Module 1 - Properties and structure of matter

Elements are pure substances made up of one type of atom that can't be broken down into simpler substances.

Compounds are pure substances made up of 2 or more different types of atoms and can be decomposed by heat, electrolysis, and high energy EM radiation. Compounds can exist in 3 ways:

- Ionic compounds (salts) - A metallic element bonded to one or more non-metallic elements forming a crystal lattice through a complete transfer of electrons. They don't exist as discrete molecules but in a ratio of atoms.
- Covalent compounds - A group of 2 or more non-metal atoms bonded by sharing electrons to form discrete molecules.
- Lattice/Network - A 3D network of atoms chemically bonded in a lattice that are not discrete molecules.

Mixtures are composed of non-chemically bonded substances and can either be:

- Homogeneous - Components are uniformly mixed and have one phase e.g. solutions, alloys, unsaturated salt water.
    - Alloys: Mixture of two or more elements with at least one of them being a metal. Alloys have different properties to the metals which they contain. This makes them more useful than pure metals. They are often harder than the metals they contain e.g. steel, brass, bronze, stainless steel.
- Heterogeneous - Not uniformly mixed and can have more than one phase e.g. muddy water, sand, rocks.

True solutions: made where a solute is dissolved in a solvent. Below 10^{-7} m particle size

Suspensions: where the solute does not dissolve in the solvent. The solute particles will settle and can be filtered out e.g. $CaCO_3$ in water. Above 10^{-5} m particle size

Colloids: particles are dispersed throughout but are not heavy enough to settle. The particles are not as small as a solution but are smaller than those of a suspension. They can be separated by filtering e.g. milk, mayonnaise, paint, fog. 10^{-5} to 10^{-7} m particle size

Physical changes only affect the form of the substance

- Substance changes its physical appearance but not composition
- Changes are reversible
- Involves the breaking of intermolecular forces but not bonds
- Particles stay the same but move differently
- A small amount of heat or energy may be taken in or given out

Chemical changes affect the chemical composition of the substance

- A new substance is formed
- A gas may be given off
- There may be a change in colour
- There may be a change in temperature
- A precipitate may form
- Changes are irreversible

STP: 0C 100kPa and SATP / RTP / NTP / SLC: 25C 100kPa unless given otherwise

Mixtures in the Spheres of the Earth

There are 4 spheres:
- Biosphere - Living organisms
  - Mixtures of carbon containing compounds
- Lithosphere - Earth's outer mantle and crust
  - Contains mixtures such as soils, rocks, sand, mineral ores, coal, oil and natural gas.
- Hydrosphere - Earth's Water
  - Mixtures of water, sodium chloride, magnesium and calcium chlorides
- Atmosphere - Gases above Earth's surface
  - Mixtures of gases e.g. N_2, O_2, CO_2, H_2O

Separation techniques and their properties:

| Separation Method	Property which enables separation
Sieving	Particle size
Evaporation	Liquid has a lower boiling point than solids
Distillation	Relatively large differences in boiling point between two substances
Fractional Distillation	Small differences in boiling point between two substances usually in the same phase
Separating funnel	Components are immiscible and have different densities
Filtration	One solid, the other a liquid or solution
Sedimentation	Density

- Qualitative analysis - Determining what substances are present
- Quantitative analysis - Determine how much of each substance is present

To calculate the percentage composition by mass or calculate the mass of each component use the formulae:
- $\frac{Mass\ of\ component}{Total\ mass\ of\ mixture} \times 100$
- *% of component × mass of the mixture*

Orbitals are geometric areas of 95% electron presence probability as determined by Schrodinger's equation in which one or two electrons can move. Principal energy levels (1, 2, 3…) are groupings of similar energy sublevels (s, p, d, f) which are in turn groupings of individual orbital lobes.
- In order to have probability in excess of 99%, an area the size of the observable universe is required
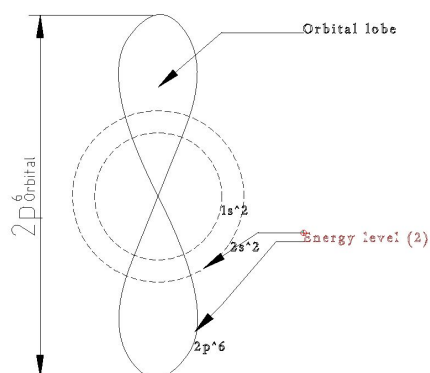
- The Aufbau principle governs that electrons fill atomic orbitals of the lowest available energy levels before occupying higher levels
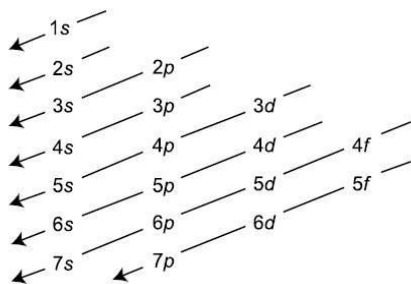
- Exceptions to Aufbau principle occur in the d block due to the reduced energy distinction between s and d levels and Coulombic repulsion (incl. Cu, Ag, Cr)
- The Heisenburg uncertainty principle states that the position and momentum of a particle (such as an electron) can not be measured accurately simultaneously
- The Pauli exclusion principle and Hund's rule states that orbitals of an energy level are always filled first by electrons with $+\frac{1}{2}$ spin and are then completed with electrons of $-\frac{1}{2}$ spin (identical fermions cannot occupy the same quantum state within a system). E.g. Oxygen
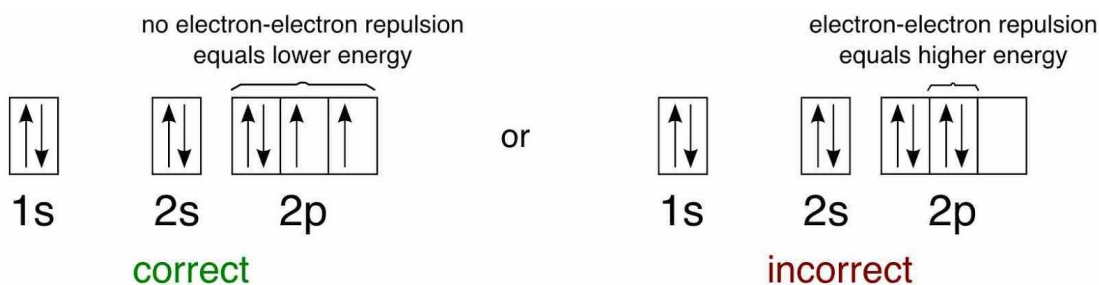
Valence electrons are the electrons present in the outermost shells of an atom
- Elements in the same group have the same number of valence electrons
- Valency is the maximum number of direct bonds formable with the element. Variable valency may occur when an atom loses or gains more electrons than the valence shell.

