

With 2017 NCEA
Exam included



NCEA Chemistry 3.4

Particles, Substances and Thermochemistry AS 91390



Achievement Criteria

This achievement standard involves describing properties of atoms, molecules, and ions, and thermochemical principles.

Properties of particles will be limited to:

- electron configuration of atoms and ions of the first 36 elements (using *s,p,d* notation)
- periodic trends in atomic radius, ionisation energy, and electronegativity, and comparison of atomic and ionic radii
- Lewis structures and shapes (up to six electron pairs about the central atom for molecules and polyatomic ions, including those with multiple bonds), polarity of molecules
- attractive forces between atoms, ions, and molecules. These will include ionic bonds, covalent bonds, and intermolecular attractions due to temporary dipoles and permanent dipoles (including hydrogen bonding).

Properties of substances will be limited to:

- melting point, boiling point and solubility
- enthalpy and entropy changes associated with spontaneity in chemical reactions (entropy calculations are not required)

Thermochemical principles will include

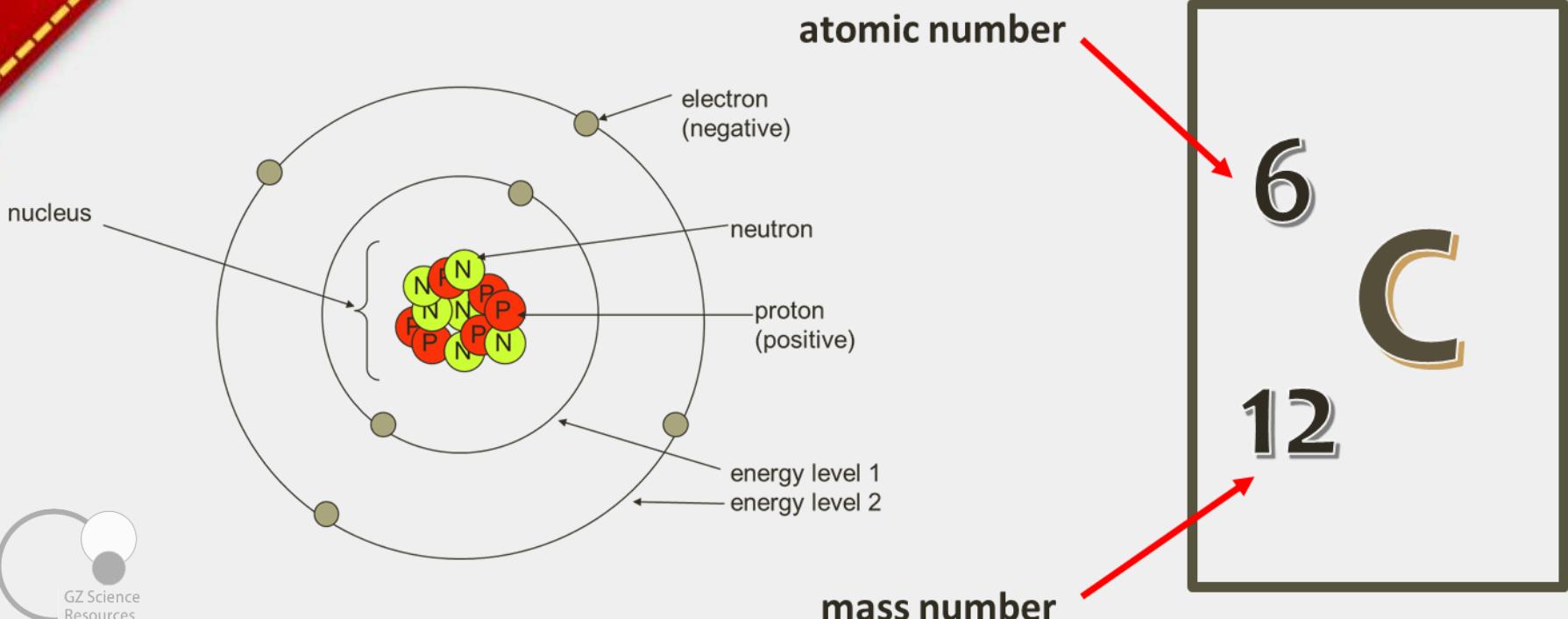
- specific heat capacity
- $\Delta_c H^\circ$, $\Delta_f H^\circ$, $\Delta_r H^\circ$, $\Delta_{vap} H^\circ$, $\Delta_{sub} H^\circ$, and $\Delta_{fus} H^\circ$
- Hess's Law including application of $\Delta_r H = \sum \Delta_f H(\text{products}) - \sum \Delta_f H(\text{reactants})$ and related calculations.



Background Knowledge

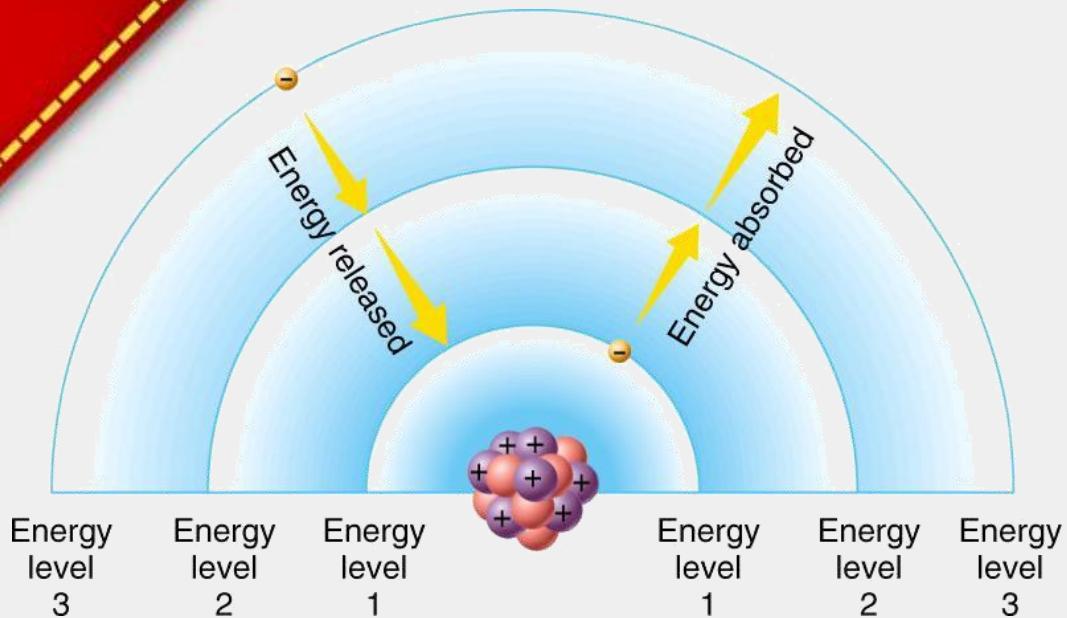
Atomic and Mass number

The **atomic number** is unique for each element. A neutral atom has the same number of electrons as protons. The periodic table is arranged in order of an elements atomic number. The **mass number** is the total number of protons and neutrons together.



Background Knowledge

Electrons orbit a nucleus of an atom at fixed energy levels.



An electron can only be found in a fixed energy level around a nucleus. A ball bouncing down a flight of stairs provides an analogy for energy levels of electrons because a ball can only rest on each step, not between steps.

An electron can move up an energy level if energy is absorbed, such as light or heat. When the electron moves back down to its lowest possible level the energy is released again, often in the form of light.

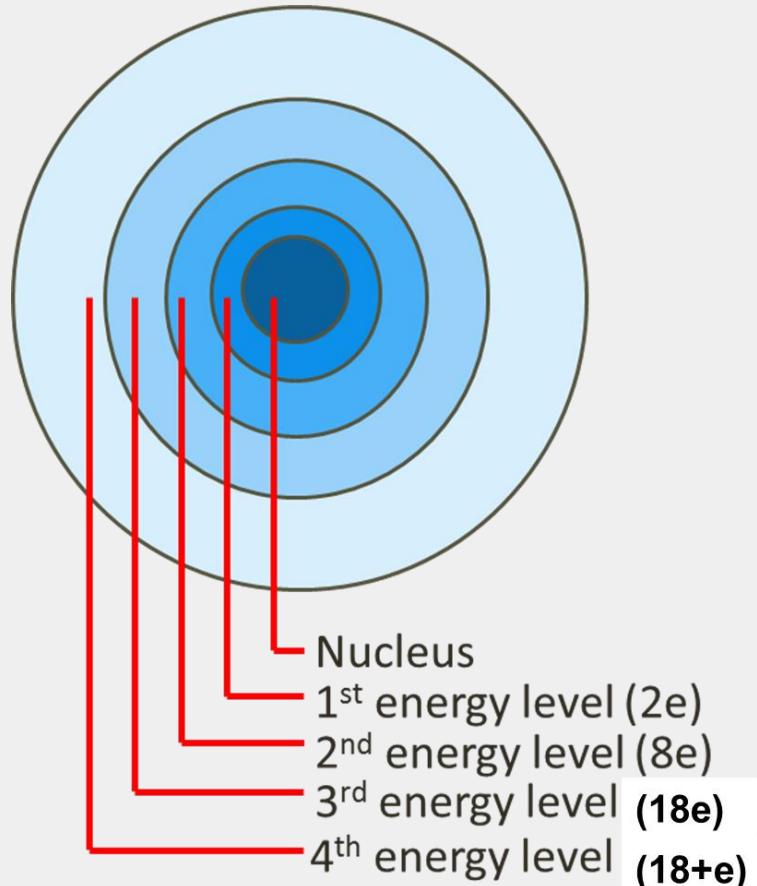
Background Knowledge

Electrons move or ‘orbit’ around the nucleus in **energy levels** or shells. The energy levels further away from the nucleus are able to fit more electrons.

The first energy level is filled first, followed by the second and so on until all the electrons (the same number of protons in an atom) have been used.

