AS Chemistry – Revision Notes
Unit 1 – Atomic Structure, Bonding And Periodicity

Atomic Structure

1. All atoms have a mass number, A (the number of nucleons), and a proton number, Z (the number of protons).
2. Isotopes have different numbers of neutrons, and have different physical properties but the same chemical properties.
3. In a mass spectrometer:
    a. Ionisation – The vaporised sample is passed through an electron beam, from an electron gun, forming cations.
    b. Acceleration – The cations are attracted to negatively charged plates, passing through a small hole to focus the beam.
    c. Deflection – The magnetic field of an electromagnet deflects the beam, so lighter ions are deflected more. The ions passing out of the electromagnet will be of the same mass.
    d. Detection – The ions reaching the detector are counted, to give the relative abundance of each isotope.
4. $$\text{Relative atomic mass }(A_r) = \frac{\text{the average mass of an atom of the element}}{\frac{1}{12}\text{ of the mass of a carbon-12 atom}}$$
5. The average mass can be determined from a mass spectrum – the peaks show the relative abundances of each isotope, which can be multiplied by the mass of each to give the average mass.
6. Electron shells are arranged into sub-orbitals (s, p, d and f), each of which can contain two electrons spinning in opposite directions due to the Pauli exclusion principle.
7. When filling orbitals:
    a. The lowest energy orbitals will be filled first (e.g. 1s before 2s).
    b. Orbitals of the same type (e.g. p) will only pair up electrons after there is one electron in each (e.g. you will get $2p_x^1\ 2p_y^1\ 2p_z^1$ rather than $2p_x^2\ 2p_y^1\ 2p_z^0$) – the Aufau principle.
    c. The 4s orbital will always fill before the 3d orbital.
    d. When forming ions, electrons will be removed from the 4s orbital before the 3d orbital.
    e. For chromium and copper, an electron will be taken from the 4s orbital and placed in the 3d orbital to make half-full or full 3d orbitals respectively.
8. The first ionisation energy is the energy required to remove one mole of electrons from one mole of atoms in a gaseous state – $X(g) \rightarrow X^+(g) + e^-$.
9. With successive ionisation energies, big increases in energy will occur between electron shells because the shell closer to the nucleus will have a greater attraction for the electrons, and less shielding from complete shells.
10. Ionisation energy trends can be explained by:
    a. The distance from the nucleus.
    b. The nuclear charge / attraction.
    c. The amount of shielding.
11. Going down a group, the first ionisation energy will always decrease because the electron is further from the nucleus, and has more shielding, even for the increase in nuclear charge.
12. Going across a period (Li to Ne):
    a. Overall increase in ionisation energy due to the increase in nuclear charge for the same distance from the nucleus.
    b. Drop from Be to B due to shielding from full 2s orbital.
    c. Drop from N to O due to electron repulsion when p electrons pair up (easier to remove).

Bonding

1. An ionic bond is the attraction between ions, creating a giant ionic lattice. Ions are formed by gaining or losing electrons to create a stable octet (the octet rule).
2. Most elements that become ions do so by becoming isoelectronic with a noble gas.
3. The strongest bonds (most reactive elements) are formed between the bottom of group I / II and the top of group VI / VII.
4. Cations will become slightly smaller and anions will become slightly bigger than their neutral atoms (e.g. Na^+ is smaller than Na; Cl^- is bigger than Cl).
5. X-Ray diffraction can be used to show the structure of an ionic compound.
6. The coordination number tells you how many ions can surround each other ion:

a. 6:6 coordination number if one ion is much smaller than the other (e.g. NaCl)
b. 8:8 coordination number if both ions are roughly the same size (e.g. CsCl)

7. A unit cell is the smallest unit of structure that has all the features of the lattice, and can build up the lattice by simple repetition.

8. A covalent bond is the sharing of a pair of electrons. The negative charge on the electron pair attracts the positive nuclei, holding the atoms together. The electron pair must lie between the nuclei for the attraction forces to outweigh the repulsion between the nuclei.