Orbital notation can be determined by filling to the appropriate orbital given the number of electrons or through the use of spdf blocks on the periodic table by counting the number of filled orbitals.
- Helium and groups 1 and 2 comprise s orbitals from energy levels 1-7
  Transition metals comprise d orbitals from energy levels 3-6

- Excluding helium, groups 13 - 18 comprise p orbitals from energy levels 2-7
 Lanthanides and actinides comprise group f from energy levels 4-5

Periodic Table of the Elements
Orbital Shell Blocks

Atomic emission spectra and flame tests are based on the excitation of electrons:
When electrons are supplied with energy they can become excited.
De-excitation causes the release of energy. The re-emission of energy
occurs as different wavelengths of light.

- Flame test: visible spectrum of light indicates ion
- Mass spectrometry analyses the spectrum of light released by
  means of dispersion through an electromagnetic lens and
  detection by an amplifier wherein positive species are detected
  and neutral species are eliminated
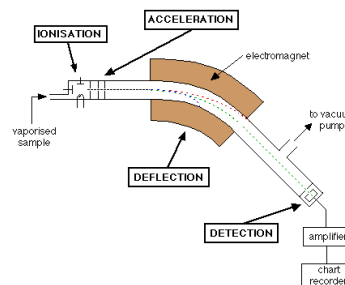
Isotopes and radioactive chemistry:
Isotopes are elements with the same number of protons and different numbers of neutrons and are named
by their mass number. Given the notation $^A_Z M$. A represents the mass number and Z represents the
atomic number.
Ionising radiation is classified into several primary types:

- <u>Alpha radiation consists of the emission of a particle of</u> $^4_2 He$ with charge +2 and a large relative
  mass and reduced penetration (typically blocked by paper)
- <u>Beta radiation consists of the emission of electrons (</u>β^-, $^0_{-1}e$<u>) or positrons (</u>β^+, $^0_{+1}e$<u>),</u> charge is -1,
  mass is minimal, and penetration is moderate (blocked by sheets of lead or aluminium)
- <u>Gamma and X-ray radiation consists of high energy electromagnetic radiation</u>, with charge 0 and
  mass 0, penetration is high (blocked by thick lead or concrete)
- Neutron radiation is able to penetrate through layers of concrete but decays quickly, has relatively
  increased mass, no charge, and high penetration (shielding typically consists of several metres of
 concrete or boron/cadmium compounds (dissolved in water) or metal)

To calculate relative atomic mass (RMS) use: $RMS = \sum(relative\ abundance\ of\ isotope \times mass\ of\ isotope)$

Technetium 99m in medicine:

It is formed by $^{98}_{42}Mo + {}^{1}_{0}n \rightarrow {}^{99}_{42}Mo \rightarrow {}^{99}_{43}Tc + {}^{0}_{-1}e$

Technetium 99m is used as a radiotracer in medical diagnostic procedures such as SPECT scans in oncological, cardiothoracic, and other fields

Band of Stability:
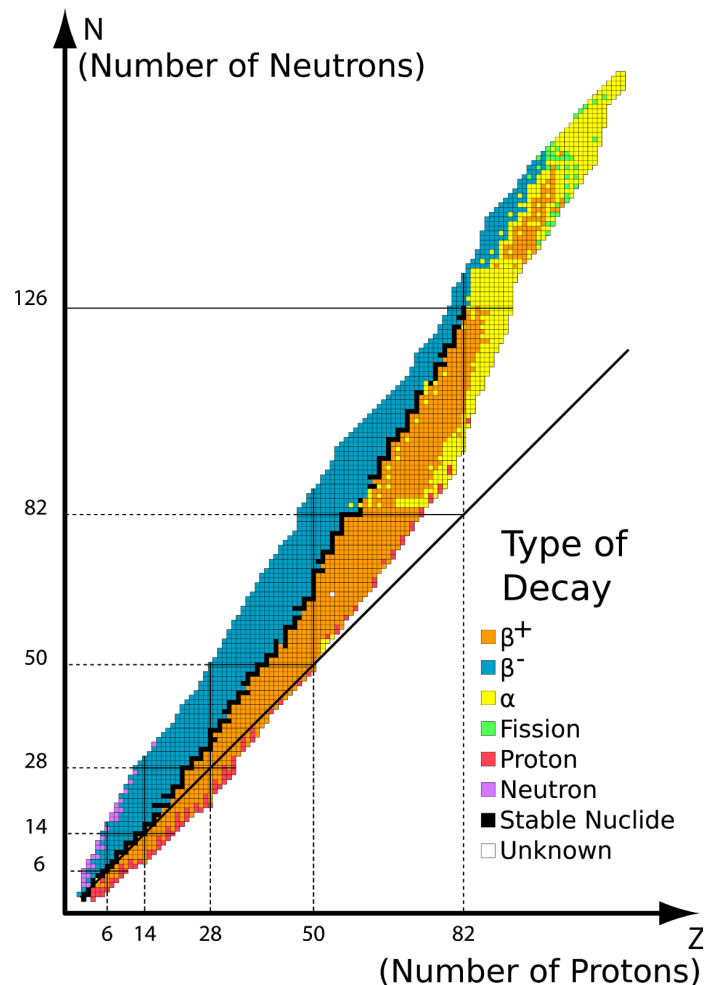
Periodicity:

Increasing from the given corner:

- Upper-right → lower left:
  - Atomic radius
  - Metallic character
- Lower-left → upper right:
  - Ionisation energy - The energy needed to remove an electron from a **gaseous** atom
  - Electron affinity
  - Electronegativity - The ability of an atom to attract electrons
  - Non-metallic character

Additionally:.

- Core Charge (The number of valence electrons) increases across a period

- Reactivity increases from the upper right corner of s, d, f-blocks and from the lower left corner in p block, excepting noble gases
- Shielding increases with period
- Melting point and boiling point increase until across the period from group 1 to group 14, then drastically drops for groups 15-18. M.p. and B.p. decrease down a group, suggesting that metallic bonds in crystals of metals are weaker as atoms get larger.
- Valency +1 for group 1, +2 for group 2, variable for d-block, and +3, -4, -3, -2, -1, 0 for p-block
  - 1,2,3,t,4,3,2,1,0

Chemical bonding and intermolecular forces:
Allotropes are different physical forms of an element in which an element can exist in a given phase.

