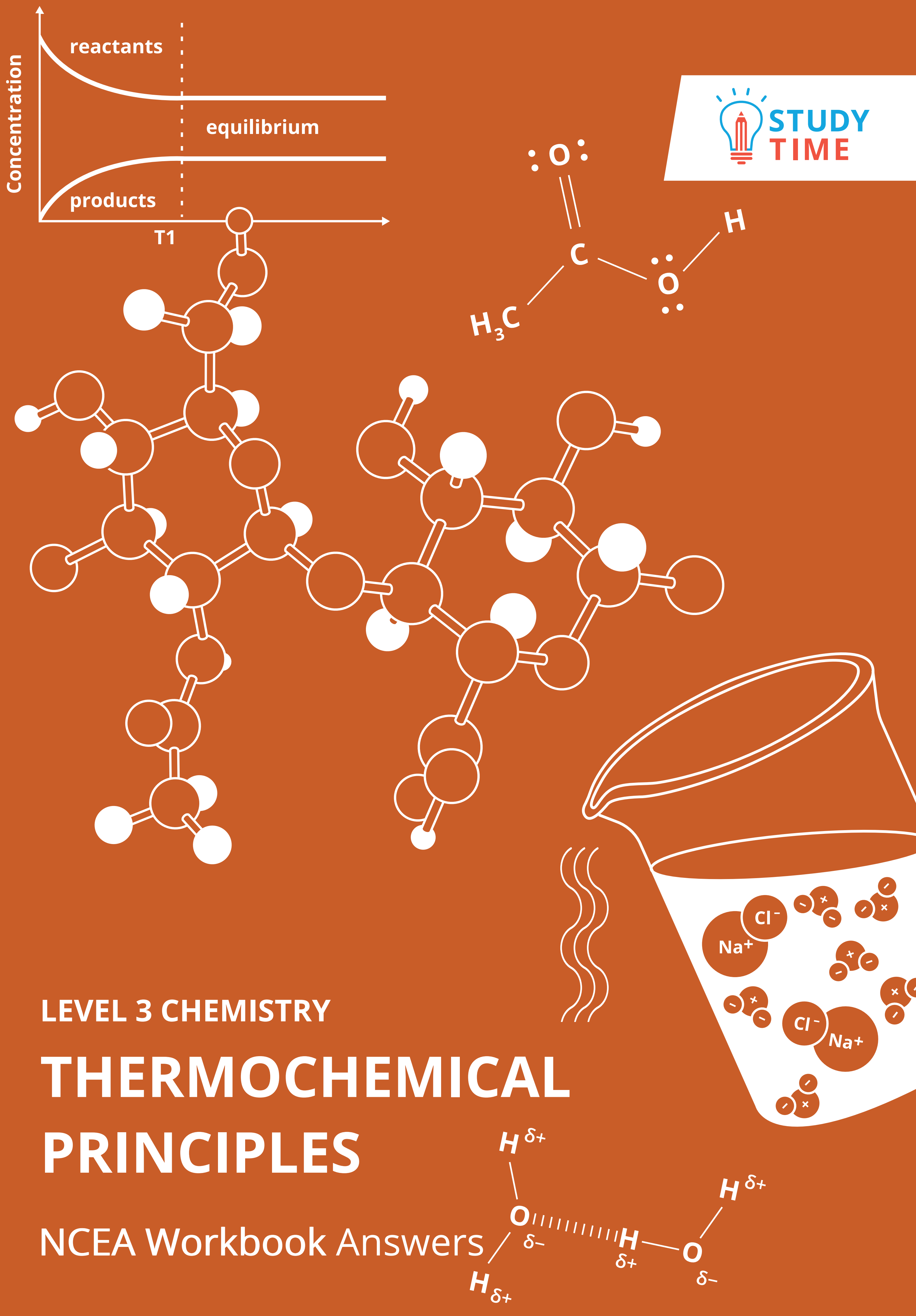
STUDY TIME



LEVEL 3 CHEMISTRY

THERMOCHEMICAL PRINCIPLES

NCEA Workbook Answers

Section One

Basic Skills & Definitions

1. Electron Configuration

a. The atomic number of an element tells you how many protons it has, which is equal to the number of electrons.

b.

i.	Nitrogen	7	*ii.*	Iron	26
iii.	Calcium	20	*iv.*	Fluorine	9
v.	Aluminium	13			

c. No. The atomic number is determined by the number of protons, which does not change when an ion is formed. Only the number of electrons changes.

d. Ionisation, the gain or loss of one or more electrons. This causes the number of electrons to be different from the number of protons. Since protons have a +1 charge, and electrons a -1 charge, when proton and electron numbers are equal (as is the case in an atom), there is no charge as they cancel out. However, as the electron number changes when an ion forms, the number of protons no longer equals the number of electrons and so a charge is created.

e. The atom will gain or lose electrons to minimise the energy or to increase stability. Usually, this is seen or explained as to have full shells, as this makes the atom/ion more stable.

f.

i.	Fe	2+ and 3+	*ii.*	Li	1+		
iii.	Al	3+	*iv.*	Br	1-	v.	Mg 2+

g. A defined region of space around an atom that can contain a pair of electrons.

h. $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^{10}$, $4p^6$. Chromium and Copper are exceptions, as it is more stable to form a half-full (in the case of Chromium, [Ar] $4s^1$ $3d^5$) or full (in the case of Copper, [Ar] $4s^1$ $3d^{10}$) sub-shells.