9. Covalent bonds result in the overlap of two orbitals:
    a. A σ bond is the overlap of two s orbitals.
    b. A π bond is the overlap of two p orbitals.
    c. A δ bond is the overlap of two d orbitals.

10. A dative covalent bond (or a coordination bond) is a covalent bond whereby both electrons come from one atom. This is shown by an arrow on the bond in the direction the electrons go. It usually occurs between an electron deficient compound, and one with a lone pair.

11. Some elements (such as Be, B and Al) bond covalently to form electron deficient compounds. These can then form dative bonds with other compounds to help to get the full octet of electrons (e.g. $AlCl_3$ bonds together to form Al_2Cl_6 dimers).

12. Electronegativity is the power of an atom to withdraw electron density from a covalent bond (it is an atom's affinity for electrons). Electronegativity increases going along a period and up a group.

13. A polar bond occurs when the two atoms have a large difference in electronegativity (if the difference is very large, then it will become completely ionic). This creates a slight negative charge (δ^-) on the more electronegative atom, and a slight positive charge (δ^+) on the other. This is a permanent dipole. Symmetrical molecules will not be polar, as the dipoles cancel out.

14. Instantaneous dipoles are produced on non-polar molecules due to the random movements of electrons – at any moment in time a very slight dipole can be created ($\delta\delta^+$ and $\delta\delta^-$).

15. Intermolecular forces act between molecules (as opposed to intramolecular bonds).

16. Van der Waals forces are very weak, acting between molecules with dipoles. There are three types:
    a. Permanent dipole – permanent dipole attraction occurs between polar molecules.
    b. Permanent dipole – induced dipole attraction occurs between a polar molecule and a non-polar molecule, whereby the polar molecule induces a dipole on the non-polar molecule.
    c. Instantaneous dipole – induced dipole attraction occurs between two non-polar molecules, whereby a dipole is instantaneously produced on one; inducing a dipole on the other.

17. Hydrogen bonding is a dipole – dipole attraction between a hydrogen atom with a δ^+ charge, and a highly electronegative atom with a lone pair of electrons (N, O or F). It is much stronger than Van der Waals forces, but still very weak. This results in unusually high boiling points in compounds such as H_2O and HF.

18. There are four types of crystal structure:
    a. Giant ionic structure – formed by ionic bonding as the close packing of ions in a lattice.
    b. Simple molecular structure – formed by covalent bonding to form molecules. Molecules are held together by intermolecular forces.
    c. Macromolecular structure – formed by covalent bonding to give a giant lattice structure. Allotropes of carbon have this structure (graphite forms layers with delocalised electrons between; diamond is tetrahedral).
    d. Metallic structure – formed by a lattice of metal cations, surrounded by delocalised electrons. There is close packing of ions.

19. Properties of ionic structure:
    a. High melting/boiling point due to very strong bonds.
    b. Dissolves as it consists of charged ions.
    c. Conducts electricity in solution or when molten.
    d. Very strong but brittle, as a shift in the layers splits the lattice.
    e. Crystalline structure, due to ionic lattice.

20. Properties of simple molecular structure:
    a. Low melting/boiling point due to weak Van der Waals forces.
    b. Poor electrical conductivity.
    c. Variable solubility in water.
    d. Very weak when solid.

21. Properties of macromolecular structure:
    a. High melting/boiling point due to very strong bonds.
    b. Very poor electrical conductivity (except graphite with delocalised electrons).
    c. Very strong and hard (graphite is brittle due to a layered structure).