Example: Carbon has multiple allotropes including: diamond, graphite and fullerenes:
- Diamond:
  - Has a high refractive index
  - Hardest natural material - used in industrial cutting, drilling equipment
  - 3D strong covalent network lattice - strong, hard, rigid
  - Every carbon is bonded to 4 other carbon atoms in tetrahedral arrangement
  - Does Not conduct electricity
  - Brittle due to rigid structure
  - As atoms are held together very strongly, it is a good thermal conductor
- Graphite
  - Carbon atoms are bonded in flat hexagonal rings in layers, but weak dispersion forces between the layers make graphite hard in one direction but slippery and soft in another direction.
  - It is a dry lubricant
  - It is a good heat insulator
  - Each carbon is bonded to 3 other carbons, leaving a free valence electron. This delocalised electron is free to move, so graphite is a good conductor of electricity
- Fullerenes
  - Made up of molecules containing carbon atoms arranged in a cage like structure
  - Similarly to graphite, it can conduct electricity
  - They can be spherical or cylindrical
  - Can be used in drug delivery systems in the body

Polarity and Intermolecular Forces:

Polarity means there is a net difference in charge between two areas in a molecule: If two bonded atoms are different, the electrons will stay closer to the more electronegative atom (has stronger pull). This produces a small charge imbalance, making one end of the bond more negatively charged δ^- than the other δ^+. The difference in electronegativity can lead to three outcomes:
- No difference → Nonpolar covalent
- Intermediate difference → Polar covalent

- Very different → Ionic

Polarity is determined by electronegativity and molecular geometry (VSEPR)

Types of intermolecular forces list by strength in descending order:

- Ionic bonding commonly occurs between negatively and positively charged ions (sodium chloride crystals)
- Ion-dipole interactions occur between polar molecules and charged ions (sodium ions in water)
- Hydrogen bonding occurs when electropositivity induced (from F, N, O) on a hydrogen ion leads to dipole-dipole-type interactions. For hydrogen bonding to occur, a hydrogen atom must be bonded to three very electronegative atoms which are F, N and O. This creates a large partial positive charge on the hydrogen and is attracted to the lone pairs on nitrogen, oxygen or fluorine. Hydrogen bonds are 10 times stronger than dipole-dipole bonds but only 1/10th the strength of an ionic or covalent bond. Hydrogen bonding is present in compounds such as water and ethanoic acid. The density of ice is less than liquid water as when water freezes, it forms a lattice, with molecules being held further apart than in liquid.
- Dipole-dipole interactions occur in molecules that have a net dipole such as in polar molecules (NH_3 - NH_3, ICl - ICl). These forces result from the electrostatic attraction between the positive and negative ends of two or more dipoles. These forces are relatively weak as the partial charges are small. However, the more polar a molecule is, the stronger the dipole-dipole forces will be.
- Ion-induced dipole interactions occur when a relatively stronger ion induces the polarisation of an electron cloud in another molecule (Fe^{2+} ion - dioxygen)
- Dipole-induced dipole interactions occur where a polar molecule with dipole moment asymmetricality induces the polarisation of an electron cloud in another molecule (HCl - dichloride)
- Dispersion forces occur when momentary dipoles are formed. Weakest of all IMFs. This temporary charge can influence a change in the charge distribution in nearby molecules. This creates a temporary charge between the negative end and a positive end of two different molecules. There are billions of these interactions being made and broken every second. The strength of a dispersion force increases as the size of the molecule increases as more electrons will increase the probability of temporary dipoles.

*Types of molecular structures:*

Crystalline structures are usually solid, non-volatile, and have high melting points:

- An attraction and combination between a cation and an anion will form an ionic lattice network. They are large structures that naturally exist due to intermolecular electrostatic attractions. They conduct electricity when molten or aqueous as for substances to conduct electricity, they must have charged particles that are free to move. Ionic compounds are hard. There are no discrete molecules and their formulas are empirical.
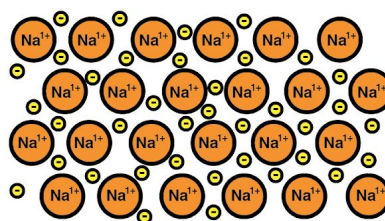
Ionic Bonding

Crystal Lattice
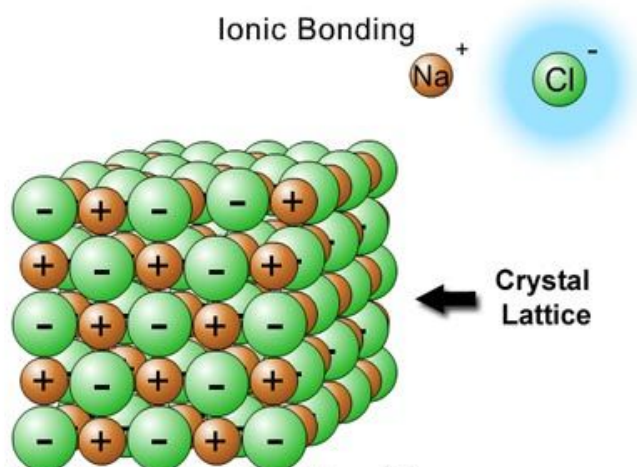
- Metallic networks have a sea of delocalised electrons surrounding a positively charged cation with electrostatic bonding and good conductivity of electricity and heat. The electrostatic attraction between the cations and delocalised electrons is called *metallic bonding*. They have lustre and are malleable. E.g. zinc and sodium
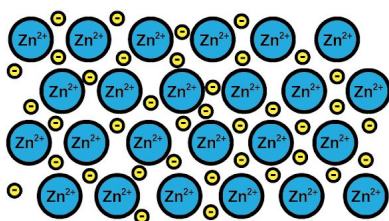

Zinc

Sodium

- Covalent lattice networks have covalent bonding throughout the structure and are similar to ionic lattice but have higher melting points and generally do not conduct electricity e.g. Diamond, Graphite, Silicon Dioxide, Silicon Carbide. They are of tetrahedral shape.
- Covalent molecular compounds are usually amorphous liquids or gases, volatile, have low boiling points, are poor conductors, and are soft.

Molecular geometry:

The octet rule states that atoms generally combine to obtain the noble gas configuration (8 valence electrons). A share of 8 valence electrons is the most stable arrangement of electrons, however it doesn't apply to certain molecules including BF_3, PCl_5 and SF_6. VSEPR is a theory used to predict the geometries of molecules with a central atom around which bonding occurs by modelling the repulsion of valence shell electrons from each other
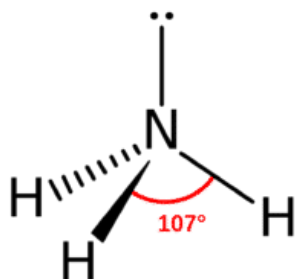
- Tetrahedral:
  - This is the most stable way for four equal electron clouds to arrange themselves
  - There are 4 bonding pairs, and no lone pairs [4,0]
  - 109.5 degree angle between atoms
  - E.g. NH_4, CH_4, $SiCl_4$, CCl_4
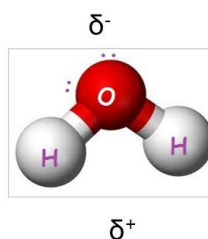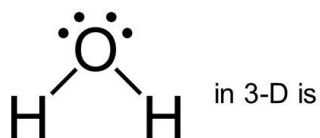
A   **B**
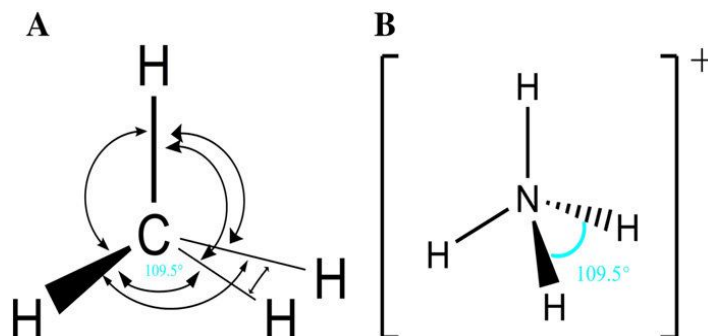
- Trigonal pyramidal:
  - Tetrahedral arrangement of electron pairs without one of the atoms.
  - Has 3 bonding pairs and 1 lone pair [3,1]
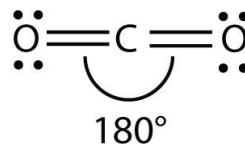 - 107 degree angle between atoms
  - E.g. NH_3, PCl_3
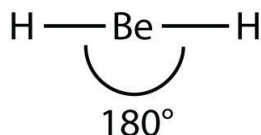
- Bent shape:
  - Tetrahedral arrangement of electron pairs but only two are bonded.
  - 2 bonding pairs and 2 lone pairs [2,2]
  - 105 degree angle between atoms
 - E.g. H_2O, H_2S, CH_2