i. 4s.

j.

i.	Ca^{2+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$
ii.	Co	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^8$ or [Ar] $4s^2\ 3d^8$
iii.	Ne	$1s^2\ 2s^2\ 2p^6$
iv.	Cu	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$
v.	Fe^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5$
vi.	K^+	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ or [Ar]
vii.	N	$1s^2\ 2s^2\ 2p^3$
viii.	Cl^-	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ or [Ar]

ix. Al $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

x. Ti^{2+} $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^2$

2. Periodic Trends: Atomic and Ionic Radius

a.
- Proton count: The greater the number of protons, the higher the positive charge. A larger positive charge leads to more attractive forces acting on the valence shell, pulling it closer to the nucleus, and therefore, decreasing the radius.
- The number of electrons: Electron-electron repulsion causes the electrons to be "pushed" further away from the nucleus, increasing the radius.
- The number of electron shells: The greater the number of electron shells, the further they are from the nucleus, resulting in an increased radius.

b.
- Removing electrons decreases the atomic radius as electron-electron repulsion is reduced, and in most cases, an entire shell of electrons is removed (e.g. $Mg \longrightarrow Mg^{2+}$) which results in a whole 'layer' less to contribute to a radius. A bit like taking a layer off an onion makes it smaller. However, adding electrons has the opposite effect, therefore increasing radius.

c. *i.* Going across the periodic table, radius decreases as the number of protons increases, therefore, increasing the attraction of the electrons to the nucleus, holding them closer. The increased number of protons is stronger than additional electrons added going across.

ii. Going down the periodic table, the atomic radius increases as additional shells of electrons are added. This adds an extra electron shell and also introduces additional shielding. When combined, these have a greater effect on the radius than the increased proton count.

d. *i.* C [✓ F] *ii.* Mg [✓ Mg^{2+}] *iii.* Si [✓ C]

iv. Fe^{3+} [✓ Fe^{2+}] *v.* [✓ Br^-] Br *vi.* K [✓ Li]

3. Periodic Trends: Electronegativity

a. Electronegativity is defined as the ability of an atom to attract a bonding pair of electrons.

b.
- The number of protons: More protons indicates a more positive charge to attract electrons.
- Shielding: Electrons in full shells can "shield" the positive charge of the nucleus from a bonding pair of electrons, reducing the attractive force on the electron pair.
- Atomic radius: The attractive force of the nucleus decreases with distance, so as the radius increases, the attractive force, and therefore, electronegativity decreases.

c. *i.* Going across the periodic table, electronegativity increases as the radius decreases. The number of protons increases with no change in the amount of electron orbitals.

ii. When going down the groups, electronegativity decreases. This is due to the radius increasing, reducing the attractive force of the nucleus. The additional shells of electrons “shield” the positive nuclear charge further, reducing the attractive force on a bonding pair of electrons. This reduction is more significant than the attraction gained due to the increased number of protons in the nucleus, and so electronegativity decreases.

d. *i.* [✓ F] Br

ii. Cs [✓ Na]

iii. [✓ O] S

iv. Ca [✓ P]

v. [✓ N] Mg

vi. [✓ C] Li

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4. Periodic Trends – Ionisation Energy

a. Ionisation energy is defined as the energy required to remove 1 mole of electrons from the outermost shell of 1 mole of atoms.

b. Second ionisation energy is the energy required to remove a second electron from 1 mole of atoms, meaning the atom/ion would then have lost 2 moles of electrons.

c. What are two factors that affect the ionisation energy of an atom?

- The number of protons: More protons indicates a more positive charge, and therefore, a stronger attractive force acting on the valence electrons, increasing the energy required to remove them.
- Shielding: Electrons in full electron shells can “shield” the positive charge of the nucleus from the valence electrons, reducing the attractive force acting on the valence electrons, decreasing the energy required to remove them.
- Atomic radius: Attractive force of the nucleus decreases with distance, so as the radius increases attractive force decreases, therefore, decreasing the energy required to remove valence electrons.

d. *i.* Going across the periodic table, ionisation energy increases because of the radius decreasing and the number of protons increasing. There is no change in the amount of shielding. This means the attractive force between the nucleus and valence electrons is increased and more energy is required to remove an electron.

ii. When going down the groups, ionisation energy decreases. This is because the radius increases, reducing the attractive force of the nucleus, and additional shells of electrons “shield” the positive nuclear charge from the valence electrons. This reduction is more significant than the attraction gained due to the increased number of protons in the nucleus, and so ionisation energy decreases.

e. Both ionisation energy and electronegativity follow the same trends, They both increase with an increase in the number of protons, decrease with additional shielding and decrease as radius increases. However, ionisation energy is about the energy required to **remove** an electron, while electronegativity is the ability to **attract** a bonding pair of electrons.

Answers

f. *i.* [✓ O] K *ii.* [✓ Mg] Na *iii.* Mg [✓ S]

iv. [✓ Cl] P *v.* I [✓ Br] *vi.* [✓ K] Li

5. Shape and Polarity of Molecules

a. A negative region or electron density refers to the space around the central atom caused by a bond (single, double, and triple bonds all count as a single negative region) or non-bonding pair of electrons.