      d.   Insoluble in water.
22. Properties of metallic structure:
      a.   High melting/boiling point due to strong attraction between electrons and cations.
      b.   High electrical and thermal conductivity.
      c.   High density, very strong, ductile and malleable.
23. In order to change state, a certain amount of energy is needed:
      a.   The energy needed to melt a solid at its melting point is the enthalpy of fusion.
      b.   The energy needed to vaporise a liquid at its boiling point is the enthalpy of vaporisation.
24. The shape of a molecule is based on the number of electron pairs that it has:
      a.   2 pairs – linear (180°)
      b.   3 pairs – trigonal planar (120°)
      c.   4 pairs – tetrahedral (109.5°)
      d.   5 pairs – triangle bipyramid (120° equatorial, 90° axial)
      e.   6 pairs – octahedral (90°)
25. Lone pair – lone pair repulsion > lone pair – bond pair repulsion > bond pair – bond pair repulsion.
26. Lone pairs give a greater repulsion, as they are closer to the nucleus. If a molecule is based on tetrahedral, then for one lone pair the angle will be reduced to 107° (e.g. NH_3), and for two lone pairs the angle will be reduced to 105° (e.g. H_2O).

Amount Of Substance
1. One mole of a substance is Avogadro's number of particles of that substance (6×10^{23} particles).
2. In practical terms, one mole of a substance is the relative mass of that substance (A_r or M_r) expressed in grams.
3. The empirical formula is the simplest ratio of atoms of each element in a compound. The molecular formula gives the actual number of atoms of each element in a molecule.
4. When calculating empirical formulae:
      a.   Write down the symbols in columns.
      b.   Write down the mass composition (either percentage or mass).
      c.   Divide by the relative mass (i.e. convert into moles).
      d.   Divide by the smallest value to get the simplest ratio of moles – i.e. the empirical formula.
5. Number of moles – $n = \dfrac{m}{M_r}$
6. Molarity of a solution – $\text{molarity} = \dfrac{\text{number of moles}}{\text{volume}} \times 1000$
7. Number of moles in a solution - $\text{number of moles} = \dfrac{\text{molarity} \times \text{volume}}{1000}$
8. The ideal gas equation – $PV = nRT$ where:
      a. P is the pressure in Nm^{-2}.
      b. V is the volume in m^3.
      c. n is the number of moles.
      d. R is the universal gas constant ($8.31\ Jmol^{-1}K^{-1}$).
      e. T is the absolute temperature in K.

Periodicity
1. Periodicity is the repetition of both physical and chemical properties of the elements both across periods and down groups. This can coincide with repetition in electronic configurations.
2. There are two definitions of atomic radius:
      a.   Covalent Radius – half the distance between the nuclei of atoms of the same element covalently bonded within the same molecule (most commonly used).
      b.   Van der Waals Radius – half the distance between the nuclei of two atoms of the same element from two different molecules (not chemically bonded).
3. The atomic radius decreases across period 3:
      a.   The nuclear charge increases, so the electrons are drawn closer to the nucleus.
      b.   There is no additional shielding for the increase in nuclear charge.
4. Electronegativity increases across period 3:
      a.   This is the power of the element to attract electrons.
      b.   The number of protons increases, so there is a greater positive charge, providing a greater attraction for the electrons in a covalent bond.