- Linear:
  - Tetrahedral arrangement of electron pairs but only one bonding pair, or 2 bonding pairs with no lone pairs (CO_2, HCN, BeH_2) [2,0] [2,3]
  - 180 degree angle
  - E.g. HCl, HF

- Trigonal planar:
  - Repulsion between electron pairs is minimised by a triangular arrangement about the central atom such that the electron pairs are in the same place.
  - 3 bonding pairs and no lone pairs [3,0]
  - 120 degree angles between atoms
  - E.g. BH_3, BF_3, SO_3, NO_3^-

Boron Hydride
BH_3

Boron Trifluoride
BF_3
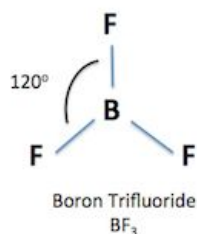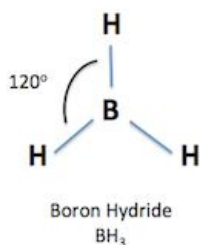
- A - Central atom X - Ligands to other atoms E - Lone pairs
- Linear: [2,0] [2,3] (CO2) Bent: [2,1] [2,2] (H2O)Trigonal pyramidal: [3,1] T-shaped: [3,2] Tetrahedral: [4,0] Disphenoidal:[4,1] Square planar:[4,2]Trigonal bipyramidal:[5,0] Octahedral: [6,0] (SF6)

Lewis diagrams:

Dots on lewis diagrams represent the number of valence electrons in the given atom (octet rule generally states a full shell is 8 valence electrons)

For ionic compounds, bracket the ion structure with the charge

Line bonds represent covalent bonds only
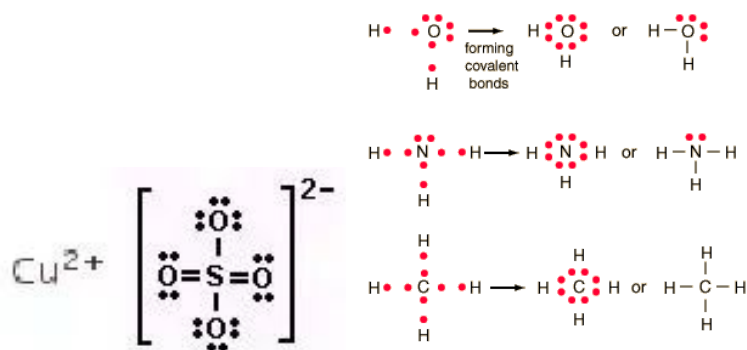
Evolution of atomic theories:

Dr. David C. Stone   University of Toronto Chemistry

Democritus:

Shit be made of atoms

Dalton: Different elements have atoms of differing size and mass

Thomson: Plum pudding model: small electrons in a large area of positive charge

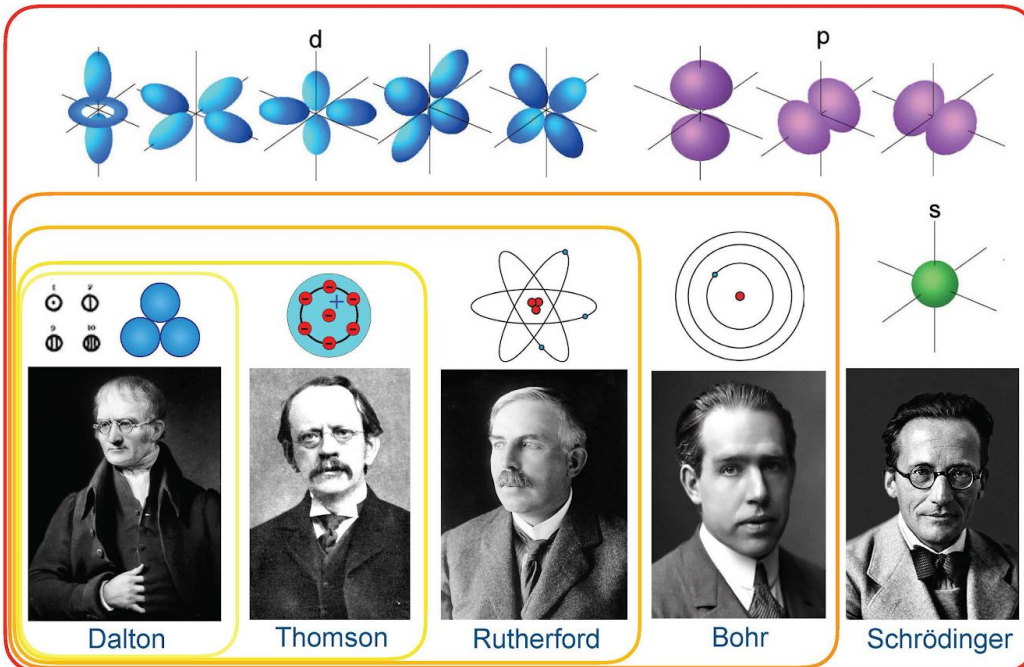Rutherford: Atom has a positively charged nucleus (gold foil experiment); electrons orbit the nucleus

Bohr: Electrons exist in discrete energy levels

Schrodinger: Quantum/geometric model of electron position (orbitals)

Chadwick: Discovery of neutrons in the nucleus

Module 2 - Quantitative chemistry

Stoichiometry

Mass, energy, and number of atoms are always conserved in reactions. Balanced chemical equations show mole ratios.

Relative atomic mass of an element is calculated by the weighted average of isotopic masses (protons and neutrons)

To calculate <u>density</u> , use the formula $d = \frac{m}{v}$. As temperature increases, density decreases.

Relative molecular mass (molecular weight) is given by the sum of the relative atomic masses of the atoms as given in the molecular formula.

