

Chemistry Notes

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Unit 1—Stoichiometric Relationships

1.1 Particulate nature of Matter and Chemical Change

Introduction

Stoichiometry—The relationship between the amounts of reactants and products during chemical reactions

Atom—The smallest particles of an element to show the characteristic properties of that element

Chemical Element—A single pure substance, made of only one type of atom

Compound—A chemical combination of different elements, containing a fixed ratio of atoms; the physical and chemical properties of a compound are different from those of its component elements

Chemical Equations

- the formation of compounds from elements is an example of **chemical change** and can be represented by a **chemical reaction**
- the total number of atoms of each element must be same on both sides of the equation

Mixtures

Pure Substance—Matter that has a constant composition, with its chemical and physical properties distinct; they physically combine to make a mixture

Mixture—Composed of two or more substances in which no chemical combination has occurred

- in the formation of a mixture, there is no chemical combination, only physical
- air is a **homogenous mixture**: it has uniform composition and properties throughout; other samples of these are salt water solution and metal alloys
- there are also **heterogenous mixtures**: there is a non-uniform composition of substances, and hence their properties vary throughout the mixture; it is usually possible to see separate component ex: oil and water

Mixture	Differences in Property of Components	Technique Used
sand and salt	solubility in water	solution and filtration
hydrocarbons in crude oil	boiling point	fractional distillation
iron and sulfur	magnetism	response to magnet
pigments in food coloring	absorption to solid phase	paper chromatography
different amino acids	net charge at a fixed pH	gel electrophoresis

States of Matter

Solid	Liquid	Gas
<ul style="list-style-type: none">- particles closely packed- inter-particles forces strong, particles vibrate in position- fixed shape and volume	<ul style="list-style-type: none">- particles more spaced- inter-particle forces weaker, particles can slide over each other- no fixed shape, but fixed volume	<ul style="list-style-type: none">- particles most spread out- inter-particles spaced negligible, particles move freely- no fixed shape or volume

Kinetic Theory of Matter

Temperature—A measure of the average kinetic energy of the particles in a substance

- the **kinetic theory of matter** states that the average kinetic energy of the particles is directly related to the temperature of the system

- the state of matter at a given temperature and pressure is determined by the strength of the forces that may exist between the particles, known as **inter-particles force**
- liquids and gases are **fluids** as they have the ability to flow

Diffusion—The process by which the particles of a substance become evenly distributed, as a result of their random movements

- **Kinetic energy (KE)** refers to the energy associated with movement or motion, determined by mass and velocity of a substance
- there is an inverse relationship between mass velocity, so substances with a lower mass diffuse more quickly than those with a greater mass at the same temperature

Changes of State

Sublimation—The direct inter-conversion of a solid to a gas without going through the liquid state

Deposition—Change of state directly from gas to solid

Evaporation—Unlike boiling (which occurs throughout the liquid) it occurs only at the surface and takes place at temperatures below the boiling point

- boiling is a volume phenomenon, characterized by particles leaving throughout the body of the liquids so bubbles occur
- it happens at a specific temperature, determined by when the vapor pressure reaches the external pressure

Heating Curve

Solid

- the solid is heated, so the vibrational energy of particles and so temperature increases

Melting Point

- vibrations are more energetic for molecules to move away from fixed positions and form a liquid
- energy added at this stage is used to break the inter-particle forces but not to increase KE, so the temperature remains constant

Boiling Point

- sufficient energy to break all of the inter-particle forces and form a gas
- this state needs more energy than melting because all inter-particle forces must be broken
- temperature remains constant as KE does not increase]
- bubbles of gas seen

1.2 The Mole Concept

Avogadro Constant

- the Avogadro constant (6.02×10^{23}) is the number of particles in one mole of a substance and has the units mol^{-1}
- a **mole** of the substance contains the Avogadro number of particles

Relative Atomic Mass

Relative Atomic Mass—The weighted average of one atom of an element relative to one-twelfth of an atom of carbon-12

Relative Formula Mass—The sum of the weighted average of the masses of the atoms in a formula unit relative to one-twelfth of an atom of carbon-12

Molar Mass—a substance's relative atomic mass or its relative formula mass expressed in grams, with the unit g mol^{-1}

One Mole—The mass of a substance that contains as many particles as there are atoms in 12 g of carbon-12

Empirical Formula

- the **empirical formula** of a compound gives the simplest ratio of all its atoms
- it is the simplest whole-number ratio of the elements in a compound
- the **molecular formula** shows all the atoms present in a molecule; it is a multiple of the empirical formula

Equations

- the limiting reactant determines the amount of product that can form
- the theoretical yield is the quantity of product that can form the complete conversion of the limiting reactant

Experiments

- qualitative analysis focuses on determining which elements are present in a compound; it can also verify the purity of a compound
- quantitative analysis enables chemists to determine the relative masses of elements which allows them to work out their exact composition

1.3 Reacting Masses and Volumes

Stoichiometry—The quantitative method of examining the relative amounts of reactants and products

Limiting Reagent—The (usually more expensive) reactant which will be completely consumed during the reaction, and it determines the amount of products formed

Theoretical Yield—The expected amount of products to be calculated

Gas Laws

- equal volumes of all gases, when measured at the same temperature and pressure, contain an equal number of particles (Avogadro's law)
- the volume occupied by one mole of gas, known as molar volume, must be the same for all gases when measured under the same conditions of temperature and pressure
- gases are separated by huge empty spaces, so most volume occupied by a gas is empty space
- gaseous particles are constantly moving in straight lines, but random directions
- gaseous particles undergo elastic collisions with each other and the walls of the container, but there is no loss of KE
- gaseous particles exert no force of attraction on other gases

Ideal Gas—A gas that obeys all the gas laws, but none exist, sadly

- no gas actually fits the description for an ideal gas (an ideal gas being one that has largely empty spaces containing free moving particles of negligible volume having no inter-particle forces)

Boyle's Law

$$V_1P_1 = V_2P_2$$

- when the temperature remains constant, there is an inverse relationship between pressure and volume

Charles's Law

$$V_1/T_1 = V_2/T_2$$

- for a fixed mass of gas at a constant pressure, the volume is proportional to the absolute temperature (in K)

Gay-Lussac's Law

$$P_1/T_1 = P_2/T_2$$

- when the volume of a gas is constant, the pressure is directly proportional to its absolute temperature

Combined Gas Law

$$P_1V_1/T_1 = P_2V_2/T_2$$

Ideal Gas Equation

$$pV = nRT$$

$R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ (universal gas constant)

Relationship: Volume and Pressure

- the volume of a gas is always the volume of its container as the particles spread out fully
- the gas pressure is a result of its particles colliding with the walls of the container, and will increase when the frequency or energy of these collisions increases
- if the temperature is constant, increasing the pressure on a fixed mass of gas decreases its volume
- the pressure of a gas is **inversely proportional** to its volume—**Boyle's law**

Relationship: Volume and Temperature

- an increase in temperature represents an increase in the average kinetic energy of the particles
- if the pressure is constant, increasing the temperature of a fixed mass of gas increases its volume
- the volume of a gas is **directly proportional** to its absolute temperature—**Charles's law**

Relationship: Pressure and Temperature

- increase in temperature increases the average kinetic energy of the particles
- this is because the particles move faster and collide with the walls of the container with more energy and more frequency, hence raising the pressure
- if the volume is constant, increasing the temperature of a fixed mass of gas **proportionately** raises its pressure
- the pressure of a gas is **directly proportional** to the absolute temperature

Ideal Gas Equation

$$PV = nRT$$

- where $n = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ R is the universal gas constant
- the SI units of $P = \text{Pa}$, $V = \text{m}^3$, $T = \text{K}$

Real Gases

- an ideal gas obeys the gas law $PV = nRT$ under all conditions but real gases show deviation from this ideal behavior (there is no such ideal gas)
- there are some trends
 - gases behave most like an ideal gas at **low pressure** and **high temperature**
 - gases show the most deviation at **high pressure** and **low temperature**

Assumptions of Ideal Gases

- the volume of gas particles is negligible
- there are no attractive forces between the particles

1. The volume of gas particles is negligible

- at low temperatures the volume occupied by gases is very low, almost negligible
- but as the pressure increases, the space between particles is reduced, so the volume occupied increases

2. There are no attractive forces between particles

- when a gas is at a low temperature the particles are widely spaced so interactive or attractive forces are unlikely
- but as the pressure increases, the particles come closer together and attractive forces increase
- low temperatures also cause deviation:
 - when the temperature is low, the particles are less likely to move so they will be closer together
 - so the lower kinetic energy of the particles increases the strength of inter-particle forces

Concentration

Solution—A homogeneous mixture of two or more substances (solids, liquids, gases, or a combination)

Solvent—The component present in the greatest quantity, in which the solute is dissolved

Concentration—The amount of solute per volume of solution in mol dm^{-3} or g dm^{-3}

Standard Solution—A solution of accurately known concentration

Dilution

- a dilution can be made from a more concentration starting solution (stock solution) by adding a solvent
- when a solution is diluted the number the moles stays constant but the concentration is decreased

Titration

- quantitate analysis includes a range of laboratory techniques used to determine the amount or concentration of an analyte (substance whose chemical constituents are being measured)
- volumetric analysis is a quantitative technique involving two solutions
- a titration involves a standard solution of known concentration until the chemical reaction is complete
- the reaction progress is monitored trough color changes using indicators

Unit 2—Atomic Structure

2.1 The Nuclear Atom

Model of an Atom

Element—a substance that cannot be broken down into simpler substances by a chemical reaction

Compound—a substance made by chemically combining two or more elements that has different properties from its constituent elements

Isotope—atoms of the same element with a different mass number

Sub-atomic Particles

Atoms are made up of smaller particles called sub-atomic particles. They are protons, neutrons (collectively nucleons), and electrons

Particle	Relative Mass	Relative Charge
proton	1	+1
electron	0.0005	-1
Neutron	1	0

Relative Atomic Mass

Relative atomic mass (A_r)—the average mass of an atom of an element, taking into account all its isotopes and their relative abundance, compared to one atom of carbon-12