You need to draw the configurations of the first 36 elements as well as knowing their names and symbols

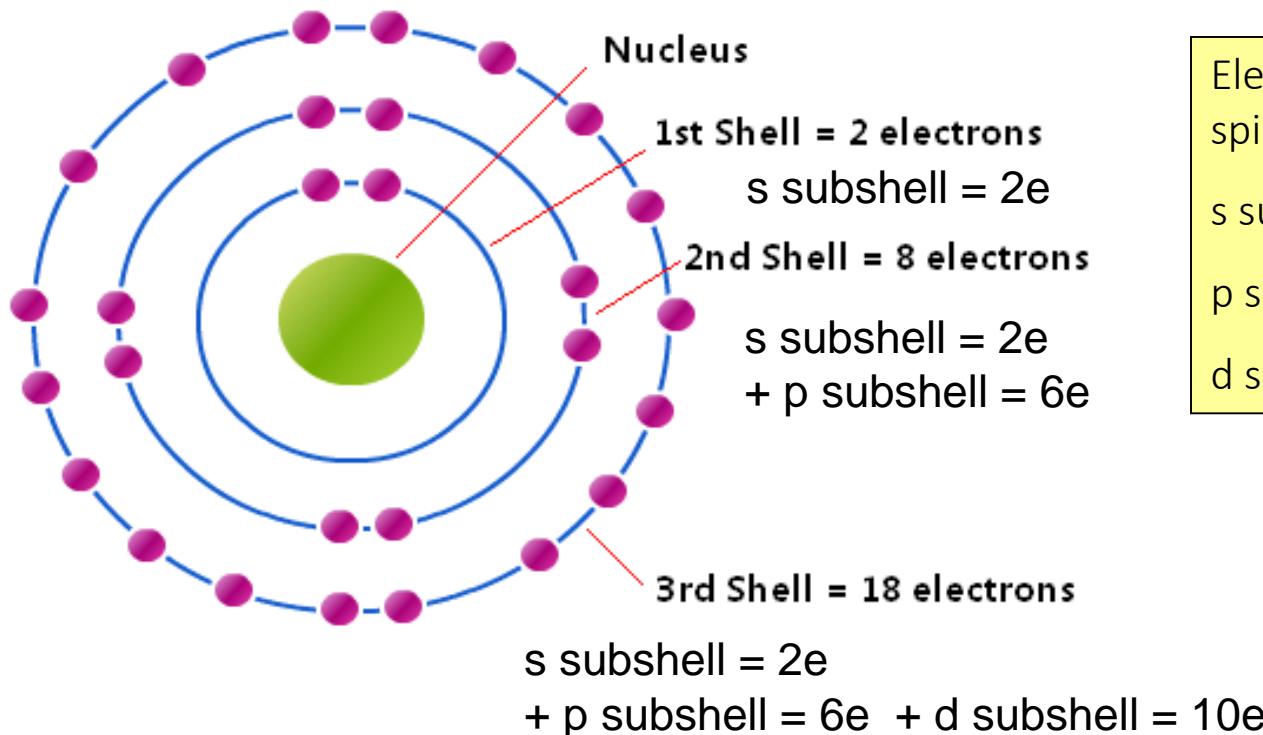
The electrons in an atom are arranged in a series of energy levels.



Electron orbitals

The major energy levels (shell) split into **subshells**. Each sub shell level made up of one or more **atomic orbitals**.

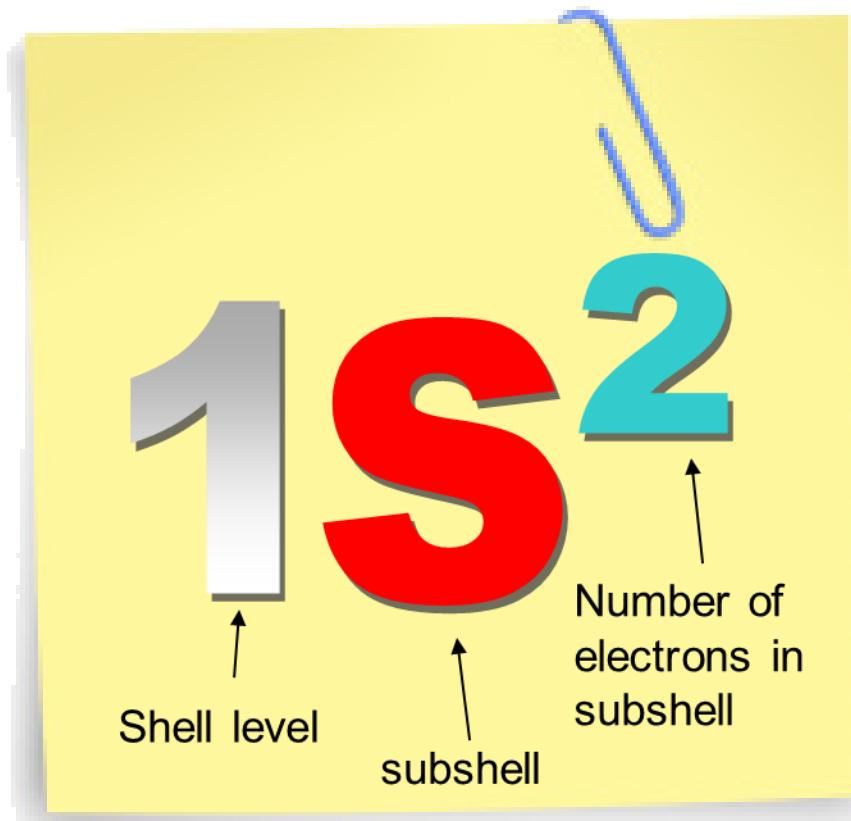
An **Orbital** is an area of space with high probability of finding a particular electron pair. Electrons orbit in pairs spinning opposite directions.



Electrons orbit in pairs
spinning opposite directions
s subshell = 1 orbital (2e)
p subshell = 3 orbitals (6e)
d subshell = 5 orbitals (10e)

Electron Configuration notation

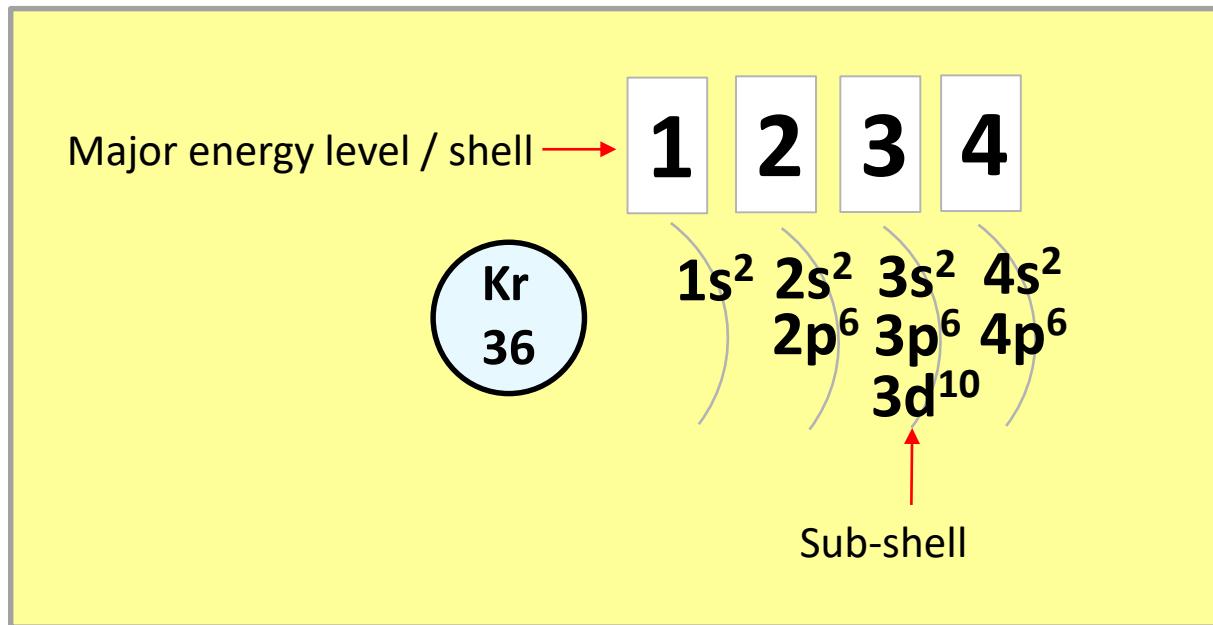
Even though the subshells are filled according to energy level, the notation is still written out in order. $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}, 4s^2, 4p^6, \dots$



Atoms and ions with the same electron configuration are said to be isoelectronic.



Energy levels and subshells



The sub shells are numbered according to the major shell/energy level they are in.

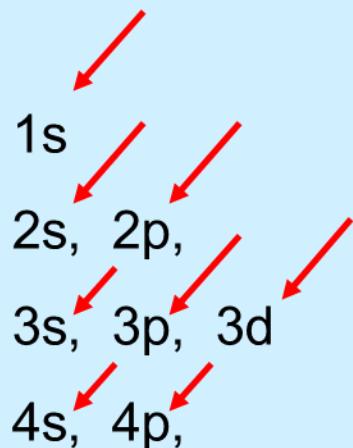
Major Energy Level	No. of orbitals of a given type			Total electrons
n	s	p	d	
1	1			2
2	1	3		8
3	1	3	5	18
4	1	3	5	18+

Order of fill

The arrangement of the electrons around the nucleus is known as its configuration.

The **Aufbau principle** states that electrons always fill the shells with the lowest energy level first.

Order of fill



1. All of the orbitals hold up to 2 electrons which make up a pair (s1,p3,d5).
2. The electron pairs spin in opposite directions indicated with arrows ↓↑
3. Electrons fill up orbitals with lower energy levels first
$$1s \rightarrow 2s \rightarrow 2p \rightarrow 3s \rightarrow 3p \rightarrow 4s \rightarrow 3d \rightarrow 4p$$
4. The most stable (lower energy) arrangement is for the sublevels to be filled with a single electron first (with the same direction spin) before pairing electrons.
(Hund's rule) Place electrons singly first showing upwards arrow.