The <u>number of moles</u> (n) can be found with $n = \frac{Mass(g)}{Molar\ Mass} = \frac{m}{MM} = \frac{Number\ of\ particles}{N_A}$

Number of atoms in a mole is given by the Avogadro constant (number of atoms in 12g of C-12):

$N_A = 6.022 \times 10^{23}$. To find the number of atoms, use $N = n \times N_A$.

The volume of 1 mol of an ideal gas at 25C and 100kPa (SATP) is 24.79 L and is 22.71L at 0C and 100kPa.

Molecular or formula mass is given as $g\ mol^{-1}$

To calculate the empirical formula from experimental data in a given compound: find the moles of each compound and find the relevant ratio of moles.

In a reaction, the Limiting reagent is a substance which does not contain enough moles for the complete reaction of another substance to occur, resulting in a leftover reactant.

Preparing solutions

Concentration is measured in three ways:
- Percentage by volume (%v/v), where both volumes are the same unit e.g. (mL/100mL).
- Percentage by mass (%w/w) where both masses are in the same unit e.g. (g/100g).
- Percentage by mass/volume (%w/v) where units are preferably (g/100mL) or (kg/100L).

Some conversions:
- ppm = mg/L = mg/kg = mL/1000L = g/1000kg
- 1g = 1000mg
- 1mg = $1000\mu g$ (micrograms)
- 1ppm = $1\mu g/g$ = 1mg/kg
- 1ppb = $1\mu g/kg$ = 1mg/tonne

Concentration of a solution in mol/L is given by: $c = \frac{n}{v}\ or\ c = \frac{m}{MM \times v}$ where v is in litres and mass is in grams. Hence, the number of moles can also be calculated by $n = c \times v$

Dilution of a given solution by the same solvent is given by $c_1 v_1 = c_2 v_2$

Additionally: 1 PPM $= 1\ mg\ L^{-1} = 1\ g\ m^{-3} = 1\ g\ /\ 1000L$

Measuring cylinders are used for approximate measurements of about ±5%, pipettes and burettes deliver variable accurate volumes of about ±0.2% to ±0.5%, whilst volumetric flask deliver fixed volumes with the same accuracy as the latter.

Preparing a standard solution:
1. Calculate the mass of a substance you need to dissolve in a certain volume to make a desired concentration for a solution using $c = \frac{m}{MM \times v}$
2. Weight the desired mass and transfer to a clean beaker.
3. Add distilled water until the mass is fully dissolved.
4. Transfer the solution to a desired volume volumetric flask using a filter funnel.
5. Rinse the beaker while transferring the washings into the volumetric flask.
6. Add distilled water until the bottom of the meniscus is on the calibration line.
7. Cork the volumetric flask and shake to ensure it is completely dissolved.

Gas laws:

Kinetic molecular theory of gases states that gases are made up of atoms or molecules, and as the temperature rises, so does the kinetic energy of the gas particles.

$Pressure = \frac{Force}{Area}$ where force is in Newtons and area is in m^2.

Units of gas pressures:

- $1n/m^2 = 1Pa$ (pascal).
- $1000Pa = 1kPa$
- $1atm$ (atmosphere) $= 101.3kPa$
- $1bar = 100kPa$

<u>Boyle's law:</u> <u>Pressure is inversely proportional to Volume</u>. Given by the formula: $P_1V_1 = P_2V_2$

<u>Charles's law:</u> <u>Volume is proportional to Temperature</u> given by the formula: $\dfrac{V_1}{T_1} = \dfrac{V_2}{T_2}$ where temperature is in Kelvin.

<u>Gay-Lussac's gas law:</u> <u>Pressure is proportional to temperature</u> Combined gas law: $\frac{PV}{T}$ is constant. Also given by the formula $\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2}$ where temperature is in Kelvin.

<u>Gay Lussac's law of combining volumes:</u> When measured at <u>constant temp and pressure, volumes of gases in a reaction show simple whole number ratios</u> to each other given by the formula: $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$ where temperature is in Kelvin.

Avogadro's Law: States that equal volumes of has at the same pressure and temperature contain an equal number of molecules given by the formulae: $V = N_A \times n$ and $\dfrac{V_1}{n_1} = \dfrac{V_2}{n_2}$

<u>Ideal gas law:</u> $PV = nRT$ where r $= 8.314$. Non-ideal gas behaviour occurs at high pressures (ideal gas laws do not account for space taken up by the molecules themselves) and low temperatures (intermolecular attractions result in decreased pressure)

For stoichiometric calculations use a BCA table.

Module 3 - Reactive chemistry

Types of reactions:
- Synthesis: reactions in which two or more substances combine to form a new substance:
    - $A + B \rightarrow AB$
- Decomposition: When a substance decomposes into two or more substances by light, heat or electricity:
    - $AB \rightarrow A + B$
- Acid-base (neutralisation) reactions: acid reacts with a base to form a salt and water depending on the reaction.
    - E.g. $HCl_{(aq)} + NaOH_{(s)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$
- Combustion reactions: When elements or compounds are burnt in oxygen. Complete combustion will form carbon dioxide and water while incomplete combustion can form carbon or carbon monoxide:
    - Complete Combustion e.g: $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$
    - Incomplete combustion e.g: $CH_{4(g)} + O_{2(g)} \rightarrow C_{(s)} + 2H_2O_{(l)}$,
      $CH_{4(g)} + \frac{3}{2}O_{2(g)} \rightarrow CO_{(g)} + 2H_2O_{(l)}$

- Precipitation reactions (double displacement): When two solutions of soluble ionic compounds are mixed together, they can either mix together completely or form an insoluble precipitate (ppt).
  - $AB + CD \rightarrow AD + CB$
  - Precipitation e.g: $AgNO_{3(aq)} + NaCl_{(aq)} \rightarrow NaNO_{3(aq)} + AgCl_{(s)}$
  - Solubility laws for precipitates:

TABLE 4.1 Solubility Rules for Ionic Compounds in Water

Compounds Containing the Following Ions Are Generally Soluble	Exceptions
Li^+, Na^+, K^+, and NH_4^+	None
NO_3^- and $C_2H_3O_2^-$	None
Cl^-, Br^-, and I^-	When these ions pair with Ag^+, Hg_2^{2+} or Pb^{2+}, the resulting compounds are insoluble.
SO_4^{2-}	When SO_4^{2-} pairs with Sr^{2+}, Ba^{2+}, Pb^{2+}, Ag^+, or Ca^{2+}, the resulting compound is insoluble.

Compounds Containing the Following Ions Are Generally Insoluble	Exceptions
OH^- and S^{2-}	When these ions pair with Li^+, Na^+, K^+, or NH_4^+, the resulting compounds are soluble.
	When S^{2-} pairs with Ca^{2+}, Sr^{2+}, or Ba^{2+}, the resulting compound is soluble.
	When OH^- pairs with Ca^{2+}, Sr^{2+}, or Ba^{2+}, the resulting compound is slightly soluble.
CO_3^{2-} and PO_4^{3-}	When these ions pair with Li^+, Na^+, K^+, or NH_4^+, the resulting compounds are soluble.