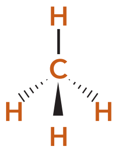
b. They repel each other, to maximum separation angles, minimising the energy of the molecule.

c. Negative regions around the central atom repel each other to minimise energy, changing bond angles. The bond angle, and therefore, the shape of the molecule, is determined by how many negative regions there are. The final shape is determined by how many of those negative regions are bonding regions vs non-bonding lone pairs.

d.

Number of negative regions	Bond angle	Molecule Geometry				
		No lone pairs	1 lone pairs	2 lone pairs	3 lone pairs	4 lone pairs
2	180°	Linear				
3	120°	Trigonal planar	Bent			
4	109.5°	Tetrahedral	Trigonal pyramidal	Bent		
5	90° and 120°	Trigonal bipyramidal	Sawhorse	T-shaped	Linear	
6	90°	Octahedral	Square-based pyramid/ square pyramidal	Square planar	T-shaped	Linear

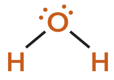
e. i.



Tetrahedral

109.5°

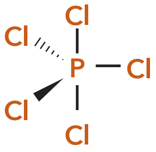
ii.



Bent

109.5°

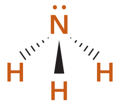
iii.



Trigonal bipyramidal

90° and 120°

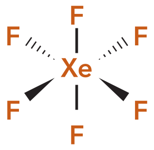
iv.



Trigonal pyramidal

109.5°

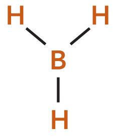
v.



Octahedral

90°

vi.



Trigonal planar

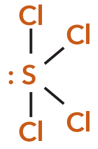
120°

vii.

Square planar

90°

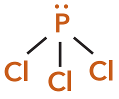
viii.



Sawhorse

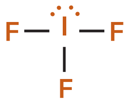
90° and 120°

f. *i.* PCl_3



Trigonal Pyramidal 109.5°

ii. IF_3

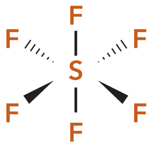


T-Shaped 90°

iii. CO_2

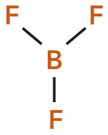
Linear 180°

iv. SF_6



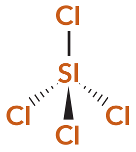
Ochtahedral 90°

v. BF_3



Trigonal planar 120°

vi. $SiCl_4$

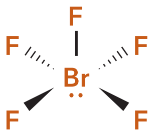


Tetrahedral 109.5°

vii. BBr_2

Linear 180°

viii. BrF_5

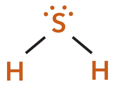


Square Pyramidal 90°

g. A bond is polar when it is between two atoms of different electronegativities. This means any bond between two different atoms is polar. Examples include (but are not limited to): H-F, C-H, O-H, Si-Cl.

h. The polar B-H bonds are effectively "cancelled out" by the other B-H bonds due to the symmetry in the molecule. The electrons (or negative charge) is evenly spread around the molecule and so there is no overall separation of charge (polarity).

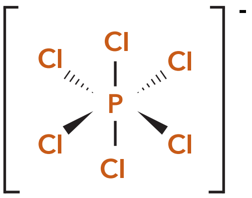
i. *i.* H_2S



Bent

The molecule is polar as there are polar bonds between H-S, and the molecular shape (bent) is non-symmetrical. A non-symmetrical shape does not result in cancellation of dipoles as the H atoms are not evenly distributed around the molecule. This results in an overall polar molecule.

ii. PCl_6^-



Octahedral

The ion is nonpolar, despite the P-Cl bonds being polar. There is no overall separation of charge (dipoles) in the molecule as each Cl is evenly distributed around the molecule. Therefore, the dipoles of each bond cancel out, resulting in a nonpolar molecule overall.

6. Intermolecular Forces

a. Hydrogen bonding, permanent dipole interactions, and temporary dipole/Van der Waals interactions.

i. Hydrogen bonds

ii. Hydrogen bonding requires hydrogen and a small electronegative atom (nitrogen, oxygen, or fluorine) to be bonded together. Examples include: H_2O, CH_3OH.
Permanent dipoles interactions form between polar molecules as the negatively-charged region of a polar molecule is attracted to the positively-charged region of another polar molecule. Examples include: H_2O, CH_3Cl, NH_3.
Temporary dipole interactions are formed by all molecules but are stronger in molecules with large numbers of electrons. This means a stronger temporary dipole can form.

b. *i.* Temporary dipoles/Van der Waals interactions.

ii. Hydrogen bonds, permanent dipoles and temporary dipoles/Van der Waals interactions.

iii. Hydrogen bonds, permanent dipoles and temporary dipoles/Van der Waals interactions.

iv. Permanent dipoles and temporary dipoles/Van der Waals interactions.

v. Temporary dipoles/Van der Waals interactions.

c. Stronger intermolecular forces require more energy to break the intermolecular bonds. This means stronger intermolecular forces (e.g. hydrogen bonds) will increase the energy required to separate molecules from each other (as is required for a change in state, e.g. liquid to gas requires breaking of intermolecular forces). Therefore, there is a direct link between the strength of intermolecular bonds and boiling and melting points of molecules.

d. Methanol has hydrogen bonds, permanent dipole interactions, and temporary dipole interactions whereas methane only has temporary dipole/Van der Waals interactions between molecules. This means the intermolecular forces between methane molecules are significantly less than that of methanol, and it requires a lot less energy to separate the methane molecules than the methanol molecules. This results in a significantly lower boiling point.