Unified atomic mass—one-twelfth of a carbon-12 atom in its ground-state

Mass spectrometer—an instrument used to determine the relative atomic mass of an elements by showing its isotopic consumption

Calculating relative atomic mass based on abundance of isotopes

Example: 2 isotopes

${}^1_1\text{X}$, natural abundance = $a\%$

${}^2_2\text{X}$, natural abundance = $b\%$

$$A_r = (z_1 * \frac{a}{100}) + (z_2 * \frac{b}{100})$$

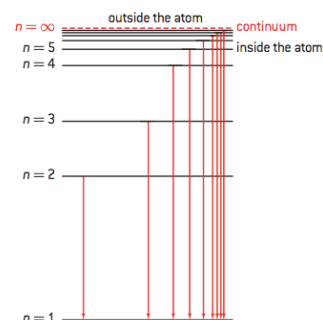
Isotopes

- they are atoms of the same mass element with a different mass number
- between isotopes and their atoms, density, atomic velocity, and radioactivity is different (these are physical properties)

2.2 Electron Configuration

Hydrogen spectrum

- an atom moves into an excited state when an electron moves into an orbit of higher energy level further from the nucleus when the atom absorbs energy
- the excited atom is unstable and the electron soon falls back to the ground state (lowest level), and a photon is released
- the energy of the photo of light is equal to the energy change in the atom
- this released energy corresponds to a certain wavelength and shows up as a line in the spectrum
- each orbit has a definite energy associated with it—the electron orbiting the positively charge center in a particular orbit is fixed or quantized (each step of



energy is analogous to an energy level which has a definite, discrete energy)

- (when electromagnetic waves are shot at hydrogen, there is an absorption spectrum as certain wavelengths of light are not shown because those are the wavelengths (photons of energy) required for exciting, and when the atom loses the energy, there is an emission spectrum where only certain wavelengths of light are shown as they energy (photons) taken to excite are now being released)
- when energy is supplied to different elements, they emit a spectrum which only contains elements at particular wavelengths
- each element has its own characteristics known as line spectrum and are not continuous
- line spectrum: radiation absorbed/emitted at specific frequencies
- continuous spectrum: radiation spread over all frequencies

Continuous spectrum—It shows an unbroken spectrum, such as the spectrum of visible light

Line emission spectrum—a spectrum that has only certain frequencies of light as it is produced by excited atoms and ions as they fall back to a lower energy level

- the line emission spectrum of H provides evidence for the existence of electrons in discrete energy levels which convert at higher energy levels

Quantization of energy

$E = h\nu = hc/\lambda$, where

h = Planck's constant = 6.63×10^{-34} Js

ν = frequency of radiation

c = speed of light = 3.00×10^8 ms⁻¹

- each characteristic wavelength corresponds to a discrete amount of energy
- E is inversely proportionate to λ —the greater the energy, the smaller the wavelength, and vice versa
- the line emission spectrum of hydrogen provides evidence for the existence of electrons in discrete energy levels, which converge at higher energy levels

Heisenberg Uncertainty principle

- electrons have wave properties
- we cannot know where an electron is at any given time
- we can only have a probability if where the electron is most likely to be
- any attempt to measure an electron's position will disturb its motion

Model of hydrogen atom

Atomic orbital—a region around the atomic nucleus in which there is a 90% probability of finding an electron

- an electron has wave properties
- when an electron is in an orbital of higher energy, it will have a higher probability of being found further from the nucleus

Orbitals

- all electrons are found in s, p, d, and f orbitals
- each orbital contains a maximum of 2 electrons at an opposite spin
- the s orbital is spherically symmetrical
- the p orbital is dumbbell-shaped

First energy level: 1s

- the first energy level has **one 1s orbital**

- it is spherically symmetrical

Second energy level: 2p and 2s

- it is dumbbell shaped
- the **2s sub-level** is made up of **one 2s orbital** and can hold a maximum of 2 electrons
- the **2p sub-level** is made up of **three 2p orbitals**: 2px, 2py, and 2pz; each can hold 2 electrons, so totally, the 2p sub-level holds 6 electrons
- the 2p atomic orbitals in the 2p sub-level are all at equal energies, they are said to be degenerate

Note

Energy level > sub-level > orbital

second EL > 2p > 2px

first EL > 1s > 1s

Aufbau principle: orbital diagrams

- the principle states that electrons are placed into orbitals of lowest energy first
- electrons are always placed and removed from the 4s orbital before the 3d orbital
- orbitals in the same sub-shell are always filled singly first (Hund's rule)
- electrons are first lost from the 4s sub-level when transitional metals form their ions, as once the 3d sub-level is occupied, the 3d electrons push the 4s electrons to a higher energy
- until Ca the 4s level is filled before the 3d level since it is lower in energy; Ca = [Ar] 4s²
- for Sc (21), the 4s level is slightly higher in energy than the 3d level so 3d is filled first; Sc = [Ar] 3d¹ 4s²
- this trend continues along for the 3d level
- for Zn (30), the 4s level is now much higher in energy than the 3d level; Zn = [Ar] 3d¹⁰ 4s²
- when 3d-block elements are ionized, the electrons are removed from the 4s before 3d levels because 4s is higher in energy than the 3d for this block of elements
- due to the stability of half-filled and full-filled 3d sub-shells, Cu and Cr have 3d filled first (half- and full-filled are more stable); in the Cu⁺ ion the electron is removed from the orbital of higher energy, the 4s level

Electronic configurations

1s 2s 2p 3s 3p 4s 3d 4p 5s 4d 5p 6s

Element	Configuration
H	1s ¹
He	1s ²
Ne	1s ² 2s ² 2p ⁶ = [He] 2s ² 2p ⁶
Al	1s ² 2s ² 2p ⁶ 3s ² 3p ¹
Cr	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹ 3d ⁵ = [Ar] 4s ¹ 3d ⁵
Zn	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹ 3d ¹⁰ = [Ar] 4s ¹ 3d ¹⁰
Kr	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ² 3d ¹⁰ 4p ⁶ = [Ar] 4s ² 3d ¹⁰ 4p ⁶

Valence electrons—the electrons in the outer energy level which are mainly responsible for the compounds formation

- copper and chromium have different electron configurations
- the 4s and 3d sub-levels are close in energy, so the configuration of chromium with a half-full d sub-level is relatively stable as it minimizes electrostatic repulsion, with 6 strongly occupied atomic orbitals
- half-filled and completely filled 3d sub-levels reduce the overall potential energy of an atom, so the electron configurations of Cr and Zn are more stable
- electrons are always placed and removed from the 4s orbital before the 3d orbital

- from Cu \rightarrow Cu⁺, the electrons is removed from 4s, not 3d

12.2 Electrons in Atoms

Ionization energy

First ionization energy—the energy needed to remove one mole of electrons from the ground state of one mole of gaseous atoms

First ionization energy: $\text{H(g)} \rightarrow \text{H}^+(\text{g}) + \text{e}^-$

Second ionization energy: $\text{H}^+(\text{g}) \rightarrow \text{H}^{2+}(\text{g}) + \text{e}^-$

- once an electron is removed from an atom, it is an infinite distance away from the nucleus, and can be considered to be in the $n=\infty$ energy level
- beyond the continuum (limit of convergence), electrons can have any energy, so are no longer under the influence of atom and nucleus (electrons outside atom; ionization has occurred)
- there is an increase in successive ionization energies
 - the process becomes **more difficult as there is an increasing attraction between higher charge positively ions and the oppositely charged electron** (each electron is being removed from an increasingly positive species, so there is a higher force of attraction between the electron and ion)
- there are jumps when electrons are removed from levels closer the nucleus
- between sulfur and phosphorus, the first ionization energy of sulfur is less because phosphorus is half-filled, so it is more stable than S—therefore, HELP

Evidence for sub-levels

- if ionization energies are plotted on a graph, we will see jumps at certain positions
- these jumps show that it is more difficult to remove the electron from that level
- so it shows that at different sub-levels, the ionization energy increases because of the **attraction between the higher charged positive ions and the oppositely charged electron**

Trends in first ionization energy

1. Ionization energy generally increases from left to right across a period as the nuclear charge increases
 - electrons are removed from the same main energy level, so there is an increase in force of electrostatic attraction between the nucleus and outer electrons (more protons in the nucleus across the period, so they attract the extra electrons added as you move across the period)
 - there are jumps when an electron is being removed from a different sub-level—this is because an electron is being removed from a full occupied sub-level
2. Ionization energy decreases down a group as a new energy level, which is further from the nucleus, is occupied
 - less energy is required to remove outer electrons that are further away from the pull of the nuclear

Example: Sodium's electronic configuration

Na: $1s^2 2s^2 2p^6 3s^1$

- the **first electron is the easiest to remove** because it is the furthest from the nucleus so there is the least attraction between the electron and nucleus—it is the valence electron
- there is a **large increase from IE_1 to IE_2** as the new electron is from the $n=2$ level, which is a fully-filled sub-level, so it is stable
 - the **second electron is also being removed from a more positive species**, and there is a higher force of attraction between the electron and ion
- for the next seven electrons the gradual increase in IE is small
- there is another from IE_9 to IE_{10} as it is associated with the removal of an electron from the $n=1$ sub-level which is closest to the nucleus, so it is the most difficult to remove due to the electrostatic attraction between the electron and nucleus

Example: Why IE_1 is lower for O than N

O: $[\text{He}] 2s^2 2p_x^2 2p_y^2 2p_z^1$

- an electron is removed from the 2p sub-level
- the most loosely-bound electron is where there is the maximum repulsion in the orbital—the one that contains paired electrons, which is $2p_x$
- so IE_1 of O is lower, also because there is electrostatic repulsion between the two electrons in $2p_x$, so less energy is required to remove it

N: $[\text{He}] 2s^2 2p_x^1 2p_y^1 2p_z^1$

- for N the most loosely bound electron is any one of the 2p electrons which are all degenerate
- there is no electrostatic repulsion, so it requires more energy to remove the electron
- ***the 2p sub-level is half-filled and hence it is more stable, so more difficult to remove an electron***

