## AS Chemistry – Revision Notes
Unit 2 – Foundation Physical And Inorganic Chemistry

Energetics

1. An enthalpy change is a change in energy at constant pressure (i.e. in normal 'open container' conditions where there is no change in pressure during the reaction).
2. A positive enthalpy (ΔH) signifies an endothermic reaction, whereas a negative enthalpy will be given by an exothermic reaction.
3. The energy released (or absorbed) in a reaction can be calculated by $E = mc\Delta T$, where c is the specific heat capacity of the reaction mixture (usually taken as water, i.e. 4200 $Jkg^{-1}K^{-1}$). The enthalpy for the reaction in $Jmol^{-1}$ can then be calculated by dividing E by the number of moles reacting.
4. A simple calorimeter measures the energy released in a reaction by using it to heat a mass of water – the increase in temperature of the water gives the energy released by the reaction. For combustion of alcohols, the mass of the burner before and after gives the mass of alcohol used, which can be used to calculate the moles used.
5. Standard enthalpy of combustion is the enthalpy change when one mole of a substance in its standard state is completely burned in air or oxygen to produce the products in their standard states, under standard conditions (298K, 101kPa). This is ΔH^{e}_{c}.
6. Standard enthalpy of neutralisation is the enthalpy change when one mole of water is produced when an acid neutralises an alkali under standard condition (298K, 101kPa). This is ΔH^{e}_{neut}.
7. Standard enthalpy of formation is the enthalpy change when one mole of a substance in its standard state is formed from its constituent elements in their standard states under standard conditions (298K, 101kPa). This is ΔH^{e}_{f}.
8. Hess' Law states that the enthalpy change of a reaction depends only upon the initial and final states of the reaction and is independent of the route the reaction takes.
9. Bond dissociation enthalpy is the enthalpy change when one mole of a substance in its gaseous state is split into individual gaseous atoms.
10. The mean bond enthalpy is the average enthalpy required to break or make one mole of a bond (e.g. C–H, C–C etc.). This is taken as an average from many (but not all) molecules containing the bond.
11. Mean bond enthalpies can be used to estimate enthalpy changes by calculating the enthalpy needed to break existing bonds (endothermic), and that when new bonds are made (exothermic).
12. Mean bond enthalpies can be calculated using the bond dissociation enthalpy for a species.