7. Enthalpy and Entropy

a. Enthalpy is the energy of a system, typically relating to the change in enthalpy caused by the breaking and creating of chemical bonds. This can result in a negative or positive change in enthalpy. Enthalpy is also often called "heat energy".

b. Exothermic processes release energy (negative enthalpy change, i.e. the energy of the system decreases), while endothermic processes absorb energy (positive enthalpy change, i.e. the energy of the system increases).

c. *i.* Change in enthalpy due to a chemical reaction.

ii. Change in enthalpy due to the formation of a molecule from the raw elements.

iii. Change in enthalpy due to combustion.

d. *i.* Solid to liquid.

ii. Liquid to gas.

iii. Solid to gas.

e. Standard conditions are the temperature and pressure at which a reaction (or phase change) is considered "standard". This is at 25°C (298K) and 1 atm (atmospheric pressure). This is important because the enthalpy of a reaction or state change differs under different conditions. An enthalpy value is shown to be under standard conditions by placing a degree symbol after the "H", for example, $\Delta_r H°$ or $\Delta_f H°$.

f. *i.* The change in enthalpy of the dissolution of NaCl in water can be measured by measuring the temperature change of the water as the NaCl dissolves.

The change in temperature can be used to calculate the energy change using the specific heat capacity of water using $q = mc\Delta T$, where q is the heat energy (change in enthalpy), m is the mass of substance (in this example, the mass of water), c is the specific heat capacity of the substance (again, in this case, water), and ΔT is the measured change in temperature. This can then be converted to enthalpy per mol by dividing the mass of NaCl used by the molar mass of NaCl and dividing the total heat energy by this value.

ii. The change in enthalpy for the combustion of coal can be measured by heating another substance, such as water, or by using a calorimeter. The change in temperature of the substance or calorimeter can then be used to calculate the change in heat energy using $q = mc\Delta T$, where q is the heat energy (change in enthalpy), m is the mass of substance (for example, of water), c is the specific heat capacity of the substance (of water or the calorimeter), and ΔT is the measured change in temperature.

g. The measured values will typically be lower than the correct value as energy will be lost to the surroundings or as other forms of heat energy, for example, light energy in the combustion of magnesium. This means that not all of the energy released is accounted for in the change of temperature.

h. *i.* Using $q = mc\Delta T$
$m = 200g$ (200mL of water = 200g of water)
$c = 4.186 \text{ J g}^{-1} \text{ °C}^{-1}$
$\Delta T = 35 - 23$
$\Delta T = 12°C$

Putting it together:

$q = 200 \times 4.186 \times 12$
$q = 10{,}046.4J$.

ii. Using $q = mc\Delta T$
$m = 25g$ (25 mL of water = 25g of water)
$c = 4.186 \text{ J g}^{-1} \text{ °C}^{-1}$
$\Delta T = 4°C$.

Putting it together:
$q = 25 \times 4.186 \times 4$
$q = 418.6J$.

i. Hess's law states that "the energy change in an overall chemical reaction is equal to the sum of the energy changes in the individual reactions comprising it". More simply put, this means that if you start with one set of reactants and finish with a set of products, no matter how you get there the enthalpy change is the same.

j. Hess's law can be helpful because it means you can break the overall reaction into different steps or reactions that you already have the enthalpies for, and add the enthalpy of each step together, to find the overall reaction enthalpy.

k. Entropy is described as a measure of the disorder in a system and uses the letter S.

l. *i.* As ice melts the entropy increases. This is because the water molecules are no longer locked in place in the solid ice structure, and can arrange themselves in a greater number of ways indicating a higher entropy.

   ii. In the combustion reaction of hydrogen, entropy decreases. This is because as the hydrogen and oxygen react to produce water, there are fewer particles as products (1 particle) than reactants (1.5). This means there are less possible ways to arrange the system as there are fewer particles. Additionally, the products are in the liquid state while reactants are gaseous, therefore, the products are able to move around and arrange themselves in fewer ways and entropy decreases.

   iii. As $MgCl_{2(s)}$ dissolves into its ions in water, entropy increases. The increased number of particles significantly increases the number of ways the system can be arranged, therefore, increasing the entropy of the system.

   iv. Condensation is a gas-to-liquid phase change, therefore, the entropy will decrease. This is because as ethanol particles are forced closer together to form a liquid, the number of possible ways to arrange the particles decreases, therefore, the entropy of the system decreases.

m. Both enthalpy and entropy play a role in determining whether a reaction or process will be spontaneous or non-spontaneous. A negative enthalpy (release of energy/exothermic process) is favoured for a spontaneous process. An increase in entropy is also favoured for a spontaneous process. If the change in entropy is positive and enthalpy change is negative, the process will be spontaneous. If the change in entropy is negative and enthalpy change is positive, the process will be non-spontaneous. If the change in entropy and enthalpy are both positive or both negative, spontaneity will be temperature-dependent.

n. *i.* This reaction will be non-spontaneous as the entropy decreases due to a decreased number of particles and the enthalpy change is positive (endothermic reaction).

   ii. This reaction will be spontaneous as the entropy increases due to an increased number of particles and the enthalpy change is negative (exothermic reaction).

   iii. This reaction will be non-spontaneous as the entropy decreases due to a decreased number of particles and a gas to liquid state change. The enthalpy change is positive (endothermic reaction) supporting the prediction that this reaction is non-spontaneous.

   iv. This reaction will be spontaneous as the entropy increases due to an increased number of particles and the products are in an aqueous state compared to a solid-state. The enthalpy change is negative (exothermic reaction) supporting the prediction that this reaction is spontaneous.