Example: Ca and Ti

- Ca^{2+} and Ti^{4+} both have the configuration $[\text{Ar}]$
- in Ti, the ionization energies increase more gradually as electrons are being removed from both, the 3d and 4s orbital, which are closer in energy compared to the 3p and 4s

Unit 3—Periodicity

3.1 The Periodic table

Periods and groups

The columns of the table are called groups and the rows are called periods

- periods are the horizontal rows in the table numbered according to the number of energy levels (shells) in the atoms in that period that have electrons
- groups are vertical columns numbered according to the number of electrons in the outer energy level of the atoms in the group
- elements whose valence electrons occupy an s sub-level make up the s block, and so on
- Al (... 3p¹) is in the p block (at the right of the table)
- the number of valence electrons can be found from the group number of the s and p block elements

Metals and non-metals

- the non-metals are found on the upper right-hand side of the p block, and metals are found on the left-hand side of the table in the s block, the central d block, and the f block
- metalloids have characteristics of both metals and non-metals

3.2 Periodic Trends

Physical properties

Periodicity—a repeating pattern of (physical and chemical) properties

Nuclear charge—is given by the atomic number

Effective Nuclear Charge—is experienced by an atom's outer electrons and increases with the group number of the element; it increases across a period but remains approximately the same down a group

- the periodicity of elements is reflected in their physical properties

Effective nuclear charge

- the nuclear charge increases by one between successive elements, as a proton is added to the nucleus
- the outer electrons determine many of the physical and chemical properties of the atom
- but valence electrons do not experience the full attraction of the nuclear charge as they are **shielded from the nucleus and repelled by inner electrons**—the core electrons in the inner non-valence energy levels of the atom reduce the positive nuclear charge experienced by the valence electron
- the presence of inner electrons reduces the attraction of the nucleus for the outer electrons
- **the effective charge experienced by outer electrons is less than the full nuclear charge**
- the effective nuclear charge (Z_{eff}) increases by one across the periods as one proton is added to the nucleus and one electron is added to the valence electron energy level
- so Z_{eff} increases with nuclear charge
- effective nuclear charge remains approximately the same across a group

Atomic radii

- the atomic radius is measured as half the distance between neighboring nuclei
- it increases down a group and decreases across a period
- it increases down the group as the number of occupied electron shells increases
- it decreases across a period as the attraction between the nucleus and the outer electrons increases as the nuclear charge increases—so the outer electrons are pulled closer to the nucleus
 - going to the right of the period, the effective nuclear charge increases as more outer electrons are present
 - so there is a higher attraction between these outer electrons and the positively charged nucleus

Ionic radii

- positive ions (cations) smaller than parent atom
 - formation of cation involves the loss of the outer shell
 - there are more protons than electrons so the valence electrons are more strongly attracted to the nucleus
- negative ions (anions) larger than parent atom
 - formation of anion involves the addition of electron(s) into the outer shell
 - the increased electron repulsion because of the electron added between the electrons the outer principal energy level causes the electrons to move further apart (**repel the inner electrons**) and so increase the radius of the outer shell
- the ionic radii decrease from Group 1 to 14—the increase in nuclear charge causes an increased attraction between the nucleus (protons) and electrons, so the outer shell is pulled closer to the nucleus
- the ionic radii increase from Group 14 to 17—the increase in nuclear charge... (same explanation)
- the ionic radii increase down a group as the number of electron energy levels increase

Ionization energies

- they increase across a period
 - the increase in effective nuclear charge causes an increase in the attraction between the outer electrons and the nucleus (valence electrons pulled closer) and makes the electrons more difficult to remove (more energy required)
 - atomic radii decreases across a period (because valence electrons pulled closer) so it is more difficult to remove an electron because of the attraction between the valence electrons and positively charged nucleus
- they decrease down a group
 - effective nuclear charge stays the same, so the increased distance between the electron and the nucleus reduces the attraction between them
- the trend in ionization energy is the reverse of the trend in atomic radii—both trends are an indicator of the attraction between the nucleus and outer electrons
- noble gases have the highest ionization energies
 - their outer energy level is full so it is more stable therefore more energy is required to remove an electron
 - they have the greatest attraction for their electrons
- ions or atoms that have the same electron configuration are isoelectronic

Electron affinity

First electron affinity—the energy change when one more of gaseous electrons is added to one mole of gaseous atoms to form one mole of gaseous ions

First electron affinity: $X(g) + e^- \rightarrow X^-(g)$

Second electron affinity: $X^-(g) + e^- \rightarrow X^{2-}(g)$

- the added electron is attracted to the positively charged nucleus so the process is generally exothermic
- for the second electron affinity, the process is exothermic as the added electron is repelled by the negatively charged ion (**and the previously added electron**)
- noble gases do not generally form negatively charged ions so they do not have electron affinity values
- the Group 17 elements have incomplete outer energy levels and a high effective nuclear charge so they attract electrons the most
- the Group 1 metals have the lowest effective nuclear charge so they attract electrons the least

Electronegativity

Electronegativity—the measure of an element's ability of its atoms to attract electrons in a covalent bond

- elements with high electronegativities have strong electron pulling power while an element with a low electronegativity has a weak pulling power
- it increases from left to right across a period because of the increase in nuclear charge, resulting in an increased attraction between the nucleus and the bond electrons
- it decreases down a group as the bond electrons are furthest from the nucleus so there is a reduced attraction

Metals—IE and EA

Metals are able to conduct electricity because their valence electrons move away from the atomic nucleus (because of low ionization energies and electron affinities)

Melting points

- they decrease down Group 1
 - these elements are held together by force between delocalized electrons and the positively charged ions, and the attraction decreases with distance
 - the atomic radii decreases
 - melting points decrease down the group as the radii of metals increase so less forces of attraction between them (and electrons??)
- they increase down Group 17
 - these elements are molecular, held by London forces which increase with the number of electron in the molecule
 - the London forces increase with an increasing number of electrons
- they generally rise across a period and reach a maximum at Group 14 and a minimum at Group 18 (example with period 3)
 - with the first 3 elements (Na, Mg, Al—with metallic bonding), the mp increases as the number of valence electrons increases
 - silicon, the metalloid, has a macromolecular covalent structure with very strong bonds resulting in a very high mp
 - elements in groups 15, 16, and 17 show simple molecular structures with weak intermolecular forces of attraction between molecules, so they have low mps
 - the noble gases exist as monatomic molecules with extremely weak forces of attraction between atoms

Chemical Properties

The chemical properties of an element are largely determined by the number of valence electrons in their outer energy level

Group 18: The Noble Gases

- they are the least reactive elements
 - colorless gases
 - monoatomic (exist as single atoms)
 - very unreactive
- their lack of reactivity is because of their high IEs
- all elements have a stable octet, but helium a complete principal first energy level with two electrons

Group 1: The Alkali Metals

- they react with water

Physical properties	Chemical properties
good conductors of electricity and heat	very reactive metals—need to be stored in oil to prevent contact with air and water
low densities	form ionic compounds with non-metals
grey shiny surfaces when cut with a knife	

Group 17: The Halogens

- they react Group 1 metals to form halides
- undergo displacement reactions—the more reactive halogen displaces the ions of the less reactive halogen from its compounds

Physical properties	Chemical properties
---------------------	---------------------

colored	very reactive non-metals; reactivity decreases down the group
show a gradual change of state from gases to liquid and solids	form ionic compounds with metals and covalent compound with other non-metals

13.1 First-row d-block Elements

Transition elements—elements whose atoms have an incomplete d sub-shell, or which give rise to cations with an incomplete d sub-shell

Physical Properties

- high electrical and thermal conductivity
- high mp and bp
- malleable—easily bent into shape
- high tensile strength—can hold large amounts of load without breaking
- ductile—can be easily drawn into wires

Chemical Properties

- form compounds with more than one oxidation number
- form a variety of complex ions
- form colored compounds
- act as catalysts

Zinc Stinks

- it is not a transition metal
- its compounds do not generally form colored compounds
- it does not display most properties that transition metals do
- in Zn or an ion of Zn, the d sub-level is complete, so it is not a transition element

Complex Ions

Ligand—a species that uses a lone pair of electrons to form a coordinate bond with a metal ion

Chelate—a complex containing at least one polydentate ligand

- transition metals in solution have a high charge density and attract water molecules which form covalent bonds with positive ions to form a **complex ions**
- **a complex is formed when a central ion is surrounded by molecules or ions which possess a lone pair of electrons** (all ligands have at least one atom with a lone pair of electrons which is used to form a coordinate bond with the central metal ion)
- the number of coordinate bonds is called the coordination number
- a coordinate bond uses a lone pair of electrons to form a covalent bond
- metals form small size d-block ions and act as Lewis acids, and attract species (ligands) that are rich in electrons
- ligands possess non-bonding lone pairs of electrons which can form coordinate covalent bonds with the metal ion to form complex ions
- the number of lone pairs bonded to the metal ions is known as the coordination number

Examples

Complex	Ligand	Coordination number	Shape
$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	H_2O	6	octahedral

MnO_4^-	O^{2-}	4	tetrahedral
$\text{PtCl}_2(\text{NH}_3)_2$	Cl^- and NH_3	4	square planar
$[\text{Fe}(\text{CN})_6]^{3-}$	CN^-	6	octahedral

Magnetic Properties

- most substances have paired electrons and so are non-magnetic
- some transition metals and their compounds are unusual in having some electrons that remain unpaired, which when aligned lead to magnetic properties
- the spinning of unpaired electrons create a small magnetic field and will line up in an applied electric or magnetic field to make transition metal complexes weakly magnetic when the field is applied—this is known as paramagnetism
- there are three magnetisms:
 - **diamagnetism**—the property of all materials; produces a very weak opposition to an applied magnetic field; it is the magnetism when all electrons in the metal complex are paired
 - **paramagnetism**—only occurs with substances which have unpaired electrons; stronger than diamagnetism; the more unpaired electrons there are in the complex, the more paramagnetism there will be
 - **ferromagnetism**—the largest effect