5. Electrical conductivity across period 3:
    a. This increases from Na to Al, because the number of delocalised electrons able to carry current increases, thus increasing the ability to conduct electricity.
    b. The elements Si to Ar have close to zero electrical conductivity, because they bond covalently, so the electrons are not free to conduct electricity.
6. Melting and boiling points across period 3:
    a. These are linked to the bond strength and structure of the elements.
    b. Na to Al are metals – the melting and boiling points increase because the nuclear charge and the size of the atoms increase, so the attraction between them is greater, and more energy is needed to melt or to boil them.
    c. Si is macromolecular – it has a great deal of very strong covalent bonds, which require a lot of energy to break. It therefore has very high melting and boiling points.
    d. P to Cl are molecular – the melting and boiling points depend on the Van der Waals forces between the molecules. The melting and boiling points are highest in sulphur (S_8), followed by phosphorus (P_4) followed by chlorine (Cl_2), as the bigger molecules are most polarisable and thus have stronger intermolecular forces. All the melting and boiling points are very low though, as Van der Waals forces are easily broken.
    e. Ar is monatomic – it has very little Van der Waals forces between atoms, and so its melting and boiling points are extremely low.
7. The atomic radius increases down group II:
    a. The number of electron shells increases, so the outermost electron is further away from the nucleus and the radius is bigger.
    b. Although the nuclear charge increases, there is more shielding from complete inner shells, so the radius will still increase.
8. Electronegativity decreases down group II:
    a. The electrons are further from the nucleus, and are shielded by complete inner electron shells as you go down the group, so the attraction for the electrons decreases, even though the nuclear charge increases.
    b. The electronegativity will therefore decrease, because the electrons aren't as strongly attracted to the element.
    c. Beryllium forms a very small highly charged ion, and so has a great attraction for electrons from a larger negative ion, forming essentially a covalent bond (the electron density is concentrated between the ions). Going down the group, the ions get larger, and so the charge is less concentrated and the attraction for electrons is less, so the electronegativity decreases.
9. Melting points down group II:
    a. All of the group are metals with high melting points.
    b. The overall trend is a decrease in melting point, because the atoms get bigger and have more shielding, even though the nuclear charge increases, so the attraction for the delocalised electrons is less. This means that less energy is required to separate the atoms, and thus the melting point decreases.
    c. Magnesium has a lower than expected melting point, due to a difference in its metallic structure meaning that the ions can't pack together as closely.
10. The reactivity of elements with water increases down group II:
    a. Beryllium does not react with cold water or steam.
   b. Magnesium reacts with steam, and very slowly with cold water:
$$Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$$
    c. Calcium, strontium and barium all react with cold water, and the reactivity increases going down the group, producing solutions of the metal hydroxide. For calcium:
$$Ca(s) + 2H_2O(l) \rightarrow Ca(OH)_2(aq) + 2H_2(g)$$
11. The solubility of group II hydroxides and sulphates:
    a. Hydroxides increase in solubility down the group. Barium hydroxide produces strongly alkaline solutions:
$$Ba(OH)_2(s) + aq \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$$
    b. Sulphates decrease in solubility down the group.
    c. Barium sulphate is insoluble, and is used as a test for sulphate ions – dilute acid (HCL or HNO_3) and a solution of barium ions (from $BaCl_2$ or $Ba(NO_3)_2$) are added, giving a white precipitate in the presence of sulphate ions:
$$Ba^{2+}(aq) + SO_4^{2-}(aq) \rightarrow BaSO_4(s)$$

d. The acid is added to remove carbonate ions which would form barium carbonate (also insoluble):

$$2H^+(aq) + CO_3^{2-}(aq) \rightarrow CO_2(g) + H_2O(l)$$
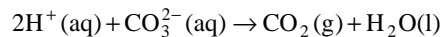
12. The atypical nature of beryllium:

a. The chlorides of other group II elements are ionic, but for beryllium, it forms a linear covalent molecule. This is because of the high-density charge on the small beryllium ion, which attracts the electron cloud between the two ions, creating a covalent bond. $BeCl_2$ is a poor conductor of electricity and is soluble in organic solvents, unlike ionic compounds.

b. The other group II element's hydroxides are basic, i.e. they dissolve in acids but not in bases:

$$Mg(OH)_2(s) + 2H^+(aq) + 4H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq)$$
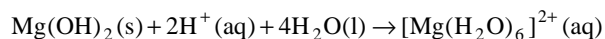
c. Beryllium hydroxide dissolves in both acids and bases – i.e. it is amphoteric:

$$Be(OH)_2(s) + 2H^+(aq) + 2H_2O(l) \rightarrow [Be(H_2O)_4]^{2+}(aq)$$

$$Be(OH)_2(s) + 2OH^-(aq) \rightarrow [Be(OH)_4]^{2-}(aq)$$
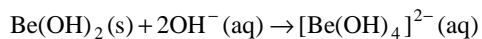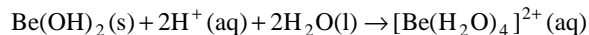
d. As the beryllium ion is so small, only four coordinate bonds can fit around it. It therefore has a maximum coordination number of 4. Other elements in group II have a maximum coordination number of 6.

e. Beryllium chloride molecules can bond together via coordinate bonds to form dimers. In this case beryllium shows a coordination number of 3.