Reaction Kinetics And Equilibria

1. The rate of a reaction can be explained using collision theory:
    a. The molecules must have a minimum amount of energy to start the reaction – the activation energy (E_A).
    b. The molecules must approach each other at the correct angle and alignment.
    c. Molecules can only react if they collide, and not all collisions lead to a reaction.
    d. Increasing the frequency of collisions will increase the rate of reaction.
2. There are four main ways of increasing the rate of a reaction:
    a. Increasing the concentration of reactants (liquids) or the pressure (gases).
    b. Increasing the temperature.
    c. Increasing the surface area of reactants (in solids).
    d. Using a catalyst (this lowers E_A).
3. The Maxwell-Boltzman distribution of molecular energies (E_{mp} is the most probable (modal) energy, $\overline{E}$ is the average (mean) energy, and E_A is the activation energy):
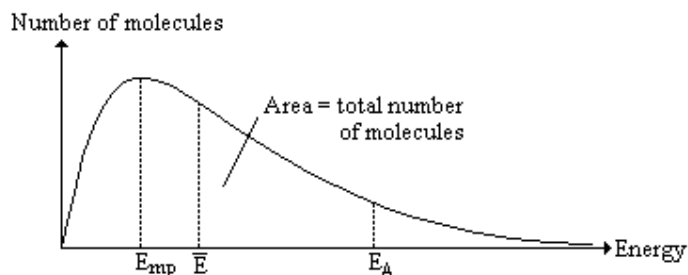
4. Increasing the temperature will cause the peak to shift to the right and downwards (to keep the area constant), meaning that more molecules have $E \geq E_A$, and will therefore be able to react if they collide. The frequency of collisions will also be increased as the molecules have more kinetic energy on average.
5. Raising the temperature by 10°C (10K) approximately doubles the rate of a reaction ($Q_{10} = 2$).
6. Energy profile diagram for a typical exothermic reaction:
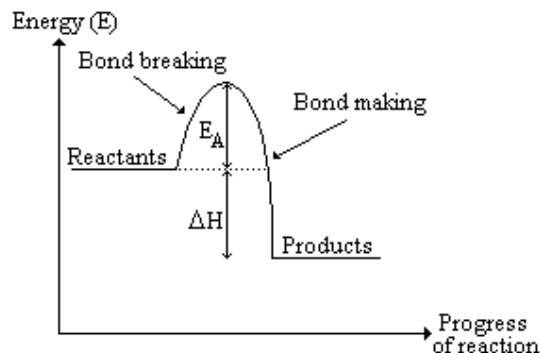
7. A catalyst lowers the activation energy for the reaction, so that for any temperature, a bigger proportion of the molecules will have $E \geq E_A$, leading to an increased frequency of reactions. There is no increase in the number of collisions.
8. Energy profile diagram for a typical catalysed reaction (E_{cat} = activation energy with the catalyst):
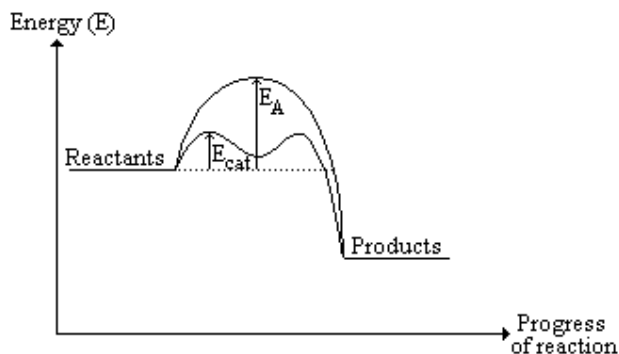
9. A reversible reaction is one that goes in both directions – Reactants $\rightleftharpoons$ Products. 'Left to right' is the forward reaction, and 'right to left' is the reverse (or backward) reaction.
10. As a reversible reaction takes place, the rate of the forward reaction decreases as the reactants are used up, and the rate of the reverse reaction increases as more products are produced. Eventually the rate will be the same for both reactions, as the overall concentration of reactants and products will stop changing.
11. Dynamic equilibrium is when there is no change in the concentration of reactants and products (the forward and backward reactions proceed at the same rate), but both the forward and backward reactions continue to take place (i.e. it is dynamic).
12. Le Chatelier's principle states that if a system at equilibrium is subjected to change, the position of equilibrium will shift so as to remove the effect of that change:
    a. Exothermic reactions give a higher yield at lower temperatures.
    b. Endothermic reactions give a higher yield at higher temperatures.
    c. Reactions with a decrease in the number of gaseous molecules from reactants to products give a higher yield at higher pressures.
    d. Reactions with an increase in the number of gaseous molecules from reactants to products give a lower yield at higher pressures.
    e. Reactions that do not involve gases, or which have equal numbers of gaseous molecules in the reactants and products do not respond (in terms of a shift in equilibrium) to pressure changes.
13. Using a catalyst in a reversible reaction does not affect the position of equilibrium – it increases the rate of the forward and backward reactions equally, so that although dynamic equilibrium will be reached more quickly, the position of this equilibrium will not be affected.

14. For the Haber Process (manufacture of ammonia), N_2 (g) $+ 3H_2$ (g) $\rightleftharpoons 2NH_3$ (g):
    a. The hydrogen is produced from methane, and the nitrogen is taken from the atmosphere.
    b. An iron (Fe) catalyst is used.
    c. The temperature is 400°C. As the forward reaction is exothermic, a lower temperature will give the highest yield of ammonia (by favouring the forward reaction). However, a lower temperature will lower the rate of reaction and so a compromise is made to give a reasonable yield at a reasonable reaction rate. This is also within the working temperature range of the catalyst.
    d. The pressure is 200atm. As the forward reaction results in a decrease in the number of moles of gas molecules, a pressure increase will increase the yield of ammonia (by favouring the forward reaction), and it will also increase the rate of reaction (due to collision theory). The higher the pressure, however, the more expensive the equipment is, and so a compromise is made at a lower pressure to save on running costs.
    e. NH_3 is condensed and tapped off as it is produced, and unreacted H_2 and N_2 is recirculated to give an overall 98% yield.