Ferromagnetism

- only occurs if there is a long range ordering of unpaired electrons
- the unpaired d electrons in large numbers of atoms line up with parallel spins in regions called domains (in Fe, Co, Ni)
- the magnetic remains after external magnetic field is removed as the domains remain aligned due to the long range interaction between the unpaired electrons in the different atoms

Paramagnetism

- shown my transition metals complexes with unpaired electrons as they are pulled into a magnetic field
- this magnetism increases with the number of unpaired electrons, so generally increases from left to right across a period
- Zn has no unpaired electrons and do is diamagnetic

Variable Oxidation States

- the variable oxidation states in the d-block elements is in contrast to the s-block metals, which have a single OS
- there is a difference because of the patterns in the successive ionization energies
- when transition metals lose electrons, the the 4s electrons first
- all transition metals show an OS of +2 and +3; some show +3 or +4 as the ionization energies are are such that up to two d electrons can be lost
- explanation of the variable OSs in terms of IEs:
 - the Ca^{3+} is energetically unstable because there is a large jump in IEs as the third electron is removed from the inner 3p orbital (not 4s)
 - the increase in successive IEs is more gradual in Ti as the 3d and 4s orbitals are closer in energy
 - Ti shows +2, +3, and +4 OSs; there is a large jump between the fourth and fifth IEs as an inner 3p electron is removed in the fifth IE, so Ti does not form a +5 OS
- there are some key points
 - all transition metals show +2 and +3 OSs; the increase in nuclear charge makes it difficult to remove a third electron
 - an OS of above +3 generally shows covalent character—ions of higher charge have such large charge density that they polarize negative ions and increase the covalent character of their compounds
 - compounds with higher OSs tend to be oxidizing agents

Catalytic behavior

Catalyst—a substance that alters a rate of reaction, by providing an alternative reaction pathway with a lower activation energy

Heterogeneous catalysts

- these are catalysts that are in different states from the reactants (usually transition metals)
- the ability of transition metals to use their 3d and 4s electrons to form weak bonds to reactant molecules makes them effective heterogeneous catalysts as they provide a surface for reactant molecules to come together with correct orientation
- this catalysis is preferred in industrial process as the catalyst can easily be removed by filtration from the reaction mixture after use

Homogeneous catalysts

- these are catalysts that are in the same state of matter as the reactants (usually ions of transition metals)
- the ability of transition metals to show variable OSs allows them to be effective homogeneous catalysts in redox reactions

13.2 Colored Complexes

- because of the partially filled d orbitals, transition metal ions are colored
- Sc^{3+} is colorless because the 3d sub-level is empty, while Zn^{2+} is colorless because the 3d sub-level is full
- in an isolated atom, d orbitals have the same energy but in a complex ion, they split into two sub-levels
- the electronic transitions between these sub-levels lead to absorption and emissions of photons of visible light, which are responsible for the color of the complex

Visible Spectrum

- the color of a substance is determined by which color(s) of light it absorbs and which color(s) it transmits or reflects
- a substance appears a certain color because it absorbs the complementary color—copper sulfate appears turquoise because it absorbs orange (orange and turquoise are complementary colors—they are opposite in the color wheel)

Absorbing Light

- transition metal compounds appear colored because their ions absorb colors
- transition metals absorb light because the d orbitals split into two sub-levels
- when light passes through a solution of a (complex ion-ligand), one 3d electron is excited to a higher energy sub-level, and a photon of a specific light is absorbed, and a photon of a complementary light color is transmitted

Crystal Field Theory

Identity of the metal ion

- crystal field splitting energy increases down a group with the metal in the same OS

Oxidation state of the metal ion

- crystal field splitting energy increases as OS increases
- the metal-ligand interaction is partially electrostatic in nature, so as the charge on the metal increases, the distance between the metal and ligands decrease
- this results in a better overlap between the metal orbital and the ligand orbital

Charge density

- ligands have different charge densities
- the greater the charge density, the greater the crystal field splitting
- if the ligand has a greater charge density, there are larger splits in the d orbitals

Unit 4—Chemical Bonding and Structure

4.1 Ionic Bonding and Structure

Ions

Ion—a charged particle formed from an atom or group of atoms by the loss or gain of one or more electrons

Valence electrons—the outer electrons of a nucleus that can be transferred when atoms react together

Polyatomic ions—ions that are made up of more than one atoms which together have experienced a loss or gain of electrons and so carry a charge

- the ionic bond is due to the electrostatic attraction between oppositely charged ions
- ionic compounds are compounds consisting of 2 or more oppositely charged ions, held by ionic bonds

Lattice structure

Ionic lattice—A predictable three-dimensional structure crystalline structure of an ionic compound; the electrostatic forces of attraction between ions in a compound cause the ions to surround themselves with ions of opposite charge

- forces of electrostatic attraction between ions in a compound cause the ions to surround themselves with ions of opposite charge, and as a result, the ionic compound takes on a predictable 3D crystalline structure known as an ionic lattice
- coordination number is the term used to express the number of ions that surround a given ion in the lattice
- lattice energy is a measure of the strength of attraction between ions within the lattice

Physical properties

Melting and boiling point

- high mps and bps as the force of electrostatic attraction between ions in the lattice are strong
- they require large amounts of energy to break
- the mps and bps are generally higher when the charge on the ion is greater, due to the increased attraction between the ions
- volatility is the term used to describe the tendency of a substance to vaporize—ionic compounds have low volatility

Solubility

- solubility refers to the ease with which a solid (solute) becomes dispersed through a liquid (solvent) to form a solution
- in general, solubility is determined by the degree to which the separated particles of solute are able to form bonds or attractive forces with the solvent
- ionic compounds are generally soluble in ionic or polar solvents but non soluble in non-polar solvents

Electrical conductivity

- ionic compounds are unable to conduct electricity in the solid state as the ions are firmly held within the lattice and so cannot move
- when the ionic compound is either present in the liquid state (molten) or dissolved in water (aqueous solution), the ions will be able to move and conduct electricity

Brittleness

- ionic compounds are usually brittle—the crystal tends to shatter when force is applied

- this is because movements of the ions within the lattice places ions of the same charge alongside each other, so repulsive forces causes it to split

4.2 Covalent Bonding

Covalent bonds

Covalent bond—the electrostatic attraction between a pair of electrons and a positively charged nuclei, formed by atoms sharing electrons

Molecule—a group of atoms help together by covalent bonds

- two non-metals react to gain a full outer electron shell to obtain the structure of a noble gas
- this is achieved by sharing electrons by covalent bonding
- molecules contain a fixed number of atoms
- the octet rule states that when atoms react, they tend to achieve an outer shell with 8 electrons

Bond lengths

Bond length—a measure of the distance between the two bonded nuclei; triple bonds are stronger and shorter than double bonds because multiple bonds have a greater number of shared electrons and so have a stronger force of electrostatic attraction between the bonded nuclei

Bond strength—bond enthalpy; multiple bonds have stronger bond strengths there is a greater number of shared electrons and hence a stronger force of attraction between the bonded nuclei

- short bonds are strong bonds
- multiple bonds gave a greater number of shared electrons and so have a stronger forces of electrostatic attraction between the bonded nuclei, hence they are shorter
- a triple bond is stronger than a double bond which is stronger than a single bond
- the single bond is longer than a double bond which is stronger than a triple bond

Polar bonds

Electronegativity—the relative attraction that an atom of an element has for the shared pair of electrons in a covalent bond

- they result from the unequal sharing of electrons
- when two atoms are covalently bonded, one atom can have a higher **electronegativity** and exert a greater pulling power on the shared pair of electrons
- this bond is **unsymmetrical with respect to electron distributions and said to be polar**
- the term dipole indicates that the bond has 2 separated opposite electric charges
 - the more electronegative atom with the greater share of electrons has become partially negative (δ^-)
 - the less electronegative atom has become partially positive (δ^+)

Example: HCl



H is partially positive; Cl is partially negative

- in a covalent bond, the greater the difference in electronegativity values of the atom, the more polar the bond
- a non-polar covalent compound is a compound where there is a bond between the same atoms, where the difference in electronegativity is zero—these are sometimes called pure covalent
- in ionic bonds the electronegativity difference between the two atoms bonded is the highest

Polar covalent bond—when one atom in the covalent bond has a greater attraction for the shared pair of electrons than the other, with on atom adopting a partial negative charge and the other adopting a partial positive charge

Pure covalent bond—the bond when the two atoms involved in the formation of the covalent bond are identical

4.3 Covalent Structures

Coordinate bonds

Dative/Coordinate bonds—covalent bond in which both the shared electrons are provided by one of the atoms; the shared pair of electrons come from only one pair of the two electrons—this atom donated both electrons to the shared pair

- both shared electrons originate from the same atom
- the other atom accepts and gains a share in a donated electron pair

Incomplete octets

- small atoms such as Be and B form stable molecules where the central atom has fewer than 8 electrons in the valence shell
- these are known as incomplete octets, and are said to be electron deficient and have a tendency to accept an electron pair from a molecule with a lone pair
- this leads to the formation of a coordinate compound in which the central atom has now gained an octet
- some molecules have an expanded octet, where their valence shell can hold 18 electrons

VSEPR theory

Electron domain—number of lone pairs of electrons or bond locations

VSEPR theory—valence shell electron pair repulsion theory—the shape of a molecule is determined by repulsion between electron domains; because electron pairs/domains in the same valence shell carry the same charge, they repel each other and spread themselves as far apart as possible

Electron domain geometry—It is determined by the positions of all electron domains, but the molecular geometry only depends on the position of the bonded atoms