Section Two

Exam Skills & Breaking Questions Down

1.

a. The electron configuration for the Na atom is $1s^2\ 2s^2\ 2p^6\ 3s^1$, while the electron configuration for the Na^+ ion is $1s^2\ 2s^2\ 2p^6$.

b. The atomic radius is affected by several factors. The number of protons (nuclear charge), number of electron shells, electron-electron repulsion, and level of electron shielding all affect the atomic radius of an atom or ion.

c. All of the above factors are affected by the loss of an electron in this example, except for the number of protons. The number of electron shells decreases from 3 to 2 with the loss of an electron, resulting in a smaller radius as there are less "layers" of electrons. When an electron is lost, electron-electron repulsion is also reduced as there are fewer electrons to repel each other outward, resulting in a decrease in the atomic radius. This has a greater effect on paired electrons, which is not the case for the ionisation of Na to Na^+. Finally, the level of electron shielding is reduced by the loss of electrons, increasing the effect of nuclear attraction, pulling the valence electrons closer to the nucleus, and therefore, decreasing the overall atomic radius for the Na^+ ion.

2.

a. Electronegativity is defined as the ability of an atom to attract a bonding pair of electrons.

b. First Ionisation energy is defined as the energy required to remove 1 mole of electrons from the outermost shell of 1 mole of atoms.

c. The definitions of electronegativity and first ionisation energy show that electronegativity is about how strongly the atom attracts a bonding pair of electrons, while ionisation energy is the energy required to remove electrons that are already part of the atom (the valence electrons, to be specific!). While they are both a measure of the attractive force on electrons, electronegativity is specifically bonding electrons while ionisation energy is the attraction towards valence electrons.

d. Going from left to right across the periodic table, electronegativity increases. This is due to an increased proton count causing a greater nuclear charge, and a smaller radius allowing a bonding pair of electrons to get closer to the attractive force of the nucleus.

e. When going across the periods from left to right, first ionisation energy increases. Therefore, it follows the same trend as electronegativity. This is due to electronegativity and first ionisation energy both being dependent on the same variables: number of protons, ionic radius, and electron shielding.

f. Going down the periodic table, electronegativity decreases. This is due to the increased levels of electron shielding decreasing the strength of the attractive nuclear force on a bonding pair of electrons, as well as the increased radius preventing the bonding pair from getting as close to the nucleus.

g. When going down the groups of the periodic table, first ionisation energy decreases just like electronegativity. This is due to electronegativity and ionisation energy being influenced by the same factors. The increased radius when going down the periodic table results in less effective nuclear charge on the valence electrons, therefore, resulting in lower energy required to remove an electron. Similarly, increased electron shielding going down the groups makes it easier to remove electrons, therefore, decreasing the ionisation energy.

3.

a. SF_6 consists of 6 negative regions (electron clouds), all of which are bonded. Negative regions repel each other to minimise their interactions, minimising the energy of the molecule. For a 6-coordinate molecule like SF_6, the maximum separation angle is 90 degrees. As all negative regions are bonded, this produces the octahedral shape.

b. The bonds between sulfur and fluorine are polar as they have different electronegativities (fluorine is the most electronegative element!). This results in fluorine pulling the electrons closer to itself, resulting in more electron density around the atom. This causes the bond to have a slightly negative charge surrounding the fluorine atom and a slightly more positive charge surrounding the sulfur atom, resulting in a polar bond.

c. The overall SF_6 molecule is nonpolar. This is because the octahedral geometry of the molecule is symmetrical, resulting in the cancellation of the dipoles in the S-F bonds, causing the overall molecule to be nonpolar.

d. H_2O is polar (due to the bent geometry) and will dissolve other polar substances. Remember the "like dissolves like" rule.

e. The SF_6 molecule is nonpolar, however, because water is polar it will not dissolve SF_6 as "like dissolves like".

4.

a. BrF_5 has 6 negative regions (electron clouds), 5 of which are bonding and 1 of which is a nonbonding pair of electrons. All of these negative regions repel to minimise energy (minimise interactions) and form maximum separation angles of 90 degrees. This gives a square-based pyramid shape (square pyramidal).

b. BrF_6^- has 6 negative regions (electron clouds), like BrF_5. However, unlike BrF_5, all 6 of these negative regions are bonded and there are has no lone pairs of electrons around the central atom. These negative regions repel to minimise energy (minimise interactions) and form maximum separation angles of 90 degrees.

c. The bonds between bromine and fluorine are polar as they have different electronegativities. This results in fluorine pulling the electrons closer to itself, resulting in more electron density/negativity around the atom. This causes the bond to be more negative at one end and more positive at the other, resulting in a polar bond.

d. The overall BrF_5 molecule is polar. This is because the square pyramidal geometry of the molecule is asymmetric, resulting in an overall dipole from the Br-F bonds, causing the molecule to be polar overall.

e. Unlike BrF_5, the overall BrF_6^- molecule is nonpolar. This is because the octahedral geometry of the molecule is symmetrical, resulting in the cancellation of the dipole in the Br-F bonds, causing the overall molecule to be nonpolar. This difference in overall geometry, asymmetric vs symmetric, causes the difference in polarity between the two molecules despite having the same polar Br-F bonds.