Redox Reactions
1. A redox reaction is one in which reduction and oxidation occur at the same time (you cannot get one without the other):
    a. Reduction involves a gain of electrons and a decrease in oxidation state.
    b. Oxidation involves a loss of electrons and an increase in oxidation state.
2. An oxidising agent will cause oxidation of another species and in doing so will itself be reduced. A reducing agent will cause reduction of another species and in doing so will itself be oxidised.
3. In calculating oxidation states (oxidation numbers):
    a. Any uncombined element has an oxidation state of zero.
    b. An ion of an element has an oxidation number equal to its charge (charges will have the sign after the number (e.g. 2+), whereas oxidation states have the sign before (e.g. +2)).
    c. Combined oxygen has an oxidation state of –2, except in the peroxides, and in compounds containing fluorine.
    d. Combined hydrogen has an oxidation state of +1, except in metal hydrides where it is –1.
    e. In a compound, the total of all the oxidation numbers is zero.
    f. In a molecular ion, the total of all the oxidation numbers is equal to the charge on the ion.
    g. Combined fluorine always has an oxidation state of –1.
4. When naming a compound, the oxidation state of an element is given in roman numerals and in brackets after the element (this is always done for transition metals), e.g. lead (IV) oxide. For an oxoanion, the oxidation number of the central atom is given after the name of the oxoanion, e.g. sodium chlorate (V).
5. When writing half equations:
    a. Only one element changes oxidation state.
    b. Write down the reactant species and the product species containing this element.
    c. Balance the number of moles of the element changing oxidation state.
    d. Add electron(s) to the right or left to balance the change in oxidation state.
    e. Add H_2O molecules to balance the number of oxygen atoms.
    f. Add H^+ ions to balance the number of hydrogen atoms (this will also balance the charge).
6. Half equations can be added together to create the overall equation for a reaction. The electrons must cancel out, and so one (or both) of the reactions will be scaled up to enable this:
    a. All reactions involving ions in either the reactants or the products require aqueous conditions.
    b. All reactions involving H^+ ions in the reactants or the products must be carried out under acidic conditions; those involving OH^- ions require alkaline conditions.

Group VII – The Halogens
1. The halogens are the most reactive non-metal group, with names ending in –ine. These will form halide ions, with names ending in –ide.
2. The electronegativity decreases down the group:
    a. The nuclear charge increases, which should provide a greater attraction for electrons.
    b. There is increased shielding of the nuclear charge from complete inner shells.
    c. The atomic radius is increased, so the electrons are further from the nucleus and the force felt by them is less.

      d.   The increases in shielding and atomic radius are greater than the increase in nuclear charge, and so the electrons are held less strongly by the nucleus.

3. The boiling point increases down the group:
   a. The halogens bond as diatomic molecules, and the intermolecular forces will be weak Van der Waals attractions (instantaneous – induced dipole).
   b. The atomic radius increases down the group, so the molecules have a greater surface area.
   c. The bigger surface area results in greater surface contact, and so the intermolecular forces are larger. These require more energy to overcome, and so the boiling point is increased.

4. Each of the halogens has different properties:
   a. Fluorine is extremely reactive and is very dangerous.
   b. Chlorine is a gas at room temperature, and forms a pale green solution.
   c. Bromine is a liquid at room temperature, and forms an orange solution.
   d. Iodine is a solid at room temperature, and forms a brown solution with water (purple / red in an organic solvent).
   e. Astatine is radioactive and so is dangerous.

5. The halogens dissolve slightly in water, but will dissolve better in an organic solvent (non-polar) such as 1,1,1-trichloroethane.

6. The halogens will undergo displacement reactions with the halides – the halogens get more reactive going up the group, whereas the halides get more reactive going down the group. A more reactive halogen (higher up the group) will displace the halide of a less reactive halogen (lower down the group).

7. The oxidising ability of the halogens depends upon:
   a. The strength of the X–X bond (this must break to form ions). This increases going down the group (the F–F bond is very weak).
   b. The affinity of an X atom for an electron (to form an X^- ion). This doesn't vary very much, so has little effect on the oxidising power.
   c. The energy released when the X^- ion goes into solution. This decreases down the group, as the charge density of the ion increases, so larger ions benefit less.

8. The halides can be tested for by their reaction with silver nitrate solution ($AgNO_3$ (aq)). Dilute nitric acid is added first to remove other ions that may form a precipitate (e.g. CO_3^{2-}):
   a. F^- ions do not form a precipitate.
   b. Cl^- ions form a white precipitate (turns lilac when exposed to light) that dissolves fully in excess NH_3 (aq).
   c. Br^- ions form a cream precipitate that dissolves partly in dilute NH_3 (aq), but fully in concentrated NH_3 (aq).
   d. I^- ions form a yellow precipitate that does not dissolve in NH_3 (aq).