- because electron pairs in the same valence shell carry the same charge, they repel each other and so spread themselves as far apart as possible
- in determining the shape of a molecule, it is important to take the electron domains into account—not only the shared electron pairs
- this is because electrons are negatively charged, so pairs of electrons (bonding or lone pairs) repel one another to be as far apart in space as possible
- there are key points in the VSEPR theory:
 - the total number of electron domains around the central atom determines the geometrical arrangement of the electron domains, and the repulsion applies to the electron domains
 - the shape of the molecule is determined by the angles between bonded atoms
 - non-bonding pairs (lone pairs) have a higher concentration of charge than a bonding pair because they are not shared between two atoms, and so cause slightly more repulsion than bonding pairs—lone pairs occupy more space than bonding pairs

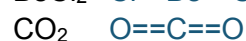
The repulsion decreases in the following order: $LP-LP > LP-BP > BP-BP$

LP = lone pair

BP = bonding pair

Two electron domains

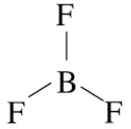
Molecules with 2 EDs will position themselves at 180° to each other, giving a **linear** shape to the molecule



(all 180° to each other)

Three electron domains

- molecules with 3 EDs will position themselves 120° to each other, giving a **triangular planar** shape to the electron domain geometry
- if all 3 EDs are bonding, the shape of the molecule will also be **triangular planar**
- if one of the EDs is a lone pair, the molecular shape will be different (the molecular shape and electron domain geometry are different if there are non-bonding electron domains)
- **O₃ has 3 EDs, so the the electron domain geometry is triangular planar, but the actual shape of the molecular is bent or V-shaped**
- the lone pair of electrons distorts the shape slightly, so the angle is slightly less than 120°



Four Electron Domains

- position themselves at an angle of 109.5° to each other
- if all 4 EDs are bonding, the shape of the molecule is **tetrahedral**
- but if one or more of the EDs is a lone pair, the shape is different
 - 4 EDs and 4 bonded EDs (0 lone pairs): **tetrahedral** 109.5°
 - 4 EDs and 3 bonded EDs (1 lone pair): **trigonal pyramidal** (3D pyramid shape) app. 107°
 - 4 EDs and 2 bonded EDs (2 lone pairs): **bent or V-shaped** (like water) app. 105°

Resonance Structures

- it is possible for Lewis structures to have identical arrangements of atoms but different arrangements of the electrons
- the individual Lewis structures that contribute to the overall structure are called resonance structures
- the actual electronic structure of the species is called the resonance hybrid
- ozone also has a resonating structure

Polar Bonds

- molecules with polar bonds are not always polar
- molecules with dipoles can be polar if the dipoles cancel out ex: CO₂, CCl₄, BF₃
- but if either the molecule contains bonds of different polarity, or its bonds are not symmetrically arranged, then all the dipoles will not cancel out, and the molecule will be polar ex: CH₃Cl, NH₃, H₂O

Allotropes of Carbon

Allotrope—different structural modification of the same element in the same state of matter

Graphite

- there are layers of hexagonal rings consisting of carbon atoms
- each atom is sp^2 hybridized
- these layers are connected by weak intermolecular forces (London forces)
- each C atom has a trigonal planar geometry
- layers can slide past each other—the London forces are weak but the covalent bonds between separate C atoms are strong
- good conductor of electricity as there are mobile delocalized π electrons

Diamond

- each carbon atom is covalently bonded to four others with a tetrahedral geometry
- each atom is sp^3 hybridized
- the valence electrons are localized in the single sigma bonds and are not mobile so no electrical conductivity
- does not conduct electricity as the valence electrons are localized in single (sigma) covalent bonds

Graphene

- is a 2D crystal (trigonal planar)
- consists of a single planar sheet of C atoms arranged hexagonally, and is only one atom thick
- each atom is sp^2 hybridized

- great electrical conductivity—same reason for graphite

Fullerene—C₆₀

- found to form when vaporized carbon condensed in an atmosphere of inert gas
- composed of individual molecules with strong covalent bonds
- trigonal planar, so sp² hybridized
- weak London forces between molecules
- do not dissolve in water; dissolve in some non-polar solvents

Silicon dioxide (Quartz)—SiO₂

- 3D covalent solid network—consisting of an array of silicon dioxide tetrahedra arranged in a lattice
- each Si atom is bonded covalently to 4 O atoms; each O atom is bonded covalently to 2 Si atoms
- very high melting point
- insoluble in water
- non-conductor of electricity

4.4 Intermolecular Forces

London (Dispersion) Forces

- the only intermolecular force that exists between non-polar molecules (occurs between all particles)
- between non-polar molecules, electrons behave like mobile clouds of negative charge, **so the density of the cloud may be at a moment greater at one region than another**
- when this occurs, a weak dipole (temporary/instantaneous dipole) is formed
- this may influence the electron distribution in a neighboring atom or molecule, **causing an induced dipole**
- this is the weakest form of intermolecular force
- relatively little energy is required to break the weak forces and separate the molecules from each other, so many non-polar elements/gases are gases at room temperature
- London forces are attractive forces between atoms, non-polar molecules (H₂), and polar molecules—so every molecule will experience London forces

the strength of London forces depends on

- molecular size—increasing the molecular size increases the forces—greater number of electrons increases the portability of temporary dipoles developing
- volume of electron cloud—in a large electron cloud, the attraction of electrons to the nucleus will not be as great as in a smaller cloud, and hence the electrons in a large electrons cloud can be polarized more easily
- shape of the molecule—straight-chain molecules allow the molecule to interact with each other across the full length of the molecule; there is a larger area of interaction because of the better contact between the molecules

Dipole-Dipole Attraction

- occurs when there is a difference in electronegativity between the bonded elements
 - one end of the molecule is electron deficient with a partial positive charge
 - the other end is electron-rich with a partial negative charge—this is known as a permanent dipole
- this permanent dipole exerts an opposite charges on neighboring molecules attracting each other, generating a force known as dipole-dipole attraction
- these forces are generally stronger than London forces as they **originate from permanent rather than temporary dipoles**
- **Van der Waal's forces—all forces between molecules that do not involve electrostatic attraction between ions or bond formation**
 - it refers to all forces between molecules that do not involve electrostatic attraction between ions or bond formation

Polarizability

- it is the ease of distortion of the electron cloud of molecular entity by an electric field

- sometimes the intermolecular forces of LDF can lead to the substance having a higher mp and bp than one with LDF and dipole-dipole forces
- for example, between CCl_4 and CH_3F , CCl_4 has a higher mp and bp, even though it has only LDF
 - the LDF is stronger—there are more valence electrons in CCl_4 than in CH_3F
 - in CCl_4 the presence of more valence electrons leads to a greater polarizability in the electron clouds, resulting in a significantly stronger LDFs which outweigh the dipole-dipole forces of CH_3F

Hydrogen Bonding

- it is when a molecule containing hydrogen is bonded to a very electronegative element (F, N, or O)
- the large electronegativity difference between hydrogen and the element results in the electron pair being pulled away from the hydrogen
- since hydrogen is small in size and has no other electrons to shield the nucleus, it now exerts a strong attractive force on a lone pair in the electronegative atom of a neighboring molecule
- note that electrostatic bonding are much stronger than the forces of hydrogen bonding; hydrogen bonding is only intermolecular force

Physical Properties of Covalent Bonds

Melting and Boiling Point

- the stronger the intermolecular forces, the more energy required to overcome the forces between the molecules
- these forces to separate the molecule are relatively weak intermolecular forces, which are significantly easier to break than the electrostatic attractions in an ionic lattice
- giant covalent structures have high mps and bps as covalent bonds (not weaker intermolecular forces) must be broken in these compounds for a change in state to occur

Solubility

- non-polar compounds are generally able to dissolve in non-polar solvents by the formation of London forces between solute and solvent: *like dissolves like*
- polar covalent compounds are generally soluble in water—a highly polar solvent
- the solute and solvent interact through dipole interactions and **hydrogen bonding**
- the solubility of polar compounds is reduced in larger molecules where the polar bond is only a small part of the total structure—the non-polar parts of the molecules are unable to associate with water, so the solubility is reduced
- giant molecular substances are generally insoluble in water as too much energy would be required to break the strong covalent bonds in their structure

Electrical Conductivity

- covalent compounds do not contain ions, so are unable to conduct electricity in solid/liquid state
- some polar compounds conduct electricity in specific conditions where they can ionize and conduct electricity—HCl dissolved in water is an electrical conductor as it dissociates to $\text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq})$
- giant molecules (graphite and graphene) are electrical conductors due to the mobile electrons

4.5 Metallic Bonding

Metallic bonding—the electrostatic attraction between a lattice of positive ions (cations) and delocalized electrons

Delocalized electrons—electrons that are not associated with a particular nucleus or metal, but instead are free to move throughout the entire crystalline lattice forming a 'sea' of mobile electrons

Alloy—a metallic material, homogenous on a macroscopic scale, consisting of two or more elements so combined that they cannot be readily separated by mechanical means; they are considered as mixtures for the purpose of their classification

- metals of low IEs, so valence electrons can be delocalized throughout the metal
- this creates a giant lattice consisting of positive metal ions surrounded by a sea of electrons
- the strength of the metallic bond depends on

- number of valence electrons
- charge of the metal ion
- ionic radius of the metallic cation

Alloys

- a mixture consisting of either two or more metals, or a metal(s) and a non-metal
- alloys have enhanced properties which differ from those of the parent metals:
 - greater strength
 - greater resistance to corrosion
 - enhanced magnetic properties
 - greater ductility
- metallic bonds within a lattice are non-directional and can slide past each other as the cations can slide past each other
- if different atoms are present in the network of cations, it becomes more difficult for the positive ions to slide past each other and change the shape of the metal—this is why alloys are generally much stronger than pure metals

14.1 Further Aspects of Covalent Bonding and Structure

Expanded Octet

There are exceptions to the octet rule:

- small atoms like Be and B form stable molecules with fewer than an octet of electrons
- atomic of elements in Period 3 and before may expand their octet by using d orbital in their valence shell
- the arrangement of an expanded octet is possible because the d orbitals available in the valence shell of these atoms have energy values relatively close to those of the p orbitals