Condensed Electron Configuration

As it is the valence shell that is of the most interest, the inner shells up to that point can be shown by the symbol for the previous inert gas element (neon)

e.g. Cl [Ne] 3s² 3p⁵ rather than 1s² 2s² 2p⁶ 3s² 3p⁵

Element	Electron Configuration
Hydrogen	1s ¹
Helium	1s ²
Lithium	1s ² 2s ¹
Beryllium	1s ² 2s ²
Boron	1s ² 2s ² 2p ¹
Carbon	1s ² 2s ² 2p ²
Nitrogen	1s ² 2s ² 2p ³
Oxygen	1s ² 2s ² 2p ⁴
Fluorine	1s ² 2s ² 2p ⁵
Neon	1s ² 2s ² 2p ⁶
Sodium	1s ² 2s ² 2p ⁶ 3s ¹
Magnesium	1s ² 2s ² 2p ⁶ 3s ²
Aluminium	1s ² 2s ² 2p ⁶ 3s ² 3p ¹
Silicon	1s ² 2s ² 2p ⁶ 3s ² 3p ²
Phosphorus	1s ² 2s ² 2p ⁶ 3s ² 3p ³
Sulfur	1s ² 2s ² 2p ⁶ 3s ² 3p ⁴
Chlorine	1s ² 2s ² 2p ⁶ 3s ² 3p ⁵
Argon	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶

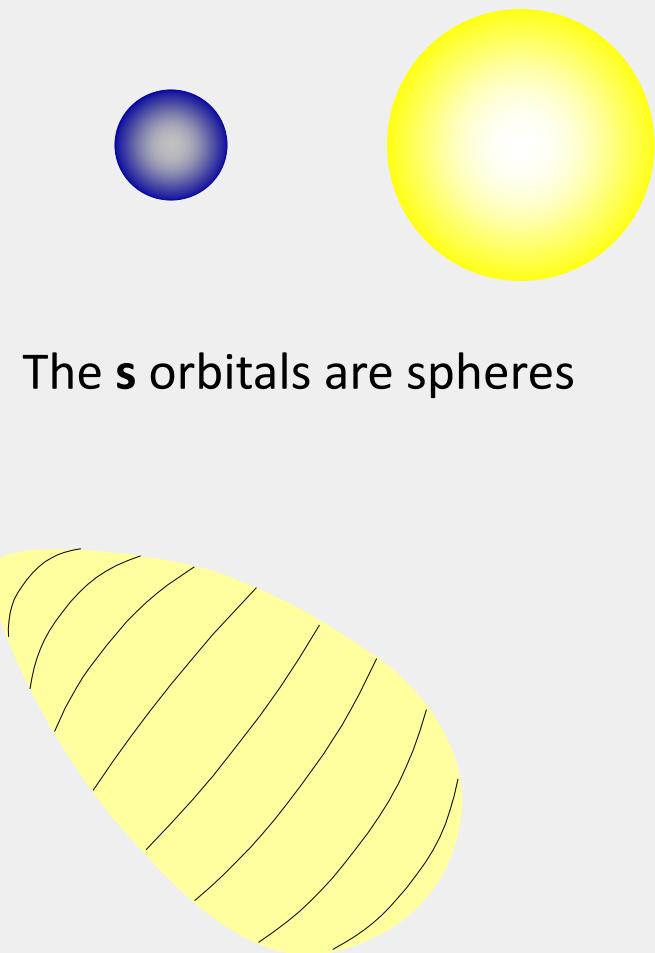
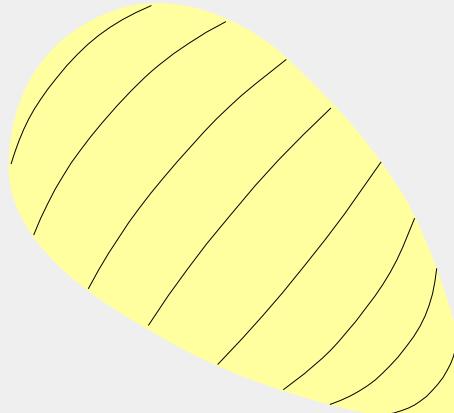
Background Knowledge

Electron orbital shapes



Science has determined where the orbitals are inside an atom, but it is never known precisely where the electrons are inside the orbitals

The area where an electron can be found, the orbital, is defined mathematically, but we can see it as a specific shape in 3-dimensional space...



The **s** orbitals are spheres

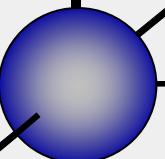
The **p** orbitals are tear shaped

Background Knowledge

z

Electron orbital shapes

The 3 axes represent 3-dimensional space. the nucleus of the atom is at the center of the three axes.

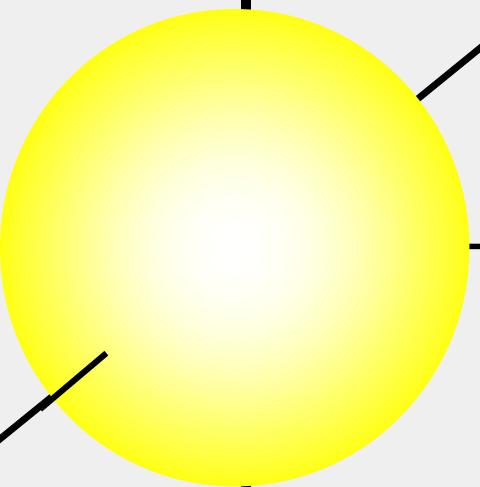


The “1s” orbital is a sphere, centered around the nucleus

Background Knowledge

Electron orbitals shapes

The 2s orbital is also a sphere.



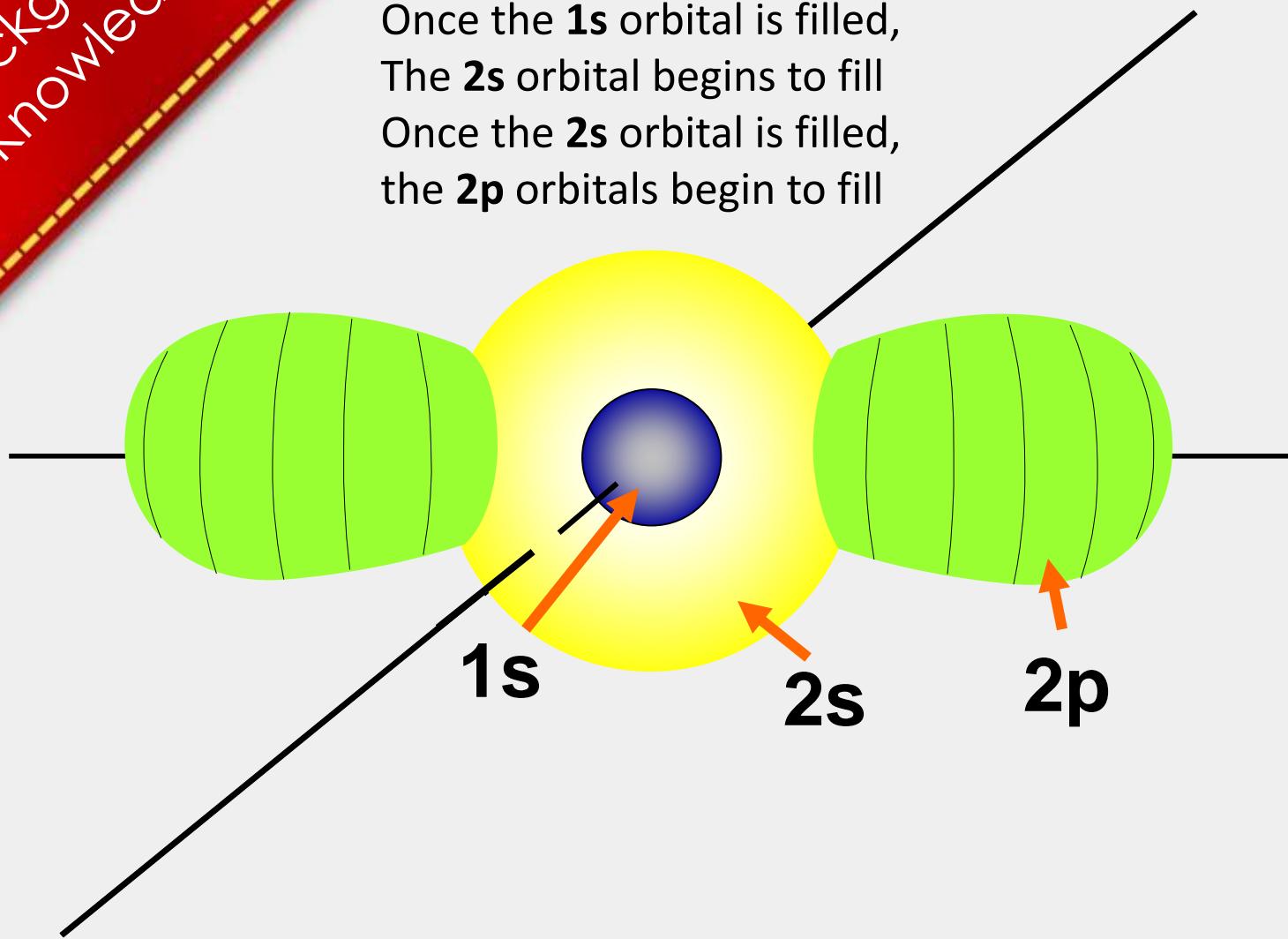
The 2s electrons have a higher energy than the 1s electrons. Therefore, the 2s electrons are generally more distant from the nucleus, making the 2s orbital larger than the 1s orbital.