9. AgCl reacts with NH_3 (aq) to form a complex silver diamine ion (the NH_3 molecules are ligands that form coordinate bonds with the silver ion):
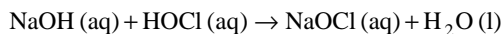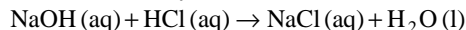
$$AgCl\,(s) + 2NH_3\,(aq) \rightarrow \left[Ag(NH_3)_2\right]^+ (aq) + Cl^-\,(aq)$$
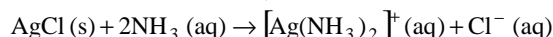
10. Sodium halide (or potassium halide) salts will react with concentrated sulphuric acid:

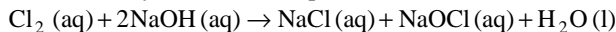| NaX	Observation	Product	Reaction
NaF	Steamy fumes	HF	NaF (s) + H_2SO_4 (l) → HF (g) + $NaHSO_4$ (l)
NaCl	Steamy fumes	HCl	NaCl (s) + H_2SO_4 (l) → HCl (g) + $NaHSO_4$ (l)
NaBr	Steamy fumes	HBr	NaBr (s) + H_2SO_4 (l) → HBr (g) + $NaHSO_4$ (l)
	Colourless gas	SO_2	RED: H_2SO_4 + $2e^-$ + $2H^+$ → SO_2 + $2H_2O$
	Brown fumes	Br_2	OX: 2HBr → Br_2 + $2e^-$ + $2H^+$
NaI	Steamy fumes	HI	NaI (s) + H_2SO_4 (l) → HI (g) + $NaHSO_4$ (l)
	Bad egg smell	H_2S	RED: H_2SO_4 + $8e^-$ + $8H^+$ → H_2S + $4H_2O$
	Purple fumes, black solid	I_2	OX: 2HI → I_2 + $2e^-$ + $2H^+$

11. For each of the sodium halides, the first reaction is a case of a stronger acid (H_2SO_4) displacing the weaker acid (the hydrogen halide) to form the salt of the stronger acid (sodium hydrogensulphate).

12. HI is a better reducing agent than HBr, as the sulphur is reduced from +6 down to –2 for HI, as opposed to +4 for HBr. These are both better reducing agents than HF and HCl, as these don not react with the sulphuric acid at all.

13. Chlorine will react with water to produce hydrochloric acid and chloric (I) acid. This is a disproportionation reaction, as the chlorine is simultaneously reduced and oxidised:

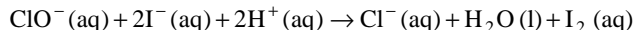$$Cl_2\,(aq) + H_2O\,(l) \rightarrow HCl\,(aq) + HOCl\,(aq)$$
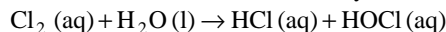
14. Chloric (I) acid will firstly turn damp litmus paper red, as it is an acid, and will then turn it white, as it is also a bleach.
15. The products of the disproportionation reaction will then neutralise a base, such as NaOH. NaOCl (sodium chlorate (I)) is used commercially as a bleach:
$$NaOH\,(aq) + HCl\,(aq) \rightarrow NaCl\,(aq) + H_2O\,(l)$$
$$NaOH\,(aq) + HOCl\,(aq) \rightarrow NaOCl\,(aq) + H_2O\,(l)$$
16. Chlorine will also react directly with NaOH to produce the same overall reaction:
$$Cl_2\,(aq) + 2NaOH\,(aq) \rightarrow NaCl\,(aq) + NaOCl\,(aq) + H_2O\,(l)$$
17. Chlorate (I) ions will readily oxidise iodide ions to iodine in acidified aqueous solution:
$$ClO^-\,(aq) + 2I^-\,(aq) + 2H^+\,(aq) \rightarrow Cl^-\,(aq) + H_2O\,(l) + I_2\,(aq)$$
18. The concentration of iodine in a solution can be calculated using a titration with sodium thiosulphate of known concentration:
    a. The indicator used is starch, but this must be added close to the end-point so that it doesn't bind too strongly to the starch. The colour change is blue/black to colourless.
    b. The iodine is reduced to iodide: $I_2 + 2e^- \rightarrow 2I^-$.
    c. The thiosulphate is oxidised to tetrathionate: $2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^-$.
    d. The tetrathionate has an averaged oxidation number of sulphur as +2.5.