Five Electron Domains

- molecules with 5 EDs will position themselves in a **triangular bipyramidal** shape with angles of 90°, 120°, and 180°
- if all 5 EDs are bonding electrons, the shape of the molecule is **triangular bipyramidal**
 - 5 EDs and 4 bonded electrons (1 lone pairs): **see-saw**
 - 5 EDs and 3 bonded electrons (2 lone pairs): **T-shapes**
 - 5 EDs and 2 bonded electrons (3 lone pairs): **linear**

Six Electron Domains

- molecules with 6 EDs will position themselves in an **octahedral shape** with an angle of 90°
 - 6 EDs and 5 bonded electrons (1 lone pairs): **square pyramidal**
 - 6 EDs and 4 bonded electrons (2 lone pairs): **square planar**

Molecular Geometry and Polarity

- if there are no lone pairs and all the atoms attached to the central atom are same, the molecules are non-polar as there is no net dipole ex: PCl_5 , SF_6
- if the atoms attached to the central atom are not the same, there may or may not be a net dipole depending on the symmetry— SBrF_5 has a net dipole and is polar; PCl_3F_2 has no net dipole due to cancellations, so is non-polar

Formal Charge

Formal Charge (FC) = number of valence electrons in unbounded atom (V)

$$- 0.5 * (\text{no. of bonding electrons}) - (\text{no. non-bonding electrons})$$

- a low FC means that less charge transfer has taken place in forming a structure from its atoms, and in general this represents the most stable or preferred structure
- if there are a number of FCs that all obey the octet rule, the most reasonable one will be
 - the one with the FC difference closest to 0
 - the one that has the negative charges located on the most electronegative atoms

Ozone

- ozone has a resonating structure of three O atoms
- triangular planar electron domain geometry, but only 2 domains are bonding, so it is a bent or V-shaped with an angle of 117°
- the double bond is composed of a sigma bond from the overlap of hybrid orbitals; the pi bond is from the overlap of unhybridized orbitals
- the electrons in the pi bond are less tightly held so become delocalized through the structure
- although there is only bonding between O atoms, it is still apolar molecule

Overlapping of Atomic Orbitals

- there are two types of covalent bonds—sigma bonds and pi bonds
- a bond forms when two atomic orbitals (each containing 1 electron) overlap to form a new molecular orbitals that is at a lower energy

Sigma Bonds

- forms when two s orbitals overlap along the bond axis (an imaginary line between the two nuclei)
- **all single bonds are sigma bonds**
- the electron density is concentrated between the nuclei of the bonded atoms

Pi Bond

- forms when two p orbitals overlap sideways, and the electron density of the molecular orbital is concentrated in two regions, above and below the plane of the bond axis
- **pi bonds are weaker than sigma bonds as their electron density is further from the positive charge of the nucleus, and so they break more easily during chemical reactions**
- **double covalent bonds contain one sigma bond and one pi bond; triple bonds contain one sigma bond and two pi bonds**

14.2 Hybridization

Excitation of Atoms

Excitation occurs when an electron is promoted within the atom from the 2s orbital to the vacant 2p orbital

Hybridization

Hybridization—the process that occurs when two different orbitals mix to form new atomic orbitals for bonding

- in methane, there are four identical carbon-hydrogen bonds, so this suggests that these orbitals have been changed and made equal. during the bonding process
- unequal atomic orbitals within an atom mix to form new hybrid atomic orbitals which are the same as each other, but different from the different orbitals

sp³ Hybridization

- when carbon forms **four single bonds**, it undergoes sp³ hybridization, producing four equal orbitals
 - the 2s sub-level has 1 electron
 - the 2p sub-level has 3 electrons
 - they hybridize to form **four sp³ hybrid orbitals**
- the orbitals orient themselves at 109.5°

sp² Hybridization

- when carbon forms a **double bond**, it undergoes sp² hybridization, producing three equal orbitals
 - the 2s sub-level has 1 electron
 - the 2p sub-level has 3 electrons (but we are only interested in 2 out of these 3 electrons)
 - they hybridize to form **three sp² hybrid orbitals** and one unhybridized p orbital
- these orbitals orient themselves at 120° (triangular planar)
- each sp² hybrid orbital overlaps with a neighboring atomic orbital, forming three sigma bonds, ex: C₂H₄
- the p orbitals in each carbon atom did not take place in hybridization and retain their dumbbell shape, and they overlap sideways and form a pi bond
- so the double bond between the carbon atom consists of one sigma bond and one pi bond

sp Hybridization

- when one carbon forms a **triple bond**, it undergoes sp hybridization, producing two equal orbitals
 - the 2s sub-level has 1 electron
 - the 2p sub-level has 3 electrons (but we are only interested in 1 out of these 3 electrons)
 - they hybridize to form **two sp hybrid orbitals** and two unhybridized p orbitals
- these orbitals orient themselves at 180°, giving a linear shape, ex: C₂H₂

Expanded Octet Hybridization

- molecules which have electrons in d orbitals can undergo hybridization with them
- PCl₅ has sp³ hybridization which produces five equivalent orbitals oriented at the corners of a triangular bipyramid

Lone Pairs and Hybridization

- non-bonding electron pairs can take part in hybridization
- in NH₃, the non-bonding pair on the N atom resides in an sp³ hybrid orbital

Hybridization and Molecular Shape

The electron domain arrangement can be predicted by the hybridization:

- tetrahedral arrangement—sp³
- triangular planar arrangement—sp²
- linear arrangement—sp

Examples

Bond	Example
s—p	H—Cl (s) (p)
p—p end-on (a single bond when the atom has valence electrons in a p sub-level)	C—O I—Cl
sp ³ —s	C—H in CH ₄ H ₂ O (tetrahedral electron domain geometry)
sp ² —s	C—H in C ₂ H ₄
sp—s	C—H in C ₂ H ₂
sp ² —p	...C=C—Cl (acyl chlorides) (sp ²) (p)

Unit 5—Energetics and Thermochemistry

5.1 Measuring Energy Changes

Energy and Heat Transfer

- energy is a measure of the ability to do work and is conserved in chemical reactions
- heat is a mode of energy transfer which occurs as a result of a temperature difference and produces an increase in disorder in how the particles behave

System and Surroundings

- the system is the area of interest in the reaction and the surroundings are everything else in the universe
- there are open systems and closed systems:
 - in an open system, energy and matter can be exchanged with the surroundings
 - in a closed system, energy but not matter can be exchanged with the surroundings

Enthalpy

- enthalpy (H) is a measure of the amount of heat energy contained in a substance
- it is stored in the chemical bonds and intermolecular forces as potential energy
- when substances react, the difference in the enthalpy between the reactants and products (at constant pressure) results in a heat change

Exothermic and Endothermic Reactions

- exothermic reactions give out heat and result in a transfer of enthalpy from chemicals to surroundings (combustion, neutralization, most other reactions); ΔH is negative
- endothermic reactions result in an energy transfer from the surroundings to system; ΔH is positive

Thermochemical Reactions

- the standard state of a substance is the pure form of the substance under standard conditions of 298 K and 1 atmosphere

Heat and Temperature Changes

- the kelvin scale emphasizes the relationship between average kinetic energy and temperature
- if the same amount of heat is added to 2 different objects the temperature change will not be the same as the average KE of the particles will not increase by the same amount
 - the object with less particles will experience a larger temperature increase as the same energy is shared amongst a smaller collection of particles
- the specific heat capacity is the property of a substance which gives the heat needed to increase the temperature of unit mass by 1 K

$$\text{heat change} = m \times c \times \Delta T$$

$$(J = g \times J \text{ g}^{-1} \text{ K}^{-1} \times K)$$

- the heat capacity (C) is defined as the heat needed to increase the temperature of an object by 1 K

$$\text{heat capacity (C)} = \text{heat change (q)} / \text{temp change } (\Delta T)$$

Enthalpy Changes

- the natural direction of change is in the direction of the lower stored energy
- the products in an exothermic reaction are more stable as they have less energy than the reactants

- endothermic reactions are less common and occur when there is an increase in disorder of the system
- combustion reactions are generally exothermic, ΔH_c is negative
- but there are some sources of inaccuracy:
 - heat could be lost to surroundings: for example when measuring energy produced by fuel, not all the heat could have been transferred to the water
 - some reactions (combustion) are unlikely to be complete, so the actual ΔH will be different from the literature one
 - the experiment could have not been performed in standard conditions

Enthalpy Changes of Reaction in Solution

- can be calculated by carrying out the reaction in an insulated system with the heat released/absorbed measured from the temperature change of water
- but all heat produced from the reaction will not always be absorbed by water, so there could be heat loss the environment
- heat is lost from the system as soon as the temperature rises above the temperature of the surroundings
- we make some assumptions in relations involving solutions:
 - all the heat is transferred to the water
 - the density of the solution is 1 g cm^3 (same as water)
 - all the heat spreads uniformly
 - the container does not absorb any heat
 - the specific heat capacity of water is same as that of the solution

5.2 Hess's Law

Enthalpy Cycles

- the enthalpy change for a particular reaction is calculated from the known enthalpy change of other reactions
- this is because of the law of conservation of energy

Hess's Law

- the law states that the enthalpy change for any reaction is independent of the route, provided the starting conditions and final conditions, reactants, and products are the same
- it allows us to calculate enthalpy changes of reactions she cannot normally measure in the lab

Standard Enthalpy Changes of Reaction

- the **standard enthalpy change of formation** (ΔH_f^\ominus) of a substance is the enthalpy change that occurs when one mol of the substance is formed from its elements in their standard states under standard conditions
- the ΔH_f^\ominus of an element in its most stable form is zero as there is not chemical change and so no enthalpy change when an element is formed

5.3 Bond Enthalpies

Breaking Bonds (Endothermic)

- endothermic processes involve the separation of particles which are held together by a force of attraction
- energy is needed to separate the atoms in a bond
- separating particles is always an endothermic process
- the average **bond enthalpy** is the energy needed to break one mole of bonds in gaseous molecules under standard conditions averaged over similar compounds

Making Bonds (Exothermic)

- exothermic processes involve the bringing together of particles which have an attractive force between them
- when a bond is formed, the compound/atoms become stable so energy is released