Background Knowledge

Z

Electron orbital shapes

Once the **1s** orbital is filled,
The **2s** orbital begins to fill
Once the **2s** orbital is filled,
the **2p** orbitals begin to fill



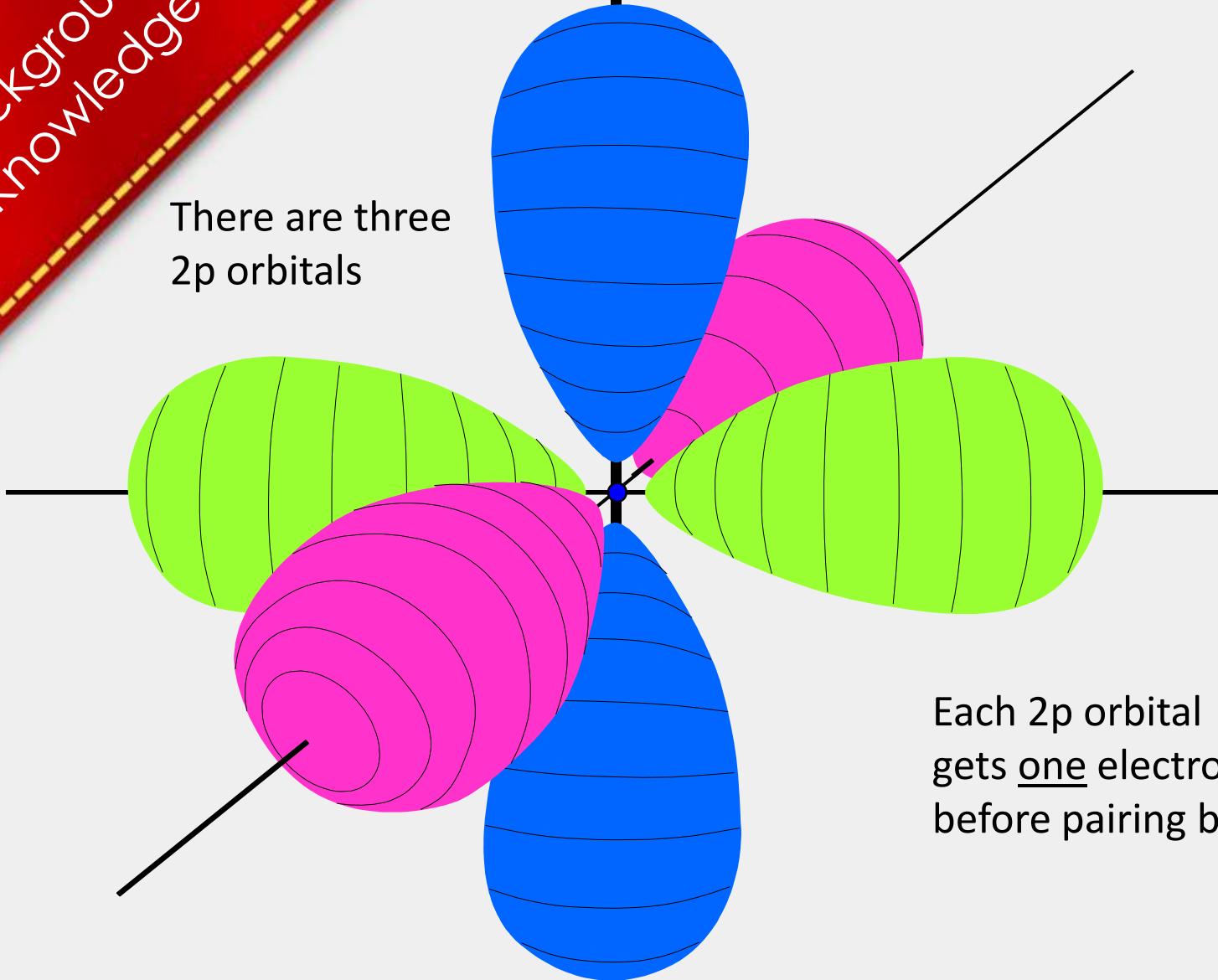
Background Knowledge

Electron orbital shapes

z

There are three
2p orbitals

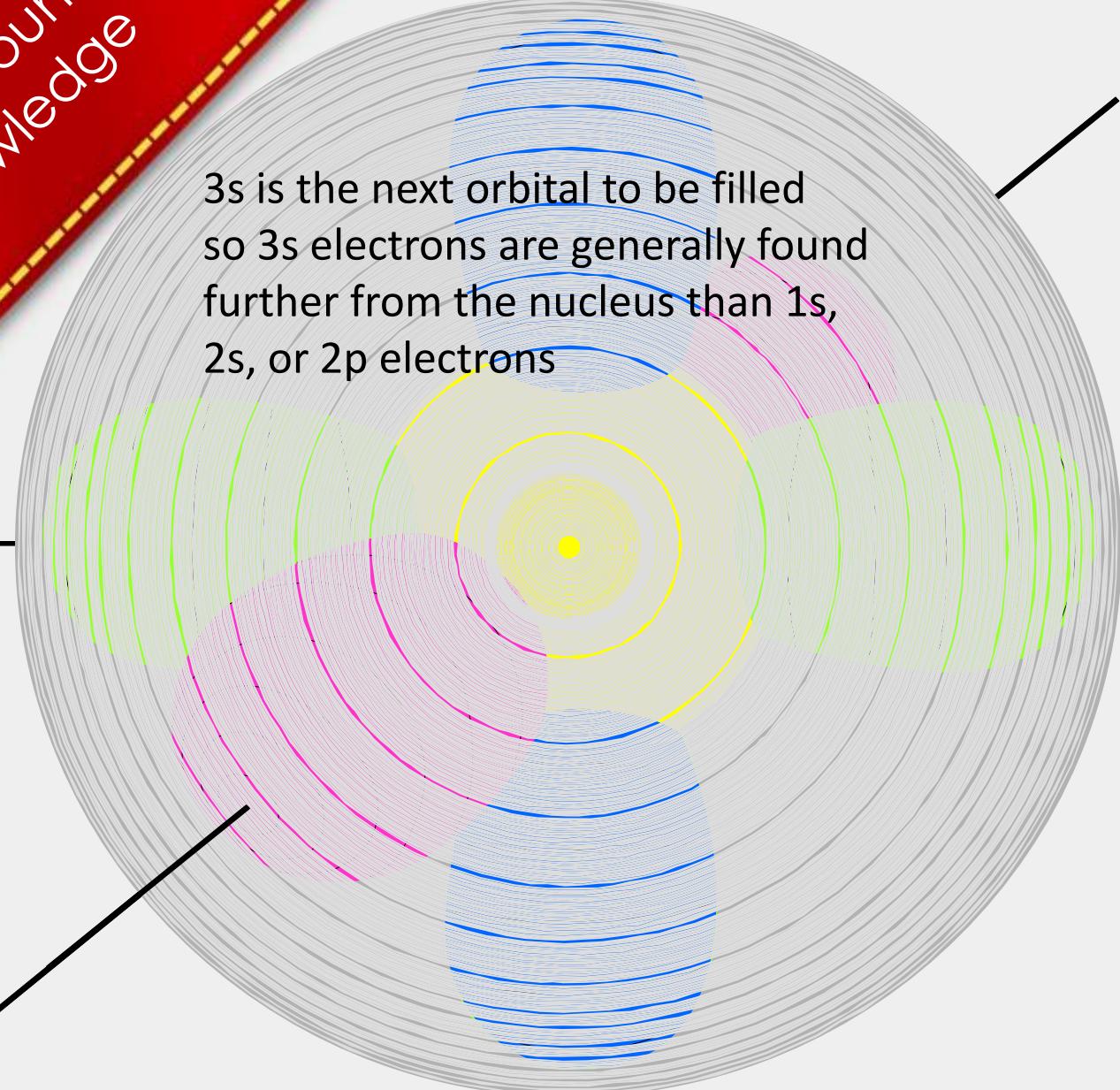
Each 2p orbital
gets one electron
before pairing begins



Electron orbital shapes

Background
Knowledge

3s is the next orbital to be filled so 3s electrons are generally found further from the nucleus than 1s, 2s, or 2p electrons



NCEA 2013 s,p,d configurations

Achieved
Question

Q 1a: Complete the following table

Symbol	Electron configuration
Se	Se: [Ar]3d ¹⁰ 4s ² 4p ⁴ or 4s ² 3d ¹⁰ 4p ⁴
V	V: [Ar]3d ³ 4s ² or 4s ² 3d ³
V ³⁺	V ³⁺ : [Ar]3d ² where [Ar]: 1s ² 2s ² 2p ⁶ 3s ² 3p ⁶

Shorthand is acceptable
spd are drawn in order not fill

In the past 5 years the spd configuration is a “stand alone” question – which case there is an Achieved point given for the majority correct. (or sometimes Merit if all correct)
In past years the following elements or ions have been used:

Al Cl Cu²⁺ Sc Zn K Cr Cr³⁺ As Se V V³⁺ Ca²⁺ Mn²⁺

NCEA 2014 s,p,d configurations

Merit
Question

Q 1a: Complete the following table

Symbol	Electron configuration
K	$K\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$ $[Ar]\ 4s^1$
Cr	$Cr\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$ $[Ar]\ 3d^5\ 4s^1$
As	$As\ 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^3$ $[Ar]\ 3d^{10}\ 4s^2\ 4p^3$

Shorthand is acceptable
spd are drawn in order not fill

In the past 5 years the spd configuration is a “stand alone” question – which case there is an Achieved point given for the majority correct. (or sometimes Merit if all correct)
In past years the following elements or ions have been used:

Al Cl Cu²⁺ Sc Zn K Cr Cr³⁺ As Se V V³⁺ Ca²⁺ Mn²⁺

NCEA 2015 s,p,d configurations

Achieved
Question

Q 1a: Complete the following table

Symbol	Electron configuration	
Al	Al	= [Ne] $3s^2 3p^1$ where $[Ne] = 1s^2 2s^2 2p^6$
Cu^{2+}	Cu^{2+}	= [Ar] $3d^9$
Sc	Sc	= [Ar] $3d^1 4s^2$ where $[Ar] = 1s^2 2s^2 2p^6 3s^2 3p^6$

Shorthand is acceptable
spd are drawn in order not fill

In the past 5 years the spd configuration is a “stand alone” question – which case there is an Achieved point given for the majority correct. (or sometimes Merit if all correct)
In past years the following elements or ions have been used:

Al Cl Cu^{2+} Sc Zn K Cr Cr^{3+} As Se V V^{3+} Ca^{2+} Mn^{2+}

NCEA 2016 s,p,d configurations

Achieved
Question

Q 1a: Complete the following table

Symbol	Electron configuration
Cl	Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$
Zn	Zn: [Ar] $3d^{10} 4s^2$
Cr^{3+}	Cr^{3+} : [Ar] $3d^3$

Shorthand is acceptable
spd are drawn in order not fill

In the past 5 years the spd configuration is a “stand alone” question – which case there is an Achieved point given for the majority correct. (or sometimes Merit if all correct)
In past years the following elements or ions have been used:

Al Cl Cu²⁺ Sc Zn K Cr Cr³⁺ As Se V V³⁺ Ca²⁺ Mn²⁺

NCEA 2017 s,p,d configurations

Achieved
Question

Q 1a: Complete the following table

Symbol of particle	Electron configuration (use <i>s, p, d</i> notation)	Charge	Atomic number
Cl	Cl: $1s^2 2s^2 2p^6 3s^2 3p^5$	0	17
Ca^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6$	+2	20
Mn^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	+2	25