- Acid-carbonate reactions: Acid reacts with carbonate to form water, salt, and carbon dioxide
  - E.g. $Na_2CO_{3(s)} + 2HCl_{(aq)} \rightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$
- Metal - Oxygen reactions: A metal burns in oxygen to form a metal oxide:
  - E.g. $2Mg_{(s)} + O_{2(g)} \rightarrow 2MgO_{(s)}$
- Metal - Water reactions: Metal reacts with water to form a metal hydroxide and hydrogen gas:
  - E.g. $2Na_{(s)} + 2H_2O_{(l)} \rightarrow 2NaOH_{(s)} + H_{2(g)}$
- Acid-metal reactions: acid reacts with a metal to form a metal salt and hydrogen gas
  - E.g. $Zn_{(s)} + H_2SO_{4(aq)} \rightarrow ZnSO_{4(aq)} + H_{2(g)}$
- Metal Displacement Reactions: The more reactive metal will displace a less reactive metal in a compound:
  - $A + BC \rightarrow AC + B$
  - E.g. $Zn_{(s)} + CuSO_{4(aq)} \rightarrow ZnSO_{4(aq)} + Cu_{(s)}$
  - Determine which metal will displace another through the metal activity series or from highest to lowest on the reduction potentials table.

- Metals with a lower ionisation energy, large atomic radius and lower electronegativities will be the most reactive.
- The metal activity series can be seen below:

Metal	Oxidation Reaction
Lithium	$Li(s) \longrightarrow Li^+(aq) + e^-$
Potassium	$K(s) \longrightarrow K^+(aq) + e^-$
Barium	$Ba(s) \longrightarrow Ba^{2+}(aq) + 2e^-$
Calcium	$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$
Sodium	$Na(s) \longrightarrow Na^+(aq) + e^-$
Magnesium	$Mg(s) \longrightarrow Mg^{2+}(aq) + 2e^-$
Aluminum	$Al(s) \longrightarrow Al^{3+}(aq) + 3e^-$
Manganese	$Mn(s) \longrightarrow Mn^{2+}(aq) + 2e^-$
Zinc	$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$
Chromium	$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$
Iron	$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^-$
Cobalt	$Co(s) \longrightarrow Co^{2+}(aq) + 2e^-$
Nickel	$Ni(s) \longrightarrow Ni^{2+}(aq) + 2e^-$
Tin	$Sn(s) \longrightarrow Sn^{2+}(aq) + 2e^-$
Lead	$Pb(s) \longrightarrow Pb^{2+}(aq) + 2e^-$
Hydrogen	$H_2(g) \longrightarrow 2H^+(aq) + 2e^-$
Copper	$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$
Silver	$Ag(s) \longrightarrow Ag^+(aq) + e^-$
Mercury	$Hg(l) \longrightarrow Hg^{2+}(aq) + 2e^-$
Platinum	$Pt(s) \longrightarrow Pt^{2+}(aq) + 2e^-$
Gold	$Au(s) \longrightarrow Au^{3+}(aq) + 3e^-$

Ease of oxidation increases

- Reduction-oxidation (redox) reactions: Oxidation refers to loss of electrons and reduction refers to the gain of electrons. A reaction is a redox reaction if there is a change in oxidation number, which can be found using the following table:

Rule	Examples (O.N is in exponent)
1. The oxidation number (O.N) of a free element is 0.	Na^0, C^0, Cl_2^0, P_4^0
2. The oxidation number of a simple ion is equal to the charge of the ion.	Na^{+1}, Cl^{-1}, Mg^{+2}, Al^{+3}, N^{-3}
3. Main group elements have an oxidation number equal to their charge on ions.	Ionic compounds: $K^{+1}Cl$, $Mg^{+2}SO_4$

4. Hydrogen in a compound has an oxidation number of +1 except for metal hydrides where it has an oxidation number of -1.	Compounds of H: $H_2^{+1}O$ Metal hydrides: NaH^{-1}, CaH_2^{-1}
5. Oxygen has an oxidation number of -2 except for: - In fluorine it has an O.N of +2 - In peroxides it has an O.N of -1	Compounds of O: H_2O^{-2} Peroxides: $H_2O_2^{-1}$, BaO_2^{-1}
6. The sum of the oxidation numbers in a neutral compound is 0.	$C^{+4}O_2^{-2}$ Note: $+4+2\times-2=0$
7. The sum of oxidation numbers in a polyatomic ion is equal to the charge on the ion.	In the polyatomic ion SO_4^{2-}, S has O.N of +6 and O has an O.N of -2. $+6+4\times-2=-2$
8. The most electronegative element is given the negative oxidation number.	$O^{+2}F_2^{-1}$

- Redox reactions can be shown in:
  - Half equations showing the transfer of electrons
  - Neutral species equation: shows the compounds involved in the reaction
  - Complete ionic equation: shows all ions present in the reaction mixture
  - Net ionic equation: shows the ions undergoing the reaction omitting spectator ions
- Deriving the different types of equations:
  - Balanced formula (neutral species) equation:
    - $2KI_{(aq)}+Pb(NO_2)_{3\ (aq)} \rightarrow PBI_{2\ (s)}+2KNO_{3\ (aq)}$
  - Total ionic equation (also complete ionic):
    - $2K^+_{(aq)}+2I^-_{(aq)}+Pb^{2+}_{(aq)}+2NO_3^-_{(aq)} \rightarrow PBI_{2\ (s)}+2K^+_{(aq)}+2NO_3^-_{(aq)}$
  - Net ionic equation
    - $Pb^{2+}_{(aq)}+2I^-_{(aq)} \rightarrow PbI_{2\ (s)}$

Galvanic cells and standard electrode potentials
Galvanic cells generate electricity through reduction-oxidation reactions
- Anode: Oxidation occurs to produce free electrons in the more reactive metal.
- Cathode: Electrons flow to the cathode and reduction occurs to create positively charged ions
- Salt bridge: completes the circuit and conserves solution neutrality. Without the salt bridge, a build-up of charge in the solutions and this would prevent further electrons or ions from forming due to chemical equilibrium. The anions flow towards the anode to balance the positive ions and the cations flow towards the cathode to balance the negative charges.