5.

a.

Molecule	Boiling Point	Intermolecular Forces
Pentane	36 °C	Temporary dipoles/Vander Waals/London dispersion forces.
1−chloropentane	108 °C	Temporary dipoles/Van der Waals/London dispersion forces and permanent dipole interactions.
Pentanol	138 °C	Temporary dipoles/Van der Waals/London dispersion forces, permanent dipole interactions, and hydrogen bonds.

b. Pentanol has the strongest intermolecular forces due to having strong hydrogen bonds in addition to permanent and temporary dipoles (Alternative names: Van der Waals or London dispersion forces).

c. Pentanol has stronger intermolecular forces than 1-chloropentane, as pentanol has hydrogen bonds in addition to the temporary dipole interactions and permanent dipole interactions of the 1-chloropentane molecules. This additional intermolecular force (hydrogen bonding) means the overall intermolecular force is stronger. Similarly, this means pentane is the weakest as it only has weak temporary dipole interactions (Alternative names: Van der Waals or London dispersion forces) as intermolecular forces.

d. Stronger intermolecular forces result in a higher boiling point as more energy is required to break the intermolecular bonds holding the molecules close together in the liquid state. If more energy is required to break these bonds, a greater temperature is needed to provide this energy, thus increasing the boiling point of the substance.

e. In the answer to part c, it was explained that pentanol has stronger intermolecular forces than 1-chloropentane, which in turn has stronger intermolecular forces than pentane. The answer to part d explains how the strength of intermolecular forces directly affects the boiling point. Therefore, we observe pentanol having the highest boiling point, pentane with the lowest, and 1-chloropentane in the middle, due to the strengths of intermolecular forces present between the molecules in each substance.

6.

a. (2) $SO_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow SO_{3\,(g)}$

b. Due to halving the overall stoichiometry of (2), the $\Delta_r H$ value will also have halved. This means the new $\Delta_r H$ will be -99 kJ mol^{-1}.

c. $S_{(s)} + O_{2\,(g)} \rightarrow SO_{2\,(g)} \quad \Delta_f H = -296\ \text{kJ mol}^{-1}$
$SO_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow SO_{3\,(g)} \quad \Delta_r H = -99\ \text{kJ mol}^{-1}$

d. $S_{(s)} + O_{2\,(g)} \rightarrow \cancel{SO_{2\,(g)}} \quad \Delta_f H = -296\ \text{kJ mol}^{-1}$
$\cancel{SO_2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow SO_{3\,(g)} \quad \Delta_r H = -99\ \text{kJ mol}^{-1}$

e. $S_{(s)} + 1\frac{1}{2}O_{2\,(g)} \rightarrow SO_{3\,(g)} \quad \Delta_f H = -395\ \text{kJ mol}^{-1}$.

f. A process is exothermic if energy is released. The negative $\Delta_f H$ value of the final answer tells us that the formation of $SO_{3\,(g)}$ is an exothermic process.

Answer tip: For a question such as this, the overall process can (and should) be simplified a lot. A typical exam answer for this kind of question would look like this:

$S_{(s)} + O_{2\,(g)} \rightarrow \cancel{SO_{2\,(g)}} \quad \Delta_f H = -296\ \text{kJ mol}^{-1}$

$\cancel{SO_2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow SO_{3\,(g)} \quad \Delta_r H = -99\ \text{kJ mol}^{-1}$

$S_{(s)} + 1\frac{1}{2}O_{2\,(g)} \rightarrow SO_{3\,(g)} \quad \Delta_f H = -395\ \text{kJ mol}^{-1}$.

$\Delta_f H$ is negative, therefore the overall reaction is exothermic.

This can make these questions fairly fast if you understand what you are doing!
Make sure you remember to reverse equations where needed and keep track of the positive and negative enthalpy values properly. Also, remember to adjust enthalpy values when adjusting the stoichiometry of the reactions.

7.

a. $B_2H_{6\,(g)} \rightarrow 2B_{(s)} + 3H_{2\,(g)} \quad \Delta_f H = -36\ \text{kJ mol}^{-1}$
$H_{2\,(g)} + \frac{1}{2}O_{2\,(g)} \rightarrow H_2O_{(l)} \quad \Delta_f H = -286\ \text{kJ mol}^{-1}$
$2B_{(s)} + 1\frac{1}{2}O_{2\,(g)} \rightarrow B_2O_{3\,(s)} \quad \Delta_f H = -1274\ \text{kJ mol}^{-1}$

Reaction (1) is reversed as in the reaction we are trying to find the enthalpy for B_2H_6, so we need to reflect this in our Hess's law calculation.

b. $B_2H_{6\,(g)} \rightarrow 2B_{(s)} + 3H_{2\,(g)} \quad \Delta_f H = -36\ \text{kJ mol}^{-1}$
$3H_{2\,(g)} + 1\frac{1}{2}O_{2\,(g)} \rightarrow 3H_2O_{(l)} \quad \Delta_f H = -858\ \text{kJ mol}^{-1}$
$2B_{(s)} + 1\frac{1}{2}O_{2\,(g)} \rightarrow B2O_{3\,(s)} \quad \Delta_f H = -1274\ \text{kJ mol}^{-1}$