Extraction Of Metals
1. The following ores are used to extract metals:
    a. Haematite – contains Fe_2O_3.
    b. Magnetite – contains Fe_3O_4.
    c. Iron pyrites – contain FeS_2.
    d. Bauxite – contains Al_2O_3.
    e. Rutile – contains TiO_2.
    f. Ilmenite – contains $FeTiO_3$.
2. Iron is extracted from its ore in the blast furnace:
    a. The furnace is lined with heat resistant bricks – the temperature ranges from 2000°C at the bottom, to 400°C at the top.
    b. Coke is added as the reducing agent, and limestone is added to remove the impurities.
    c. Hot air is blasted into the furnace through tuyères.
    d. Iron is tapped of from the bottom of the furnace (it is molten). This is 'pig' or cast iron, and contains about 4% carbon impurity.
    e. Slag is tapped off, as it floats above the iron. This is used for road building, building foundations and fertilisers.
3. Equations for the blast furnace:
    a. C (s) + O_2 (g) → CO_2 (g)   –ΔH
    b. CO_2 (g) + C (s) → 2CO (g)   +ΔH
    c. 3CO (g) + Fe_2O_3 (s) → 3CO_2 (g) + 2Fe (s)   –ΔH
    d. $CaCO_3$ (s) → CaO (s) + CO_2 (g)   +ΔH
    e. CaO (s) + SiO_2 (s) → $CaSiO_3$ (s)
    f. CaO (s) + Al_2O_3 (s) → $CaAl_2O_4$ (s)
4. Steel is made by the basic oxygen steelmaking (BOS) process:
    a. Molten pig iron, scrap steel, and calcium oxide are placed into the converter, along with any alloying elements that are needed for the steel.
    b. Oxygen is blasted onto the mixture through a water-cooled oxygen lance.
    c. The slag forms as a layer on top that can be poured off, and the steel can be tapped off separately.
5. Aluminium ores will not be reduced by carbon, so it is extracted by electrolysis:
    a. Bauxite is purified with NaOH, to remove impurities (e.g. iron (II) oxide and sand).
    b. This is dissolved in molten cryolite, reducing the melting point of Al_2O_3 to save costs (the temperature used is about 850°C).
    c. The mixture is electrolysed in a cell – the anodes are blocks of graphite (these must be regularly replaced as they are oxidised to CO_2), and the cathode is the graphite lining of the cell, at which aluminium is formed and can be tapped off.
6. Half equations for the electrolysis of bauxite:
    a. Anode: $2O^{2-}$ (l) → O_2 (g) + $4e^-$.

b. Cathode: Al^{3+} (l) + $3e^-$ → Al (l)

7. Titanium and tungsten cannot be reduced using carbon, as carbides are formed, which result in impurities in the metal.

8. Titanium is extracted from rutile using the Kroll process (a batch process):
    a. Titanium (IV) chloride is obtained from reactions of pure titanium (IV) oxide.
    b. Titanium (IV) chloride is purified by fractional distillation.
    c. Magnesium or sodium metals are used to displace the titanium from titanium chloride at about 1000°C in an argon atmosphere (to prevent other reactions).
    d. The reaction mixture is heated for 4 days, and then cooled for 4 days. The $MgCl_2$ is removed by heating this mixture. NaCl can be removed by being dissolved in dilute sulphuric acid.

9. Equations for the Kroll process:
    a. Production of titanium (IV) chloride: TiO_2 (s) + $2Cl_2$ (g) + 2C (s) → $TiCl_4$ (g) + 2CO (g).
    b. With magnesium: $TiCl_4$ (g) + 2Mg (l) → Ti (s) + $2MgCl_2$ (l).
    c. With sodium: $TiCl_4$ (g) + 4Na (l) → Ti (s) + 4NaCl (l).

10. Summary of the three methods of extraction:
    a. Reduction with carbon – very cheap, but some metals are too reactive for this method, and it can produce carbides as impurities.
    b. Reduction with metals (e.g. sodium or magnesium) – very expensive, but will produce a pure product. This is only used if the extracted metal is very expensive.
    c. Electrolysis – produces a very pure product, but is very expensive in terms of running costs.

11. Uses of the extracted metals:
    a. Iron – very common and cheap, widely used.
    b. Aluminium – cooking foil, drinks cans, aeroplane parts etc.
    c. Titanium – alloys in aircraft, missiles and car engines (very strong and low density).

12. Pollution problems:
    a. Carbon monoxide produced is poisonous, but is burnt during the extraction process.
    b. Carbon dioxide is a greenhouse gas, and constitutes to global warming.
    c. Gases such as SO_2 and NO_x cause acid rain.
    d. Fine dust is produced in Al extraction, which is emitted through tall chimneys, causing problems elsewhere. The impurities from Al extraction form a red mud.

13. Increasing amounts of recycling take place nowadays, to save money, reduce litter, and solve the problem of declining resources.