The standard hydrogen half-cell consists of platinum metal immersed in a 1 mol/L solution of H+, with hydrogen gas being bubble over the electrode at 100kPa

For reactions occurring in the direction of reduction ($K^+ + e^- \rightarrow K\,(s)$): a higher value indicates a stronger tendency to form the non-ionic form whilst a lower value indicates a tendency to form ions

Voltage of a galvanic cell under standard conditions is given by:
$$E^o_{total} = E^o_{reduction} + E^o_{oxidation}$$

- Galvanic cells are spontaneous when the cell voltage is positive
- Oxidising agents themselves are reduced and vice versa
- Galvanic cell notation $X(s)\,|\,X^+(aq)\,||\,Y^+(aq)\,|\,Y(s)$ where the left is the anode / oxidation

Example of a Galvanic Cell:

- Copper is gaining electrons, and hence the cations attach themselves to the cathode and become neutral atoms -> the cathode becomes bigger
- Zinc is losing electrons and the neutral atoms are becoming ions dissolved in the water -> the anode becomes smaller
- Electron loss in a reaction is denoted on the RHS, whereas gain is on the LHS
- $Zn\,(s)\,|\,Zn^{2+}(aq)\,(1M)\,||\,Cu^{2+}\,(aq)\,(1M)\,|\,Cu\,(s)$ for the given example
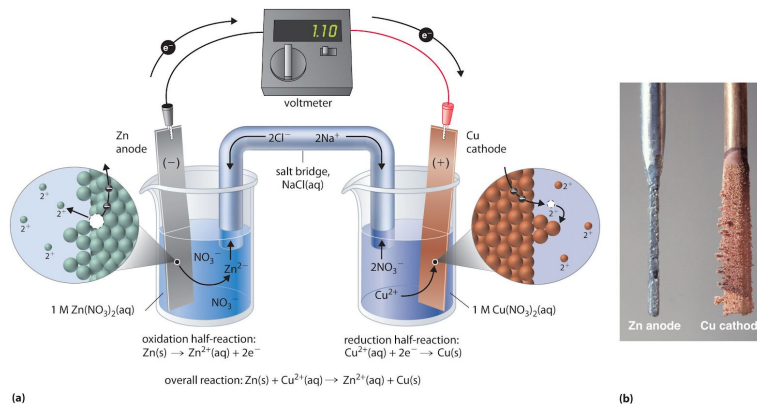
Rates of reactions
Collision theory: States that reactions occur as a result of collisions between the reacting particles. It is based on the kinetic energy of particles. For a reaction to occur, the reactant particles must:

- Collide with each other
- Collide with sufficient energy to break the bonds within the reactants and reach the activation energy
- Collide with the correct orientation to break the bonds within reactants to allow for the formation of new products

Activation energy: The minimum energy that a collision must possess for a reaction to occur.
The rate of reaction can be measured through time or loss of mass.
Factors that change the rate of reaction include:

- Surface area - Higher surface area provides more surface for collisions to occur.
- Temperature - Higher temp increases kinetic energy, increasing the probability of collisions.
- Concentration - Higher concentration means there are more particles, increasing the probability of collisions.
- Pressure (gases) - Higher pressure moves particles closer together, increasing the probability of collisions.
- Presence of a catalyst. Catalysts speed up the rate of reaction but are not used up themselves. They provide an alternative pathway for a reaction which has a lower activation energy. Due to

this, more particles will be able to collide with sufficient energy for a reaction to occur Examples are:

- ○ Iron (Fe) - used in the production of ammonia
    - ■ $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$ $\Delta H = -92kJ/mol$
- ○ Platinum (Pt) - Used in cars to catalyse carbon monoxide into carbon dioxide.
    - ■ $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$
- ○ Potassium permanganate ($KMnO_4$) - Used to decompose hydrogen peroxide into water and oxygen.
    - ■ $2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$
- ○ Biological catalysts (enzymes) - Chlorophyll in leaves increases the rate of reaction of photosynthesis.
- Heterogeneous catalysts are of a different phase to reactants (example: gas - liquid)
- Homogeneous catalysts are of the same phase to reactants.
- Homogeneous reactions occur in a single phase (example: liquid - liquid)

Module 4 - Drivers of reactions

All chemical substances hold chemical potential energy.
Bond Breaking requires energy while bond making releases energy.
Exothermic reactions release heat into the surroundings whilst endothermic reactions absorb heat into the system:

- In exothermic reactions, the energy released when making bonds is greater than the energy needed to break bonds.
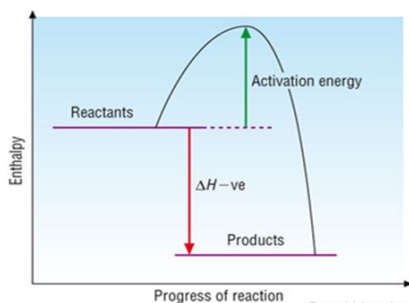
- Endothermic reactions require a constant input of heat and cannot be self-sustaining i.e. the energy required to break bonds is larger than the energy released when making bonds.
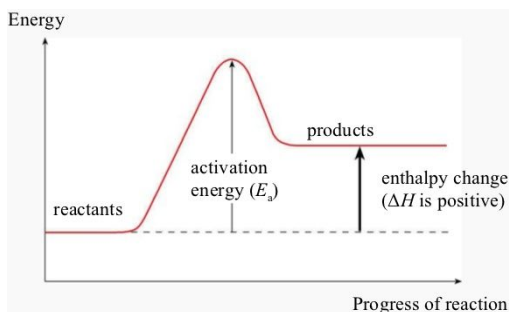
Enthalpy represents the total heat content of a system and is given in joules (J)

- Change in enthalpy is given as ΔH. It can be calculated using the formula:

$$\Delta H = H_{products} - H_{reactants}$$ where H is the heat content of a substance.

Heat of combustion (ΔH_c) is the energy released when 1 mol of a substance combusts completely at SLC. To determine energy released when n mole of a fuel burns use: $Energy\ released = n \times \Delta H_c$ when ΔH_c is given. The determine the heat of combustion from an experiment, use: $q = mc\Delta T$ where q is the amount of energy in joules, c is the specific heat capacity (usually water (4.18)), and ΔT is the change in temperature.

Specific heat capacity is the amount of energy (joules) needed to increase 1g of a substance by 1K. The specific heat capacity of water is very high (4.18), meaning it takes more energy to raise the temperature of water than other substances.

The molar heat of combustion (ΔH) is the heat energy absorbed/released per mole of that substance. It is calculated by: $\Delta H = \frac{q}{n}$ where q is in kJ and ΔH is in kJ/mol. If a reaction is exothermic, $\Delta H < 0$ and if endothermic, $\Delta H > 0$.

Calorimetry is the process by which heat transfer is measured. The efficiency of calorimetry is a measure of how efficiently heat energy is transferred from the combustion of a material to the heating of water. It can be calculated by: $\%\ efficiency = \frac{expected\ energy\ absorbed}{actual\ energy\ supplied} \times 100$. The expected energy absorbed will always be lower than actual energy supplied as heat is always lost to surroundings.

Dissolution of an ionic lattice in water:
When compounds are added to water, the positive ends of the water molecule are attracted to the anion and the negatively charged end is attracted to the cation. This is an ion-dipole attraction. If the ion-dipole attractions are strong enough, the ions can be separated and become surrounded by water molecules. These are said to be hydrated. The process of separating ions from a lattice is called dissociation.
There are three steps in dissolving:
- Ionic bonds with the crystal lattice are broken (endothermic)
- Hydrogen bonds between the water molecules are broken (endothermic)
- Ion-dipole attractions form between ions and polar water molecules (exothermic)

To measure the enthalpy of dissolution, use: $\Delta H_{aqueous\ solution} = \frac{-mc\Delta T}{n}$.