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In past years the following elements or ions have been used:

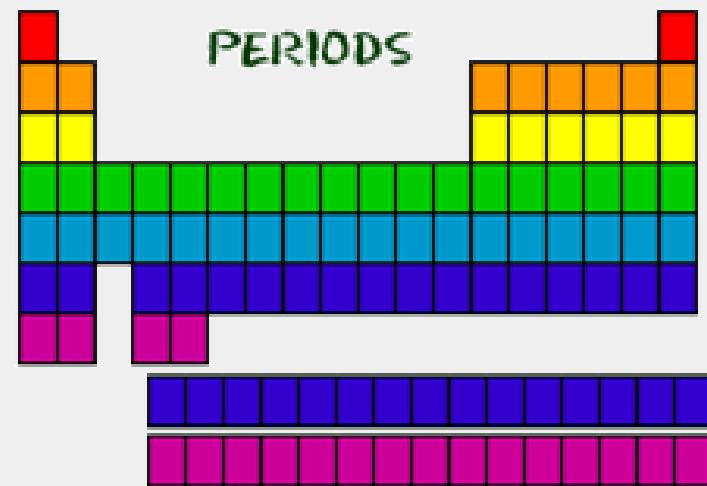
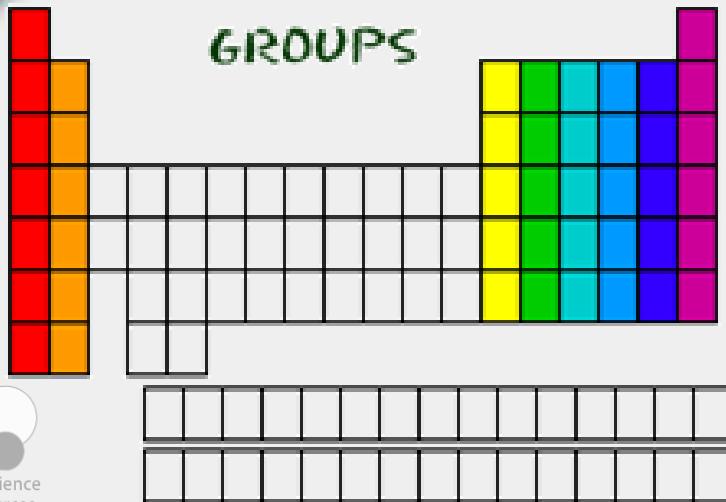
Al Cl Cu²⁺ Sc Zn K Cr Cr³⁺ As Se V V³⁺ Ca²⁺ Mn²⁺

Background Knowledge

Periodic Table

The columns (downwards) of a periodic table are called groups.

The rows (across) of a periodic table are called periods.



Elements in the same **group** all have the same number of electrons in their outer (or **valence**) shells.

Elements in the same **period** all have the same number of shells of electrons in their atoms

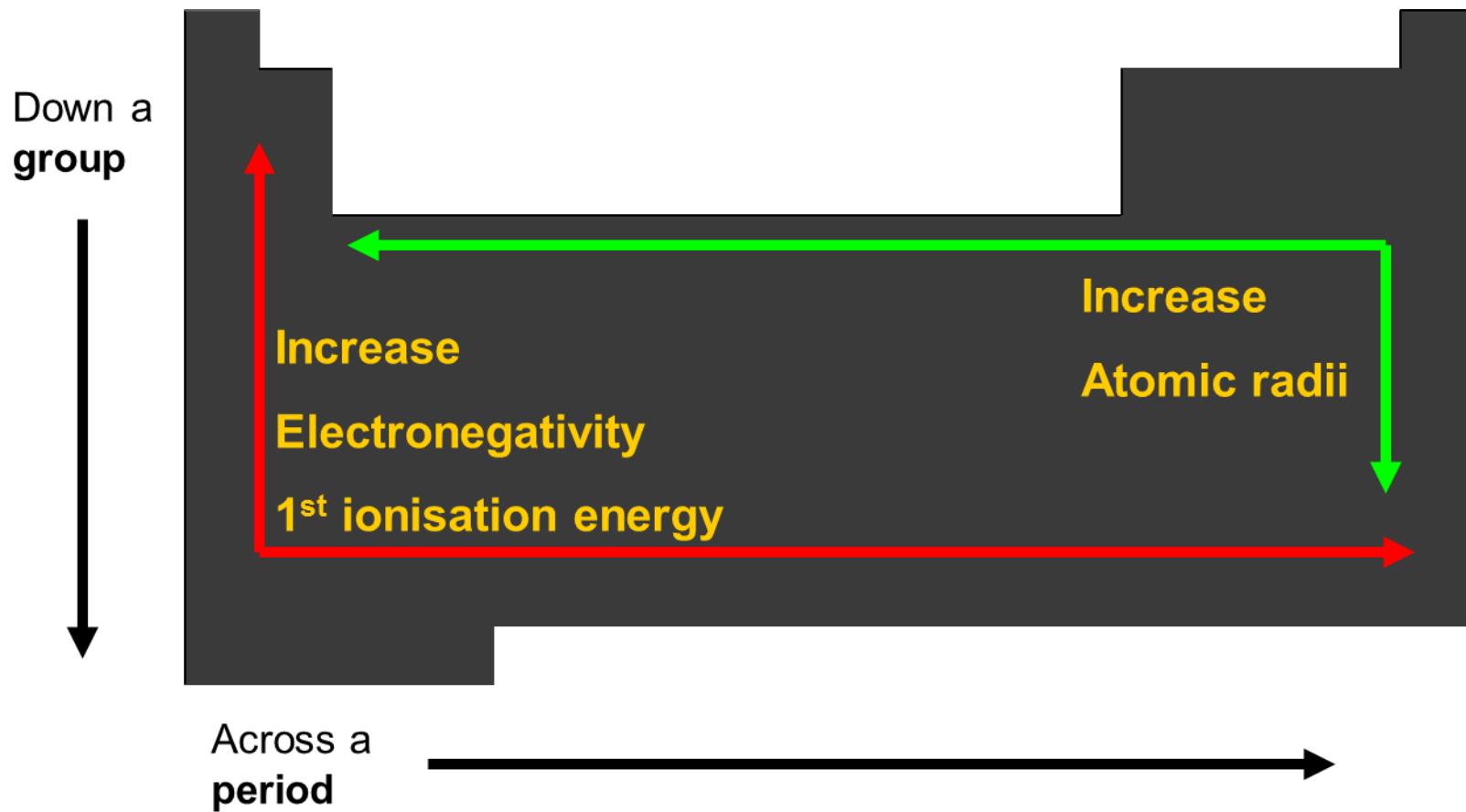
Background Knowledge

Periodic Table

		1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18																																																																																																																																																																																																																																																																							
1	H	Hydrogen	1.0	2	Li	Lithium	6.9	4	Be	Beryllium	9.0	11	Na	Sodium	23.0	12	Mg	Magnesium	24.3	19	K	Potassium	39.1	20	Ca	Calcium	40.1	21	Sc	Scandium	45.0	22	Ti	Titanium	47.9	23	V	Vanadium	50.9	24	Cr	Chromium	52.0	25	Mn	Manganese	54.9	26	Fe	Iron	55.9	27	Co	Cobalt	58.9	28	Ni	Nickel	58.7	29	Cu	Copper	63.6	30	Zn	Zinc	65.4	31	Ga	Gallium	69.7	32	Ge	Germanium	72.6	33	As	Arsenic	74.9	34	Se	Selenium	78.9	35	Br	Bromine	79.9	36	Kr	Krypton	83.8	37	Rb	Rubidium	85.5	38	Sr	Strontium	87.6	39	Y	Yttrium	88.9	40	Zr	Zirconium	91.2	41	Nb	Niobium	92.9	42	Mo	Molybdenum	95.9	43	Tc	Technetium	98	44	Ru	Ruthenium	101	45	Rh	Rhodium	103	46	Pd	Palladium	106	47	Ag	Silver	108	48	Cd	Cadmium	112	49	In	Indium	115	50	Sn	Tin	119	51	Sb	Antimony	122	52	Te	Tellurium	128	53	I	Iodine	127	54	Xe	Xenon	131	55	Cs	Caesium	133	56	Ba	Barium	137	72	Hf	Hafnium	179	73	Ta	Tantalum	178	74	W	Tungsten	184	75	Re	Rhenium	186	76	Os	Osmium	190	77	Ir	Iridium	192	78	Pt	Platinum	195	79	Au	Gold	197	80	Hg	Mercury	201	81	Tl	Thallium	204	82	Pb	Lead	207	83	Bi	Bismuth	209	84	Po	Polonium	210	85	At	Astatine	210	86	Rn	Radon	222	87	Fr	Francium	223	88	Ra	Radium	226	104	Rf	Rutherfordium	261	105	Db	Dubnium	262	106	Sg	Seaborgium	263	107	Bh	Bohrium	262	108	Hs	Hassium	265	109	Mt	Meitnerium	266	110	Ds	Darmstadtium	266	111	Rg	Roentgenium	280	112	Cn	Copernicium	285	113	Nh	Nihonium	286	114	Fl	Flerovium	289	115	Mc	Moscovium	289	116	Lv	Livermorium	293	117	Ts	Tennessee	294	118	Og	Organesson	294
Alkali Metals		Alkaline Earth		Transition Metals																										Halogens																																																																																																																																																																																																																																																																													
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57	La	Lanthanum	139	58	Ce	Cerium	140	59	Pr	Praseodymium	141	60	Nd	Neodymium	144	61	Pm	Promethium	147	62	Sm	Samarium	150	63	Eu	Europium	152	64	Gd	Gadolinium	157	65	Tb	Terbium	159	66	Dy	Dysprosium	163	67	Ho	Holmium	165	68	Er	Erbium	167	69	Tm	Thulium	169	70	Yb	Ytterbium	173	71	Lu	Lutetium	175																																																																																																																																																																																																																																																
89	Ac	Actinium	227	90	Th	Thorium	232	91	Pa	Protactinium	231	92	U	Uranium	238	93	Np	Neptunium	237	94	Pu	Plutonium	239	95	Am	Americium	241	96	Cm	Curium	247	97	Bk	Berkelium	249	98	Cf	Californium	251	99	Es	Einsteinium	254	100	Fm	Fermium	257	101	Mendelevium	258	102	No	Nobelium	256	103	Lr	Lawerencium	262																																																																																																																																																																																																																																																	

