenol has electron withdrawing groups substituted (i.e.  $\text{NO}_2$ ), however, this again decreases the negative charge on the  $\text{O}^-$ , thus making them stronger acids. 2,4,6 trinitrophenol has a  $K_a$  of about  $10^{-4}$ . Electron donating groups, however, will make for weaker acids.

### H.9.2

Substituted alkanolic acids :

Again, electron withdrawing groups result in increased bond polarity which gives a reduced charge on the resulting ion and is therefore more stable and a stronger acid. Conversely, electron donating groups result in decreased bond polarity and a weaker acid.

### H.9.3

The basic nature of ammonia, amines and amides comes from the fact that nitrogen has 5 valence electrons. 3 of these form covalent bonds, and two are left in a lone pair, which is capable of forming a dative covalent bond with protons.

**Ammonia and amines** : Amines are really just ammonia with R groups replacing the H atoms, and so they fit into a series. Each time another R group is added, the

electron density donating effect creates a larger  $\delta^-$  charge on the N atom, making it better at attracting and bonding with protons. This means that Ammonia is weaker than primary amides, which are weaker than secondary amides. Unfortunately, tertiary amides fall between primary and secondary, due to the the fact that the increasing non-polar alkyl groups make tertiary amides less soluble in water, which more than accounts for the increased inductive effect. This is obviously a pain, but you'll just have to remember it. A phenol amide is weaker than all of them because the lone pair becomes part of the delocalised Pi system.

**Amides** : These are very weak bases due to the electron withdrawing effect of the C=O group, which reduces the negative charge on the N atom, making it less able to attract protons, and less stable once it has one.