The molar heat of neutralisation ΔH_{neut} is the energy liberated per mole of water produced during a neutralisation reaction. It is calculated by $\Delta H_{neut} = \frac{q}{n(water\ produced)}$

The implications of water's specific heat capacity on Earth and its climate;
- Lakes and oceans are slow to freeze. They must lose a lot of energy for the temperature to fall to freezing point.
- Oceans and other bodies of water moderate the climate by acting as a thermal reservoir to absorb heat from the air without large changes in the temperature of the water. Cities near the ocean will have less extreme temperatures.
- It is possible for aquatic life to survive strong climate fluctuations as temperature variations in water are not extreme.

- Heat capacity and density means that waterways don't freeze solid which makes aquatic life viable under ice.
- The temperature of water in ponds stays the same overnight.
- Water in a car radiator can absorb a large amount of heat from the engine of the car without the heat rising too much.
- Since the Earth's surface is 70% water, oceans buffer atmospheric temperatures, providing a liveable climate.

The <u>enthalpy of vaporisation</u> (ΔH_{vap}) is the amount of energy required to transform 1 mol of a substance from a liquid into a gas at 1atm pressure. All values will be given to calculate it.

The <u>latent heat of fusion</u> (ΔH_{fus}) is the energy needed to melt 1 mol of a solid to a liquid at 1atm pressure. Data values will be given to calculate it.

<u>Bond energy:</u> refers to the amount of energy required to break 1 mol of a covalent bond into its constituent gaseous atoms at SLC. Bond energies will be provided. To calculate ΔH using bond energies, add up the energy required to break the reactant bonds and subtract the energy released when making the product bonds. Some bond energies are stronger than others due to a smaller atomic radius.

<u>Hess's Law:</u> The enthalpy change for a reaction is independent of the reaction pathway taken.

- In the following reaction, $\Delta H_1 = \Delta H_2 + \Delta H_3$
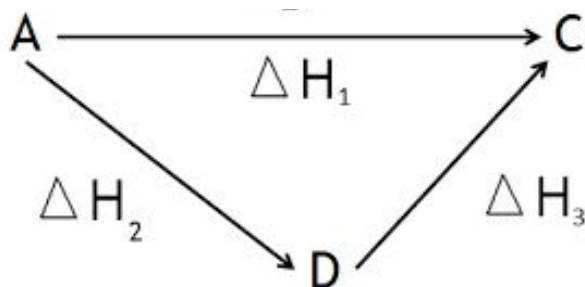
- When determining ΔH using Hess' law, some reactions may need to be reversed. <u>When a reaction is reversed, the sign of ΔH changes</u>.

The <u>standard enthalpy of formation</u> (ΔH_f^o) is the change in enthalpy that occurs when 1 mol of a compound is formed in its standard state from its constituent elements in their standard state at SLC. These values will be given. When a substance is in its elemental state, its enthalpy of formation is 0. To calculate the enthalpy change using enthalpies of formation use the formula:

$$\Delta H^o_{reaction} = \sum \Delta H^o_{f(products)} - \sum \Delta H^o_{f(reactants)}$$

The types of <u>systems</u> are:

- Open systems - energy and matter can be exchanged with the surroundings
- Closed systems - only energy can be exchanged with the surroundings
- Isolated systems - neither matter nor energy can be exchanged with the surroundings

You will need to know how to calculate the enthalpy change for:

- Photosynthesis (endothermic)

- $6CO_{2(g)} + 6H_2O_{(l)} \rightarrow C_6H_{12}O_{6(s)} + 6O_{2(g)}$ $\Delta H = 2804.8\ kJ/mol$
- Respiration (exothermic)
  - $C_6H_{12}O_{6(s)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$ $\Delta H = -2804.8\ kJ/mol$

Laws of Thermodynamics:
- The First Law of Thermodynamics: Energy cannot be created or destroyed in an isolated system
- The Second Law of Thermodynamics: The entropy of any isolated system always increases with time
- The Third Law of Thermodynamics: The entropy of a system approaches a constant value as the temperature approaches absolute zero

Entropy (S) represents the degree of disorder in a system or the energy not available to do work and is given in joules per kelvin (J/K). Factors which lead to a change in entropy are:
- A larger system (with more particles) has more energy than a smaller system
- A hotter system (more KE) has more entropy than a cooler system
- A liquid has more entropy than a solid
- A gas has more entropy than a liquid

The change in entropy of a system (ΔS) can be calculated the same way as enthalpy:

- $$\Delta S^o_{system} = \sum \Delta S^o_{products} - \sum \Delta S^o_{reactants}$$

For any spontaneous process: $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings} > 0$

Gibbs free energy (ΔG) represents the maximum amount of work a system can complete at constant T and P and is given in kilojoules per mole (kJ/mol). It is calculated by the:

- Gibbs-Helmholtz equation: $\Delta G^o = \Delta H^o - T\Delta S^o$ where ΔS^o must be converted to kJ and T is in Kelvin..
- The three outcomes of gibbs free energy are:
  - $\Delta G^o < 0$ - The reaction is spontaneous
  - $\Delta G^o = 0$ - The reaction is neither spontaneous or non spontaneous
  - $\Delta G^o > 0$ - The reaction is nonspontaneous

	ΔH > 0 (endothermic)	ΔH < 0 (exothermic)
ΔS > 0 (increase in entropy)	ΔG < 0 at high temperature ΔG > 0 at low temperature Process is spontaneous at high temperature	ΔG < 0 at any temperature Process is spontaneous at any temperature
ΔS < 0 (decrease in entropy)	ΔG > 0 at any temperature Process is nonspontaneous at any temperature	ΔG < 0 at low temperature ΔG > 0 at high temperature Process is spontaneous at low temperature

To <u>calculate the temperature at which a reaction becomes spontaneous</u> let $\Delta G^o = 0$ and solve for T given that you have already found ΔH^o and ΔS^o.

Types of enthalpy:

- ΔH^o_{rxn} Enthalpy change of a given reaction at STP
- ΔH^o_{comb} Enthalpy change of combustion of 1 mole of substance with excess diatomic oxygen at STP
- ΔH^o_f Enthalpy change when 1 mole of a product is produced from its constituents at STP
- ΔH^o_{fus} Enthalpy change required to melt or freeze 1 mole of a substance
- ΔH^o_{vap} Enthalpy change required to vaporise or condense 1 mole of a substance
- ΔH^o_a Enthalpy required to convert 1 mole of an element in its standard state to its gaseous state at STP
- $\Delta H^o_{L(diss)}$ Enthalpy required to convert 1 mole of a solid lattice to its gaseous state at STP