Periodic trends

Periodic trends can be seen in atoms and ions as you move across a period and down a group. The trends investigated will include Atomic and ionic radii (distance from the centre of the nucleus to the valence energy level), electronegativity and the 1st ionization energy



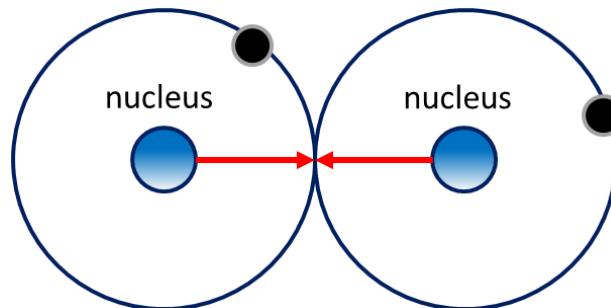
Atomic Radii

Atomic Radii is affected by two main factors :

(1) nuclear charge (number of protons) : The stronger the pull the electrons have to the protons with electrostatic attraction, then the smaller the size of the atom radii

(2) number of energy levels: The greater the number of energy levels the larger the atomic radii. The internal energy levels “shield” and reduce electrostatic attraction of the valence electrons to the protons. Addition of another electron does not result in a fractional decrease in the electrostatic attraction to any **given** electron, but it does increase the electron-electron repulsion, so an **overall decrease in Nett attractive force**.

[The most important factor is nuclear charge – atoms are neutral and as the number of protons increases, the number of electrons increases at the same rate. The more electrons in the valence shell, because of an increased number of equivalent protons they will be pulled in tighter and therefore show a smaller atomic radii.]



Atomic radius is half the distance between the nuclei of two bonded atoms

A 3rd factor that is also important: The electrons repel each other (**electron-electron repulsion**) and spread out to maximum distance in each energy level.

Atomic Radii Trends

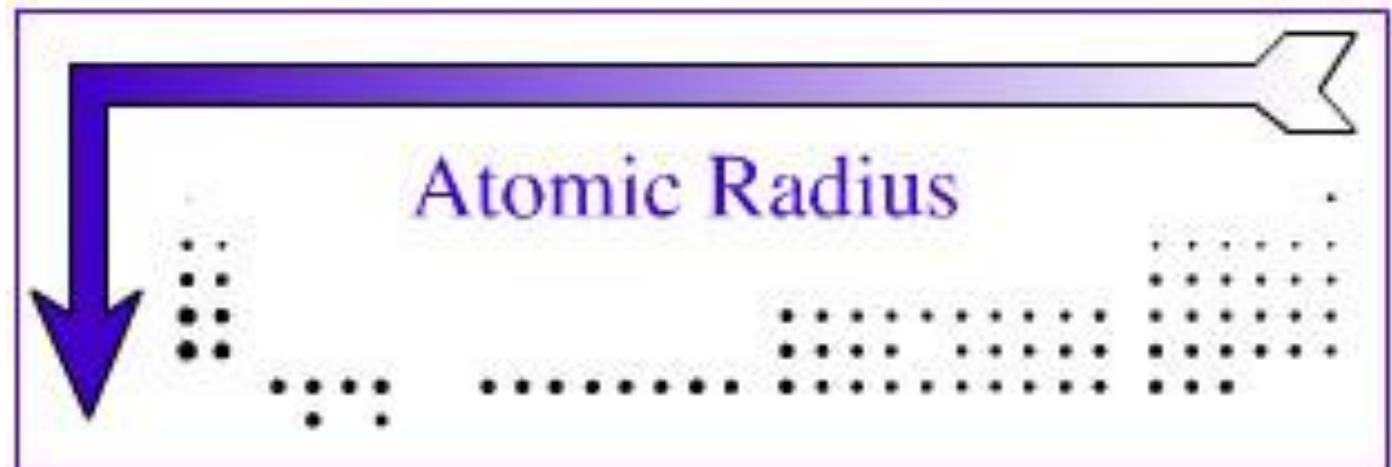
Addition of another electron does increase the electron-electron repulsion, but this is over come with increased nuclear charge which effectively increases the **nett attractive force**



Across the period the Atomic radii **decreases**

e.g. Li → Ne in **period 2**

As the nuclear charge increases across the period, so does the electrostatic attraction and so outer electrons are pulled closer to nucleus. The electron repulsions are balanced by the nuclear charge attractions, and as the nuclear charge gets larger, so the electrons get closer together. The net attractive electrostatic attraction is increased as the nuclear charge increases.

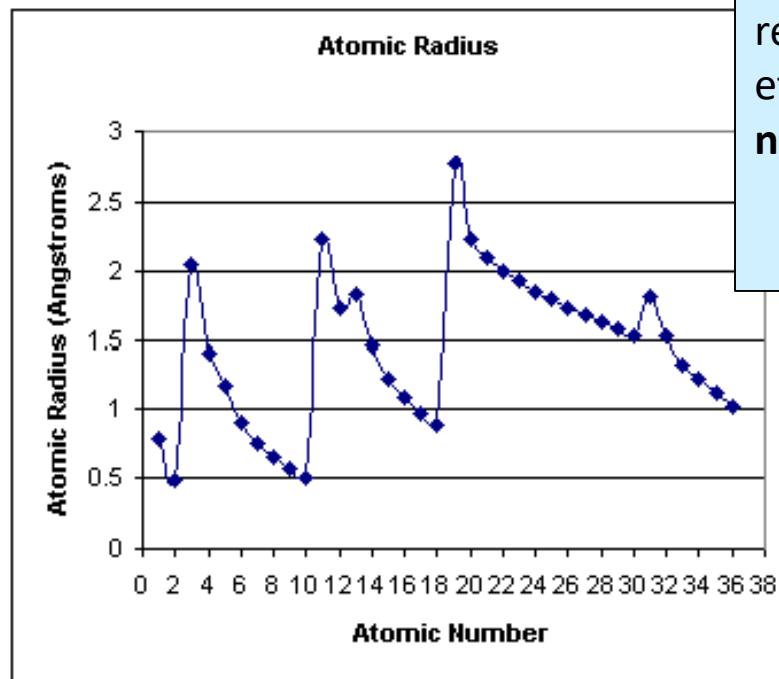


Atomic Radii trends

Down the group the Atomic radii **increases**

e.g. Li → Fr in **group one**

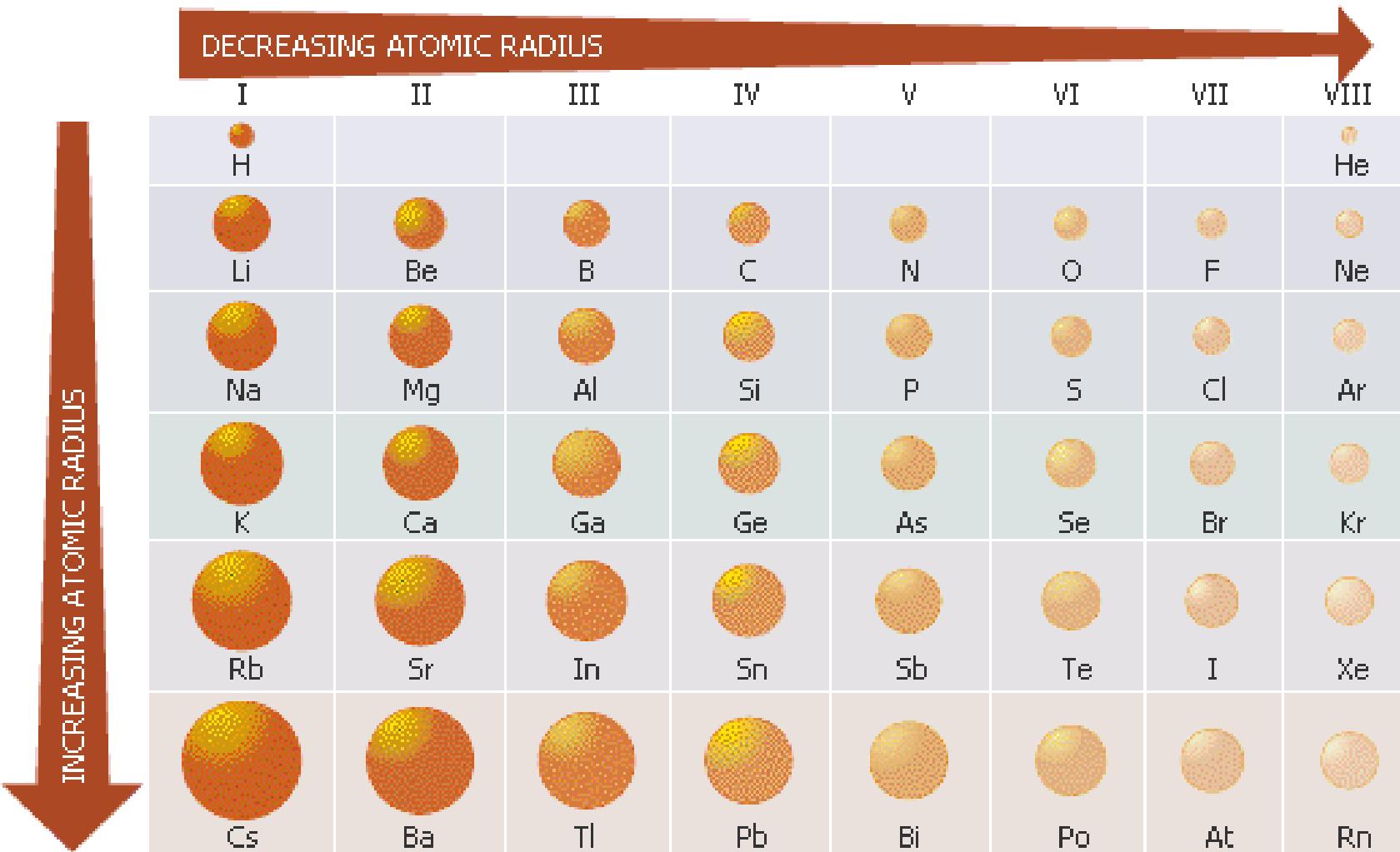
Electrons are being added to successive shells and both charge on nucleus and electron repulsion increase in step to “cancel each other out”. However, successive shells are further from the nucleus therefore, there is a subtle increase in atomic radii and an overall decrease in Net electrostatic attraction.