Stoichiometries of reaction (2) is multiplied by 3 to produce $3H_2O$, as is done in the overall combustion of diborane (the reaction we are trying to find).

c. $B_2H_{6\ (g)}$ → ~~$2B_{(s)} + 3H_{2\ (g)}$~~ $\Delta_fH = -36\ kJ\ mol^{-1}$
~~$3H_{2\ (g)}$~~ $+ 1½O_{2\ (g)}$ → $3H_2O_{\ (l)}$ $\Delta_fH = -858\ kJ\ mol^{-1}$
~~$2B_{(s)}$~~ $+ 1½O_{2\ (g)}$ → $B2O_{3\ (s)}$ $\Delta_fH = -1274\ kJ\ mol^{-1}$

d. Total enthalpy can be calculated by adding together the enthalpy of each 'step'.

$-36 + -858 + -1274 = -2186\ kJ\ mol^{-1}$

$B_2H_{6\ (g)} + 3O_{2\ (g)}$ → $B_2O_{3\ (s)} + 3H_2O_{\ (l)}$ $\Delta_cH = -2168\ kJ\ mol^{-1}$

8.

a. $KOH_{\ (s)}$ → $K^+_{\ (aq)} + OH^-_{\ (aq)}$

b. Simply plugging the values we are given into the equation we get:

$q = -120g \times 4.186\ J\ g^{-1}\ °C^{-1} \times 10.2°C$
$q = -5123.664\ J$.

Report final values to 3 significant figures (5120J) but keep the earlier value for later calculations! Also make sure to use the mass of water here, not the mass of KOH used.

c. Using $n = \frac{m}{M}$ and plugging in the mass used and molar mass of KOH provided, we get:

$n = \frac{5g}{56.1g\ mol^{-1}} = 0.0891\ mol.$

d. We can calculate the enthalpy per mole by dividing the enthalpy change by the number of moles used. This is done as follows:

$\frac{-5123.664J}{0.0891mol} = -57{,}487.5\ J\ mol^{-1}$.

Rounding to 3 significant figures gives:

$-57{,}500\ J\ mol^{-1}$. This works out as $-57.5\ kJ\ mol^{-1}$.

e. The negative enthalpy value tells us this process is exothermic. The entropy change will be positive because there is a change from solid to aqueous, as well as an increased number of particles as the KOH is dissolved, thus, causing an increase in possible arrangements of the system, and therefore, increase in entropy. Positive entropy change and negative enthalpy results in a spontaneous process.

Section Three
Practice Exam

Answers

Question One

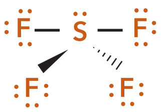
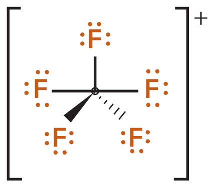
a.

Symbol	**Electron Configuration**
P^{3+}	$1s^2\ 2s^2\ 2p^6\ 3s^2$ or $[Ne]\ 3s^2$
Cl	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$ or $[Ne]\ 3s^2\ 3p^5$
Cl^-	$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ or $[Ne]\ 3s^2\ 3p^6$ or [Ar]

b. The Cl atom has a smaller radius than the Cl^- ion. Both the Cl atom and Cl^- atom have the same nuclear charge, however, the additional electron present in the Cl^- ion increases electron-electron repulsion, increasing the radius of the ion.

c. First ionisation energy is defined as the energy required to remove 1 mole of electrons from the outermost shell of 1 mole of atoms. When going across the periods from left to right, first ionisation energy increases. This is due to increased proton count causing a greater nuclear charge, and a smaller radius. This means the valence electrons are closer to the attractive force of the nucleus, and therefore, require more energy to remove. When going down the groups of the periodic table, first ionisation energy decreases. The increased radius when going down the periodic table results in less effective nuclear charge on the valence electrons, resulting in lower energy required to remove an electron. Similarly, increased electron shielding going down the groups makes it easier to remove electrons, therefore, decreasing the first ionisation energy. Because of fluorine's small radius and the low number of electron shells, it has a very strong attraction between nucleus and valence electrons. This results in high first ionisation energy. Comparatively, sodium has a much larger radius and more electron shielding due to the increased number of shells, and so there is a significantly less attractive force on the valence electrons. This means it is significantly easier to remove an electron, and therefore, sodium has lower first ionisation energy.

d. *i.*

	SF_4	SF_5^+
Lewis Diagram		
Name of shape	Sawhorse	Trigonal bipyramidal

ii. SF_4 would be expected to dissolve in water. The S-F bond is polar due to F being more electronegative than S, resulting in a negative dipole at the F end of the bond and a positive dipole at the S end of the bond. The shape of the molecule, seesaw, is asymmetric. This means no cancellation of the dipoles occurs and so the overall molecule is polar. Water is also polar, and since "like dissolves like", SF_4 would be expected to dissolve in water.