Ozone Depletion [needs a redo]

- the bonds in oxygen and ozone are broken by UV of different wavelengths
- the double bond in O₂ is stronger than the 1.5 bond in O₃ so is broken by radiation of higher energy and shorter wavelength
 - ozone has two resonating structures so a bond order of 1.5, so it requires a shorter wavelength to break
 - UV light of a higher energy (shorter wavelength, higher frequency) will be required to break the stronger bond in oxygen
- O₂ when with UV light breaks down to two free radicals; one of these free radicals reacts with O₂ to form O₃
$$\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g}) + \text{O}(\text{g})$$
- the above is the most **endothermic** step as oxygen has a bond order of 2, so it needs more energy than the below step
$$\text{O}(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{O}_3(\text{g})$$
- the above reaction is **exothermic**; it raises the temperature of the stratosphere
- but the bonds of ozone are weaker than the double bond of oxygen so UV light of lower energy is required to break them down (to oxygen free radical and oxygen: O₂)
$$\text{O}_3(\text{g}) \rightarrow \text{O}(\text{g}) + \text{O}_2(\text{g})$$
- the ozone reacts with another oxygen molecule to form two oxygen molecules
$$\text{O}_3(\text{g}) + \text{O}(\text{g}) \rightarrow 2\text{O}_2(\text{g})$$
- this is **exothermic** but produces very little heat, so it helps maintain the high temperature of the stratosphere

Energy

Planck's equation:

$$E_{\text{photon}} = h\nu$$

where ν = frequency and h = Planck's constant

using the frequency equation,

$$E_{\text{photon}} = \frac{h * c}{\lambda}$$

- oxygen has the strongest bond, so a shorter wavelength (higher frequency) is needed to break the bonds

15.1 Energy Cycles

Ionization Energy and Electron Affinity

- the first **ionization energy** is the minimum energy required to remove one mole of electrons from one mole of gaseous atoms
- the first **electron affinity** is the enthalpy change when one mole of gaseous electrons is added to one mole of gaseous atoms
- the second EA is higher than the first EA because when the second electron is being added, it is repelled by the first one
 - so EA1 (exothermic) can be negative while EA2 can be positive (endothermic)

Lattice Enthalpy

Lattice Enthalpy—The enthalpy change that occurs when one mole of a solid ionic compound is separated into gaseous ions under standard conditions

- the electron transfer process between a cation and anion is **endothermic** despite it leading to the stable noble gas electron configuration
- the oppositely charged gaseous ions come together to form an ionic lattice, and this is a very endothermic process as there is a strong attraction between oppositely charged ions

The Born-Haber Cycle

- this is an energy cycle based on Hess's law and it shows the steps of the formation of an ionic compound

- there is a process follows with different energy change:
 - enthalpy of atomization of cation
 - enthalpy of atomization of anion
 - ionization energies of cation
 - electron affinities of anion
 - lattice enthalpy of ionic compound

Enthalpy Change of Atomization (ΔH°)—The enthalpy change that occurs when one mole of gaseous atom is formed from the element in its standard state

Lattice Enthalpies and Ionic Model

- there are two factors affecting lattice enthalpy:
 - an increase in the ionic radius of one of the ions decreases the attraction between the ions
 - an increase in the ionic charge increases the ionic attraction between the ions
- so, a **decrease in ionic radius** and an **increase in ionic charge** increases the lattice enthalpy

Enthalpies of Solution

Enthalpy Change of Solution—The enthalpy change when one mole of a solute is dissolved in a solvent to infinite dilution under standard conditions

- enthalpies of solution are calculated by calculating the temperature change in a solution
- some ionic compounds are dissolved readily as the ions are strongly attracted to the polar solvent water
 - the partial positive charge on hydrogen atoms in the water molecules are attracted to the negative ions
 - the partial negative charge on oxygen is attracted to the positive ions
- the ions are separated as they get surrounded by water molecules—they are said to become hydrated

Hydration Enthalpy

- the enthalpy change of hydration of an ion is the enthalpy change that occurs when one mole of gaseous ions is dissolved to form an infinity dilute solution of one mole of aqueous ions under standard conditions

15.2 Entropy and Spontaneity

Entropy

Spontaneous Changes—Changes that occur naturally without the need to do work; a spontaneous reaction occurs without adding energy (beyond that to overcome activation energy)

Entropy (S)—The distribution of available energy among particles

- spontaneous changes can be reversed, but work will have to be done (energy needs to be spent)
- when there are more ways the energy can be distributed, the entropy is higher
- ordered states (with small energy distribution) are said to have low entropy
- energy always disperses in a way of leading to the widest energy distribution

Predicting Entropy Changes

- solid states are more orders and gaseous states are more disordered, so the entropy of the system increases as a solid changes to a liquid and as a liquid changes to a gas
- doubling the number of particles present in a sample also increases the chance for a system to become disordered and for the entropy to increase
- entropy increases:
 - from solid to liquid to gas
 - as number of particles increases

Examples

$\text{Br}_2(\text{l}) \rightarrow \text{Br}_2(\text{g})$: one mole of liquid changes to one more of gas, so more disorder, so ΔS increases

$2\text{Cu(s)} + \text{O}_2 \rightarrow 2\text{CuO(s)}$: decrease in number of moles, so reduction in disorder of particles, so ΔS decreases

Absolute Enthalpy

- this value can be calculated and depends on temperature and pressure
- it increases from solid to liquids to gas
- a perfectly ordered solid at absolute zero has an entropy of zero and all other states which are more disordered have positive entropy values

Spontaneity

- entropy increases during spontaneous reactions, but some reactions occur with a decrease in spontaneity

Entropy Changes of Surroundings

- adding heat to the surroundings results in a general dispersal of heat in the surrounding universe (exothermic reactions)
- so $\Delta S(\text{surroundings})$ is proportional to $-\Delta H(\text{system})$; it's negative) (because exothermic reactions lead to an increase in the entropy of the universe)
- this is why exothermic reactions are more common than endothermic reactions

Entropy and Absolute Temperature

- the impact of the transfer of heat to the surroundings depends on the current state of disorder in the surroundings
- so ΔS is proportional to $1/T$
- the impact of addition of heat depends on the present state of disorder
- if the system was at absolute zero, a small amount of heat energy would lead to an infinite increase in entropy

Endothermic Reactions

- endothermic reactions can only occur if the change in entropy of the system can compensate for the negative entropy change of the surroundings as heat flows from the surroundings of the system

Gibbs Free Energy

$$\Delta G(\text{system}) = \Delta H(\text{system}) - T * \Delta S(\text{system})$$

- the $\Delta G(\text{system})$ must be negative for a spontaneous reaction

Feasibility of Reaction

- all reactions which have a positive value of $\Delta S(\text{system})$ can be feasible at high temperatures even if they are endothermic

Unit 6—Chemical Kinetics

6.1 Collision Theory and Rates of Reactions

Rate of Reaction—The increase in concentration of products or the decrease in concentration of reactants per unit time

- when calculating the rate of a reaction, we measure the time
- rate of reaction is used to describe how quickly a reaction happens
- the concentration of reactants decreases and the concentration of products increases as a reaction proceeds and when reactants are converted to products, and the rate of reaction depends on how quickly either of these happen

$$\text{rate of reaction} = \frac{\text{increase in product conc}}{\text{time taken}} \text{ or } \frac{\text{decrease in reactant conc}}{\text{time taken}}$$

$$\text{rate} = \frac{\Delta[P]}{\Delta t} \text{ or } -\frac{\Delta[r]}{\Delta t}$$

- the negative sign indicates that the reactant concentration is decreasing, but rate is expressed as a positive value
- rate is measured in $\text{mol dm}^{-3}\text{s}^{-1}$
- in a graph with **rate** against **time**, the gradient is a measure of the change in concentration per unit time, or the rate of reaction
 - the gradient shows that the reaction rate is greatest at the start and slows down as the reaction proceeds
 - the rate is greatest at the start because the reactant concentration is the greatest, but it decreases over time
- the rate at a particular time can be calculated measuring the gradient of a tangent drawn to that point

Measuring Rate

Change in Volume of a Gas

- the graph of volume against time can be plotted
- a gas syringe can be used to measure the change in volume of a gas
- the gas can also be collected by displacement of water from an inverted burette (only if the gas has a low solubility in water)
- data loggers can be used for continuous monitoring of volume change against time

Change in Mass

- if a gas is given off, the change in mass can be measured (of the flask with reactants) by standing the reactant mixture directly on the balance
- however, this method may not work well if a gas such as hydrogen is released as the change in mass will be too small to give a significant change in mass
- this method works well with continuous changes in mass

Change in Transmission of Light: Colorimetry/Spectrophotometry

- this can be used if one of the reactants or products is colored as it will give characteristic absorption in the visible region
- sometimes an indicator can be added to generate a colored compound that can be used in the reaction
- a colorimeter/spectrophotometer works by passing light of a selected wavelength through a solution being studied and measures the intensity of the light transmitted by the reaction components
- when the concentration of the colored compound increases, it absorbs proportionately more light, so less is transmitted

Change in concentration measured using titration

- the concentration can be measured, and it can be titrated against a known standard
- to do this, a sample must be withdrawn from the reaction mixture at intervals and then analyzed, but the reaction will still take place
 - to solve this problem, a quenching will be done—a substance is introduced which stops the reaction in the sample at the moment it is withdrawn
 - so accurate measurements can be taken

Changes in concentration measured using conductivity

- the total electrical conductivity of a solution depends on the total concentration of its ions and on their charges, so if this changes when reactants are converted to products, it can be used to follow the progress of the reaction
- conductivity can be measured using a conductivity meter
- the apparatus can be calibrated using solutions of known concentrations

Clock reactions

- the time taken to reach a certain point in the reaction can be measured, an arbitrary end point
- but it only provides an average rate
- examples: time taken for certain size pieces of magnesium ribbon to react completely with dilute acid until it is no longer visible; time taken for solution of sodium thiosulfate and acid to react by measuring opacity by looking at a drawn cross on a sheet of paper