Addition of another electron does not result in a fractional decrease in the electrostatic attraction “shielding” to any given electron, but it does increase the electron-electron repulsion which effectively reduces the **nett attractive force**



Atomic Radii trends



Ionic Radii

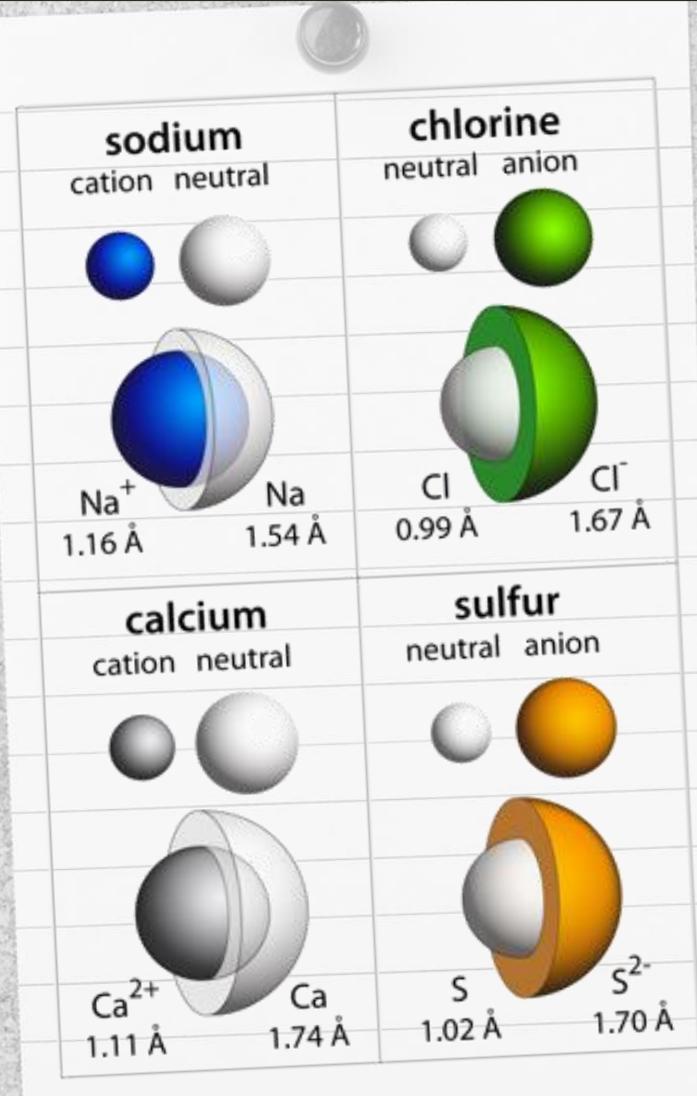
Cations (metal ions) are smaller in radii than their atoms

The outside energy level of electrons are removed but the nuclear charge (number of protons) remains the same creating **smaller radii than the atom**

Anions (non-metal ions) are larger in radii than their atoms

Extra electrons are added to the outside valance shell that have to be accommodated for and there is no change to the nuclear charge. Electron-electron repulsion spreads the electrons out further creating **larger radii than the atom**

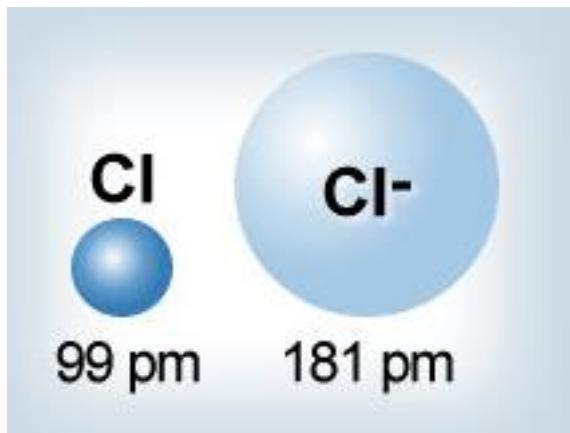
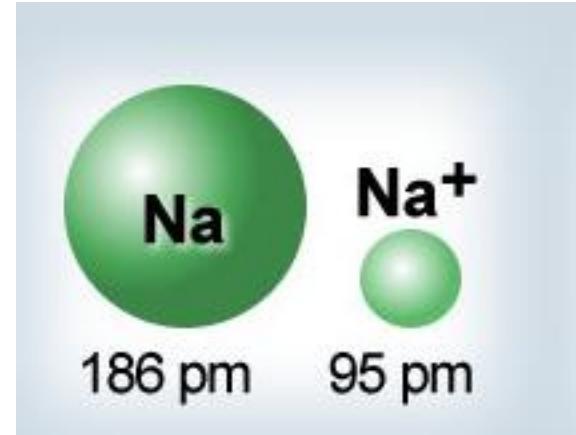
There is less of a trend seen across a periodic table of ions



Ionic Radii trends

Cations i.e. Na to Na⁺

The inter-electronic repulsion experienced by the electron cloud of the cation is **less** than the neutral atom, and since both species have the same amount of nuclear charge, the net electrostatic attractive force on the electron cloud in the cation is greater than the neutral atom resulting in a smaller cation size.

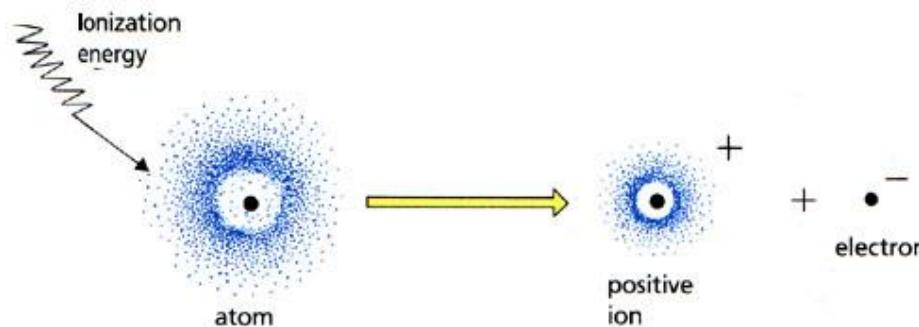


Anions i.e. Cl to Cl⁻

The inter-electronic repulsion experienced by the electron cloud of the cation is **greater** than the neutral atom, and since both species have the same amount of nuclear charge, the net electrostatic attractive force on the electron cloud in the cation is less than the neutral atom resulting in a larger anion size.

1st ionisation energy

The first ionisation energy is the **energy required to remove one mole of electrons from the outside valence shell of 1 mole of atoms in a gaseous state.**

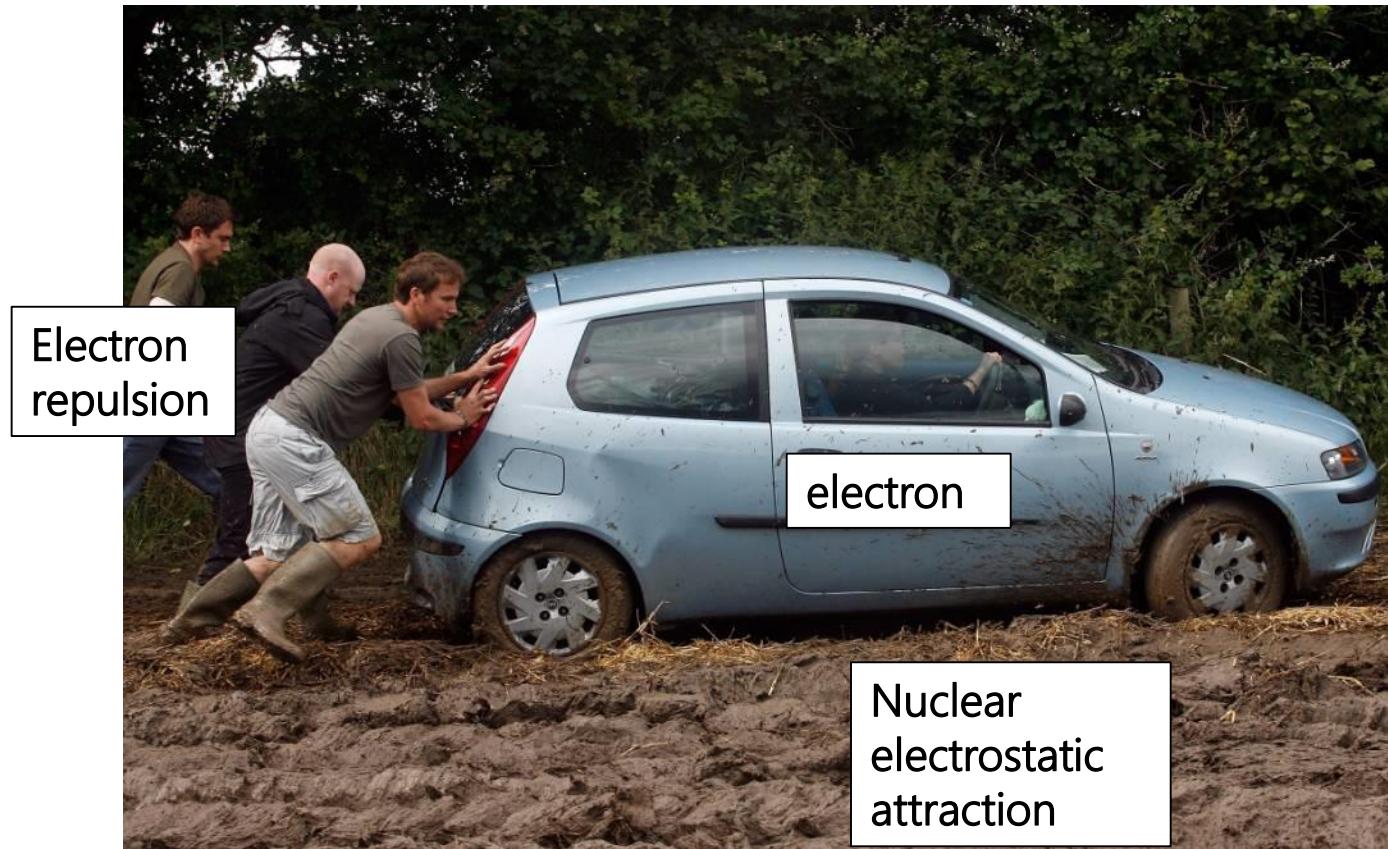


If the ionisation energy is high, that means it takes a lot of energy to remove the outermost electron. If the ionisation energy is low, that means it takes only a small amount of energy to remove the outermost electron.