Question Two

a. This symbol represents the enthalpy of vaporisation (liquid to gas state change) at standard conditions (as indicated by the degree symbol).

b. *i.*

Molecule	$\Delta_{fus}H°$ (kJ mol^{-1})	Attractive Forces
NH_3	5.65	Temporary dipoles/Van der Waals/London dispersion forces, permanent dipole interactions and hydrogen bonds.
CH_4	1.1	Temporary dipoles/Van der Waals/London dispersion forces.
CH_3F	1.4	Temporary dipoles/Van der Waals/London dispersion forces and permanent dipole interactions.

ii. CH_4 has the lowest enthalpy of fusion as it has the weakest attractive forces between molecules of any of the 3 molecules. This is because CH_4 only has temporary dipole interactions (alternatively Van der Waals or London dispersion forces) which are very weak. This means it requires very little energy (or enthalpy) to separate the molecules in the solid-state to create a liquid, resulting in low enthalpy of fusion. Fluoromethane has a higher enthalpy of fusion as it has permanent dipole interactions in addition to temporary dipole interactions. Since permanent dipole interactions are significantly stronger, this results in greater energy (or enthalpy) to separate solid fluoromethane molecules into the liquid, resulting in a higher enthalpy of fusion. NH_3 has the highest enthalpy of fusion as it has strong hydrogen bonds between molecules in addition to permanent and temporary dipole interactions, as the H will bond to the electronegative N of neighbouring NH_3 molecules. This makes NH_3 molecules harder to separate into the liquid phase, therefore, requiring more enthalpy for fusion.

c. *i.*

$$\begin{array}{llll} \cancel{2H_{2\,(g)}} + O_{2\,(g)} & & 2H_2O_{(l)} & \Delta_rH = -572 \text{ kJ} \\ N_2H_{4\,(l)} & \rightarrow & N_{2\,(g)} + \cancel{2H_{2\,(g)}} & \Delta_rH = -50.6 \text{ kJ mol}^{-1} \\ & & & \\ N_2H_{4\,(l)} + O_{2\,(g)} & \rightarrow & N_{2\,(g)} + 2H_2O_{(l)} & \Delta_cH = -622 \text{ kJ mol}^{-1} \end{array}$$

The first reaction is doubled (including enthalpy) to make the stoichiometry consistent with the overall combustion reaction, and the second reaction is reversed (including enthalpy) for the same reason. These values can then be added to get the enthalpy of combustion of -622 kJ mol^{-1}.

ii. As hydrazine has the formula N_2H_4, we know it has N-H bonds. This means N_2H_4 molecules will hydrogen bond. Water can also form hydrogen bonds due to the O-H bond, and so will have strong intermolecular interactions with hydrazine, dissolving it effectively. However, octane cannot form these hydrogen bonds and so will not be able to dissolve hydrazine effectively, as intermolecular bonds between hydrazine molecules will be favoured over intermolecular bonds between hydrazine and octane. Hydrazine is also a polar molecule, making it much easier to dissolve in water, which is also polar, than the nonpolar octane.

d. The entropy change for the formation of hydrazine will be negative, as there is both a reduction in the number of molecules and gas to liquid state change. This means the number of ways the system can be arranged significantly decreases, and so entropy decreases. The enthalpy change for the reaction is positive, meaning energy must be absorbed for the reaction to occur. Since the change in enthalpy is positive, and the change in entropy is negative, the formation of hydrazine will be non-spontaneous.

Question Three

a. Ethane is nonpolar and is not able to form hydrogen bonds, so the only intermolecular forces present are temporary dipole interactions.

b. Hexane is a significantly larger molecule than ethane, with 6 carbons compared to 2, and 14 hydrogens compared to 6. This means hexane also has significantly more electrons. This results in a much larger electron cloud that will have a larger separation of charge due to temporary dipole interactions. This means the induced dipole will be much stronger in hexane, causing stronger interactions, and therefore, more energy required to separate molecules and a higher boiling point compared to ethane.

c. *i.* Using $q = mc\Delta T$, we know:

$c = 294\text{J}\ ^{\circ}\text{C}^{-1}$
$\Delta T = 101 - 25$
$\Delta T = 76^{\circ}\text{C}$.

In this case, we do not need a mass as we are using the total heat capacity of the calorimeter in $\text{J}\ ^{\circ}\text{C}^{-1}$ (there is no per gram, so no mass needed to cancel units!).

Putting these into the equation we get:

$q = 294\text{J}\ ^{\circ}\text{C}^{-1} \times 76^{\circ}\text{C}$
$q = 22{,}344\text{J}$.

The reaction is exothermic (releases heat to surroundings) so the q value is -22,344J. The number of moles, n, can be calculated using $n = \frac{m}{M}$:

$n = {}^{0.5}/_{94}$
$n = 0.005319$ mol.

To calculate enthalpy per mol we divide the change in enthalpy by the number of moles:

$\frac{-22{,}344}{0.005319} = 41{,}800{,}671\ \text{J mol}^{-1}$.

Finally divide by a thousand to convert to kilojoules:

$\frac{41{,}800{,}671\text{J mol}^{-1}}{1000} = 4{,}180\ \text{kJ mol}^{-1}$ (rounded to 3 significant figures).

ii. When the enthalpy change is measured, it is assumed that 100% of the energy released is absorbed by the calorimeter. This will not be entirely true as some will be absorbed by the air inside and surrounding the calorimeter as well as potentially being lost to sound or light energy in the process of combustion.

d. A process can be spontaneous despite having a positive enthalpy change (endothermic) if the increase in entropy is significant enough. Ammonium nitrate will readily dissolve in water at room temperature because this causes an increase in the number of particles and a change in state from solid to aqueous for these particles. This dramatically increases the number of possible arrangements for the system, therefore, increasing entropy and causing the reaction to be spontaneous despite the endothermic nature.