3.2 Chemistry: Redox Reactions, Reaction Kinetics

Redox Reactions

- Oxidation and reaction occurs simultaneously in a complementary manner
- One substance is oxidized and another is reduced
- Involves the transfer of electrons between molecules/atoms/substances
- The number of electrons lost by one species always equals to the number of electrons gained by another

Definitions and terms:

- The substance that oxidizes other atoms/molecules/ions is the oxidizing agent (but is itself reduced)
- The acceptor of the electrons is the oxidizing agent
- The substance that reduces other atoms/molecules/ions is the reducing agent (but is itself oxidized)
- The donor of the electrons is the reducing agent
- A substance is oxidized when a reactant loses electrons during the reaction
- A substance is reduced when a reactant gains electrons during the reaction
- An element is oxidized when its oxidation state increases
- An element is reduced when its oxidation state decreases
- Disproportionation reaction: the same reactant undergoes **both oxidation and reduction at the same time**

Half Equations:

- Reactions involving a transfer of electrons can be viewed as two halves
- For NaCl (where $2Na+Cl_2 \rightarrow 2NaCl$)
  - $2Na \rightarrow 2Na^+ + 2e^-$
  - $Cl_2 + 2e^- \rightarrow 2Cl^-$

1) Check that the number of electron lost and gain are the same (if not, multiply by a suitable number)
2) Put the left hand side formulae together with the right hand side formulae and cancel away the electrons on both sides to combine the ions

Oxidation States and Oxidation Numbers:

- A number given to an element preceded by + or – sign
- The number is the charge of the atom of the element would have if it exists as an ion in a compound (even if the compound is covalently bonded)

Assigning Oxidation Numbers:

1) Elements that are uncombined with other elements is always 0
2) In simple monoatomic ions, the oxidation number is simply the charge on the ion
3) In polyatomic ions, the sum of oxidation numbers equals to the charge on the ion
4) The oxidation number of hydrogen in all its compounds is +1, except in metal hydrides where its oxidation number is -1
5) The oxidation number of oxygen in all its compounds is -2, except in peroxides where its oxidation state is -1
6) The oxidation number of Group I elements in their compounds is +1, for Group II elements in their compounds is +2, and for aluminium in its compounds is +3
7) There are many oxidation numbers for Group VII elements in their compounds but the usual one is -1
8) The sum of the oxidation numbers of all the atoms in a molecule or a compound is 0

<u>Reducing and Oxidizing Agents:</u>

Potassium Manganate (oxidizing agent):

	MnO_4^- manganate (VII) ion	Mn^{2+} manganese ion
Oxidation Sate of Mn	+7	+2
Colour	Purple	Colourless

- Used to test for reducing agent (for an unknown substance)
- The potassium manganate must be acidified in order to speed up the reaction

Potassium Dichromate (oxidizing agent)

	$Cr_2O_7^{2-}$ dichromate (VI) ion	Cr^{3+} chromium (III) ion
Oxidation state of Cr	+6	+3
Colour	Orange	Green

- Used to test for reducing agent (for an unknown substance)
- The potassium dichromate is acidified to speed up the reaction

Potassium iodide (reducing agent)

	I^- iodide ion	I_2 iodine
Oxidation State of I	-1	0
Colour	Colourless	Purple/Brown

- Used to test for oxidizing agent (for an unknown substance)

List of Common **Oxidizing Agents**	List of Common **Reducing Agents**
▪ O_2 ▪ Cl_2, F_2 and Group 7 elements ▪ $KMnO_4$	▪ H_2O_2 (will not release oxygen gas) ▪ I^- or all iodides ▪ Cl^- or all chlorides (and all halides)

▪ $K_2Cr_2O_7$ ▪ H_2O_2 (when oxygen gas is released) ▪ Fe^{3+}, Pb^{4+} or transition metal ions with higher oxidation states compared to ions of the same element (as Fe^{2+} and Pb^{2+} have comparatively lower oxidation states)	▪ Most metals (in their neutral state) ▪ CO ▪ SO_2 ▪ Sulphites, eg. Na_2SO_3 (to become SO_4) ▪ Thiosulphates, eg. $Na_2S_2O_3$ (to become SO_4)

Reaction Kinetics

Explanation:

- For a chemical reaction to occur, there must be collisions between the reactant particles, and only a small fraction of the collisions result in a reaction, these are effective collisions
- The rate of reaction depends on the frequency of the effective collisions between reactant particles

Activation Energy:

- All colliding particles require a minimum amount of energy before a reaction can occur (Activation Energy): below this level, a collision cannot occur to produce a reaction
- When the activation energy is high, the reaction is slow, since only a few of the collisions give sufficient energy to produce a reaction (needs catalyst)
- When the activation energy is low, the reaction is fast, since many colliding particles have energies equal to or greater than the activation energy
    - Catalysts make reactions more energetically efficient, and lower the activation energy
    - Catalysts provide a new pathway for reactions (with a lower activation energy) but the original pathway still remains and molecules can use either pathway (unchanged ΔH)

Factors of Rate of Reaction:

I. Increase the **temperature**

- At a higher temperature, the particles have more kinetic energy and they move faster, colliding with each other harder, thus increasing the frequency of effective collisions
- An increase in the number of reactant particles having the activation energy (derived from heat)
- A rise in 10 degrees Celsius will help in doubling the rate of reaction (for most)

II. Increase the **concentration of reactants** (only for liquid/aqueous reactants)

- At a higher concentration, there are more particles per unit volume, thus the particles are closer to each other and the frequency of effective collision increases, increasing the reaction rate
- Increasing the concentration of a reactant would also result in the increase in the amount of products (which does not occur for other factors)

III. Increase the **pressure** (only for gaseous reactants)
- At a higher pressure for gaseous reactants, the particles are in closer proximity and collide more frequently, increasing the reaction rate
- Pressure is used to increase the speed of cooking in a pressure cooker (which increases the number of steam molecules in contact with the food, compared to when steam and water are used at normal atmospheric pressure)

IV. Increase the **surface area of reactants** (only for solid reactants)
- An increased surface area means that the area of contact between the reactants increases thus the number of effective collisions per unit time also increases
- Small pieces of solid have a larger total surface area than large pieces of the same mass (surface area to volume ratio): stirring will cause larger solid particles to break into smaller pieces to increase the rate of reaction
- Flour dust in flour mills and coal dusts in coal mines are hazardous because they can react very quickly, resulting in an explosion

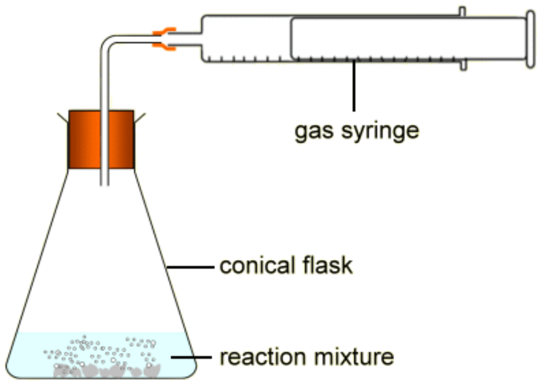
V. Presence of **catalysts**
- Provides an alternative pathway which has a lower activation energy, providing a site for reaction
- Small amount of catalyst can give a large effect (hydrogen peroxide catalyst)
- Enzymes are organic catalysts which control the rate of biochemical reactions in living organisms: they are protein in nature and are destroyed by heat
- Misconception: "A catalyst speeds up the reaction but does not take part in it"
    - Catalysts take part in the reaction, but is itself not chemically reacted

<u>Role of Catalysts:</u>
- Reactions occur more rapidly
    - Catalysts react with the reactants to form an intermediate compound (which then breaks back down into products and catalyst)
    - Lowers the activation energy since the particles can collide with catalyst as well as with each other (more particles have sufficient energy to get over the new energy barrier: this increases the rate of reaction)
- Catalysts are not sued or consumed during the reactions and do not appear as either the products or reactants of a reaction
- Importance in chemical industry: to produce products at an economical rate
    - Use of simple trial and error: most are transition metals (over 2500 catalysts tried for Haber process: production of ammonia)

- Heterogeneous catalyst: of another state compared to the reactants (most catalysts are heterogeneous and are in their solid form)
- Homogeneous: has the same state as the reactants
- Note: catalyst can become poisoned if certain molecules are preferentially adsorbed or permanently attached to the surface of the catalyst (reduces number of active sites and makes catalysts less effective): works the same way as enzyme inhibitors

Measuring the Rate of Reaction:

- Measuring the decrease in the mass of the reaction mixture
- Measuring the increase in the volume of gas formed
- The steeper the slope of the graph at any particular time, the faster the reaction at that time (usually graphs show that the reaction rate is fastest at the start of the reaction when the reactants are at their highest concentration)
- The steepness of the gradient decreases over time, hence the rate of reaction decreases



- When the gradient is zero, the reaction has stopped
- Assumption: one of the products must be a gas