Collision Theory

Kinetic energy and temperature

- the kinetic molecular theory states that particles in a substance move randomly as a result of the kinetic energy that they possess
- there is a random movement so only an average kinetic energy of the particles can be taken —this value of kinetic energy is related to the absolute temperature
- increasing the temperature means an increase in average kinetic energy
- when we heat a substance, the kinetic energy increases, so the temperature rises

Kinetic-molecular theory of gases

- gas contains particles moving at high velocities in random directions
- the size of gaseous particles is negligible; the volume is also considered negligible even though some gas particles have mass (because at normal pressure, the space between atoms or molecules is very large compared to the size of the atom or molecule)
- collisions between gaseous particles are elastic, so when particles collide, there is no net loss in energy, it is transferred
- the average kinetic energy is proportional to absolute temperature

Maxwell-Boltzmann distribution curve

- this distribution curve explains that particles in a gas at a particular temperature show a range in their values of kinetic energy
- the curve shows the number of particles having a particular kinetic energy, and the area under the curve represents the total number of particles with that energy

Reactions

- kinetic energy in particles causes them to collide together, and these collisions result in some bonds between reactants being broken and new bonds forming and hence products forming
- for a reaction to be successful, the energy of the collision and geometry of the collision need to be suitable
- in order to react, particles must collide with kinetic energy greater than the activation energy and have the correct collision geometry

Energy of collision

- this energy is necessary for overcoming repulsion between molecules, and for breaking bonds before they react

- for the collision to lead to a reaction, there needs to be a certain minimum activation energy
- when the energy is being supplied, the reactions achieve the transition state from which products can form
- in general, reactions with a high activation energy proceed more slowly than those with low activation energy

Geometry of collision

- the orientation of the molecules is crucial in determining whether the reaction is successful

Factors affecting rate of reaction

Temperature

- increasing the temperature increases the average kinetic energy of the particles
- as the temperature increases, there is an increase in collision frequency due to the higher kinetic energy
- and an increasing number of the particles that collide have the activation energy or higher
- so more successful collisions

Concentration

- as the concentration increases the frequency of the of collisions between reactant particles increases
- with a higher concentration, there are more reactants present so a higher chance of collision (increased frequency of collisions)
- so the frequency of successful collisions increases too

Particle size (surface area)

- smaller particles sizes (but same total volume) increase the total surface area and therefore allows more contact between reactants
- so more chance of successful collisions as a higher area to collide with

Pressure (gases only)

- high the pressure of the gas, higher the concentration, so higher the frequency of collisions

Catalyst

- a catalyst is a substance that increases the rate of a chemical reaction without itself undergoing permanent chemical change
- catalysts work by providing an alternate route for the reaction that has a lower activation energy (catalysts work by lowering the activation energy of a reaction)
- so without changing any of the other four factors, reactants will have kinetic energies greater than the activation energy
- in a reversible reaction, catalysts bring an equal reduction in activation energy for both the forward and backwards reaction, so the position of the equilibrium is not changes, it is only reached faster so more efficient
- biological reactions are controlled by catalysts called enzymes

16.1 Rate Expression and Reaction Mechanism

Rate law

- it is derived purely from experimental data
- **rate constant**, k , is constant for a particular reaction at a specified temperature
- the **order of reaction** with respect to a particular reaction is the power to which the concentration is relied in the rate equation, and the overall order from the reaction is the sum of the individual orders all reactions

Order of the reaction and k

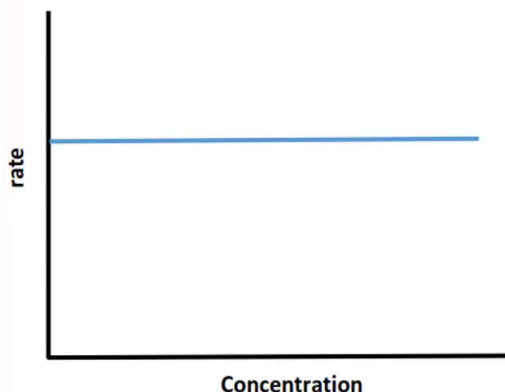
- for different orders of a reaction, k has a different value

Zero order	First order	Second order	Third order
$\text{mol dm}^{-3}\text{s}^{-1}$	s^{-1}	$\text{mol}^{-1}\text{dm}^3\text{s}^{-1}$	$\text{mol}^{-2}\text{dm}^6\text{s}^{-1}$

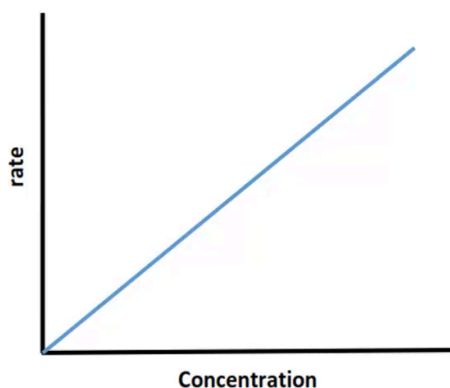
Graphical representations of reaction kinetics

Rate vs concentration

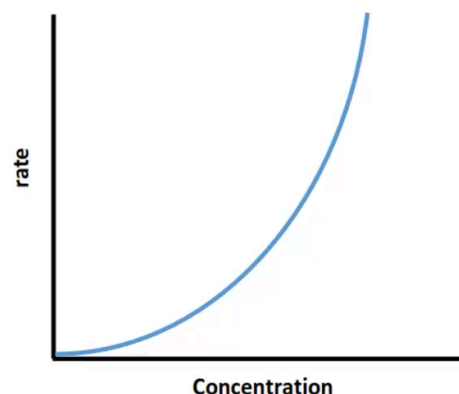
Zero order



First order



Second order



rate = k

- concentration of A does not affect the rate of reaction
- order of reaction = 0 with respect to A, so it is not included in the rate expression

rate = k[A]

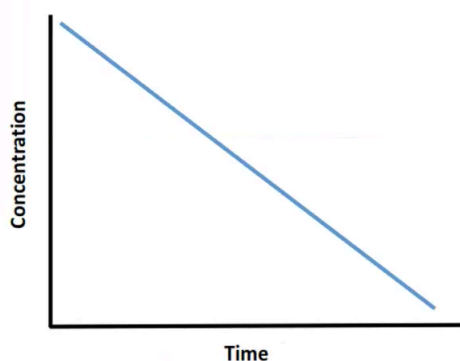
- rate of reaction is directly proportional to the concentration of A

rate = k[A]²;

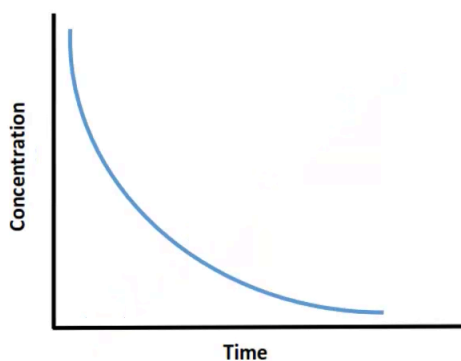
- rate proportional to square of A, so it is a curved line

Concentration vs time

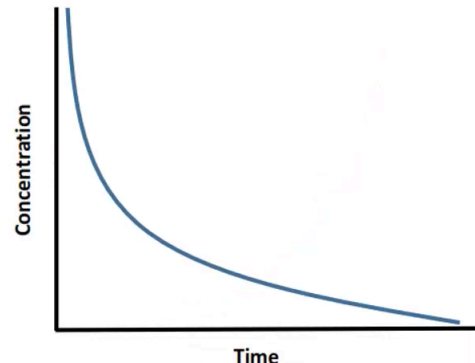
Zero order



First order



Second order



rate = k

- constant rate
- gradient of line = k

rate = k[A]

- rate = k * [A]
- rate decreases with concentration
- concentration reduces with time as reactants get used up

rate = k[A]²;

- curved line

Half-life

- **first-order** reactions have a constant half-life
- in a **first-order** reaction, the times taken for concentration to reach half its value is independent of the starting concentration
- a constant half-life is only a feature of first-order reactions
- if a reaction has a constant half-life, then the reaction must be first order with respect to that reactant

Determining the order of reaction

- if changing the concentration of A has no effect on the rate, the reaction must be **zero-order** with respect to A
- if changes in concentration of A produce directly proportional changes in the rate of the reaction, the reaction must be **first-order** with respect to A
- if changes in the concentration of A lead to the square of that changes in the rate of the reaction, then the reaction must be **second-order** with respect to A

	Changes in rate of zero-order reaction	Changes in rate of first-order reaction	Changes in rate of second-order reaction
[A] doubles	no change	rate x2	rate x4
[A] triples	no change	rate x3	rate x9
[A] quadruples	no change	rate x4	rate x16

- in zero-order the concentration of A has no effect on the rate of reaction, so [A] does not affect the rate

Reaction mechanism

- reactions occur at a measurable rate, in simple steps, each involving a small number of particles, and this sequence is known as the **reaction mechanism**, with individual steps called **elementary steps**, which cannot be observed directly
- the mechanism is a theory about the sequence of events on progressing from reactants to products
- in a reaction, the products of a single step in the mechanism are used in subsequent steps, so they only exist in the reaction as **intermediates**
- molecularity is used in reference to an elementary step to indicate the number of reactant species involved
 - unimolecular refers to an elementary step that involves a single reactant particle
 - bimolecular refers to an elementary step with two reactant particles
 - there is very low probability of more than two particles colliding at the same time with sufficient energy and correct orientation (**termolecular** reactions)

Rate-determining step

- the slowest step in a reaction mechanism is the RDS, and this step determines the overall rate of reaction
- products of the reaction can only appear as fast as the products of this elementary step
- the RDS is the step in the reaction mechanism whose transition has the highest energy

(to be completed)

16.2 Activation Energy

Rate constant k

- the rate constant k is temperature dependent
- it is not a rule of nature that the rate doubles for every 10°C increase in temperature
-