Ionisation energy is affected by two factors:

- (1) **Nuclear charge:** As it increases, there is a stronger pull to the electrons by electrostatic attraction.
- (2) **Number of energy levels:** Electrons in a lower energy level are much closer to the nucleus and thus have much stronger net electrostatic attraction to it. Electrons in a lower energy level shell have electron repulsion but are closer together. Electrons in higher energy level shells are experience less net electrostatic attraction to the nucleus, as they are further away.

1st ionisation energy Analogy



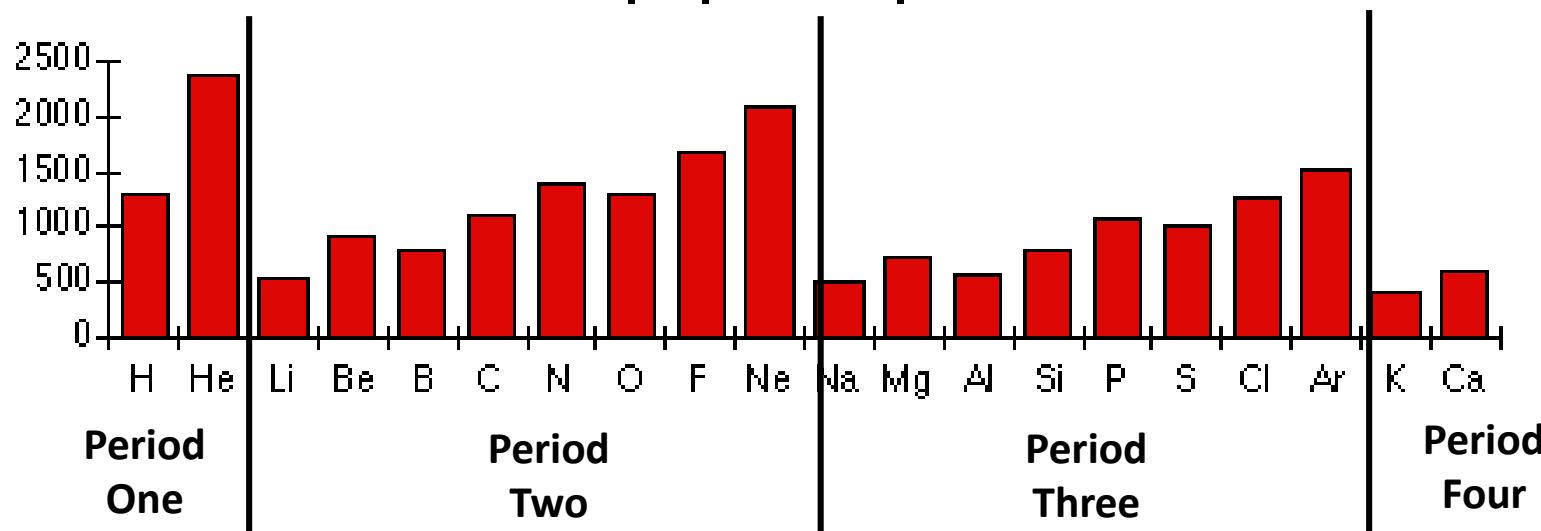
In order to remove an electron from an atom you need to overcome the nuclear attraction of its protons holding it around order. This can be shown by the mud that the car is stuck in. The more mud (nuclear attraction) the more energy to remove the car (electron). However, other electrons in the atom are repelling the electron to be removed – so the more people pushing the car (electron repulsion) the easier it is to extract the car (electron)

1st ionisation energy trends

Across a period the 1st ionisation energy **increases**

As the **nuclear charge increases**, the attraction between the nucleus and the electrons increases and it requires more energy to remove an electron from the outermost energy level and that means there is a higher ionisation energy. As you go across the periodic table, nuclear charge is the most important consideration. Therefore, going across the periodic table, there should be an increase in ionisation energy because of the increasing nuclear charge.

First ionisation energies from hydrogen to calcium
(kJ per mole)



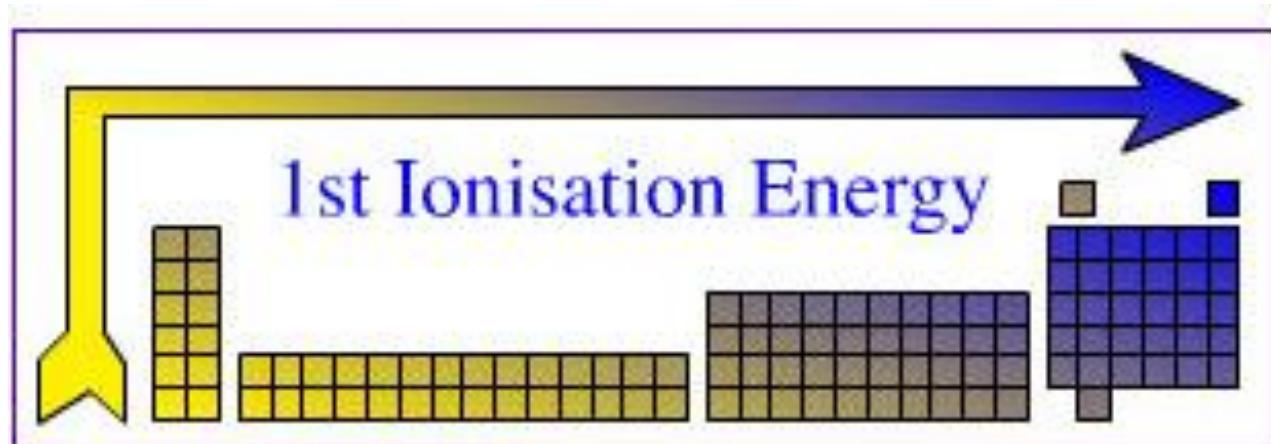
1st ionisation energy trends

All bonding is electrostatic and is characterised by **Coulombs Law** ($F = kQq/r^2$) which is an inverse square law so distance from nucleus really does matter



Down a group the 1st ionisation energy **decreases**

Going down the table, the effect of increased nuclear charge is weighed against the effect of **increased electron repulsion**, and the number of energy levels becomes the predominant factor. With more energy levels, the outermost electrons (the valence electrons) are **further from the nucleus** and are not so strongly attracted to the nucleus, and therefore there is a reduction in net electrostatic attraction. Thus, the ionisation energy of the elements decreases as you go down the periodic table because it is easier to remove the electrons. The more stable elements have higher ionisation energies.



The more stable elements have higher ionisation energies.

Sample questions – Ionisation energy (Part A)

For each of the following sets of atoms, decide which has the highest and lowest ionisation energies and why.

S, Si, Mg (period 3)

All are in the same period and use the same number of energy levels.
Mg has the lowest I.E. because it has the lowest effective nuclear charge. S has the highest I.E. because it has the highest effective nuclear charge.

Mg, Ca, Ba (group 2)

All are in the same group and have the same effective nuclear charge.
Mg has the highest I.E. because it uses the smallest number of energy levels. Ba has the lowest I.E. because it uses the largest number of energy levels.

F, Cl, Br (group 17)

All are in the same group and have the same effective nuclear charge. F has the highest I.E. because it uses the smallest number of energy levels. Br has the lowest I.E. because it uses the largest number of energy levels.

Sample questions – Ionisation energy (Part B)

For each of the following sets of atoms, decide which has the highest and lowest ionisation energies and why.

Where trends conflict e.g. IE down a group, the increased radius factor will outweigh the increased nuclear charge because it is a squared function.

Ne, Cu, Ba

All are in different groups and periods, so both factors must be considered. Fortunately both factors reinforce one another. Ba has the lowest I.E. because it has the lowest effective nuclear charge and uses the highest number of energy levels. Ne has the highest I.E. because it has the highest effective nuclear charge and uses the lowest number of energy levels.

N, P, Si

Si has the lowest I.E. because it has the lowest effective nuclear charge and is tied (with P) for using the most energy levels. N has the highest I.E. because it uses the fewest energy levels and is tied (with P) for having the highest effective nuclear charge.

1st ionisation energy

	H															He			
1	1312.0															2372.3			
2	Li	Be																	
3	520.2	899.5																	
4	Na	Mg																	
5	495.8	737.7	3	4	5	6	7	8	9	10	11	12							
6	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
7	418.8	589.8	633.1	658.8	650.9	652.9	717.3	762.5	760.4	737.1	745.5	906.4	578.8	762.2	944.5	941.0	1139.9	1350.8	
8	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
9	403.0	549.5	599.9	640.1	652.1	684.3	702	710.2	719.7	804.4	731.0	867.8	558.3	708.6	830.6	869.3	1008.4	1170.3	
10	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
11	375.7	502.9	538.1	658.5	728.4	758.8	755.8	814.2	865.2	864.4	890.1	1007.1	589.4	715.6	703.0	812.1			
12	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup				
		Lanthanides																	
13	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu					
14	534.4	528.1	533.1	538.6	544.5	547.1	593.4	565.8	573.0	581.0	589.3	596.7	603.4	523.5					
15	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr					
16	608.5	568	597.6	604.5	581.4	576.4	578.1	598.0	606.1	619	627	635	642	472.8					
17		Actinides																	

In general Atoms that lose electrons easily have low ionisation energy and atoms that gain electrons have high ionisation energy

An Ionisation equation can be written as: (M representing an atom)



Electronegativity

Electronegativity is the **tendency of an atom to attract bonding electrons from another atom**. Higher electronegativity values mean a higher tendency to attract electrons. Atoms with high E.N. are strong oxidants (gain electrons). Electronegativity is affected by two factors:

Nuclear charge: As an atoms nuclear charge increases, there is a stronger pull on electrons of another atom by electrostatic attraction.

Number of energy levels: the more energy levels an atom has the lower the net electrostatic attraction and the radii of the atom is larger. Because this then creates a bigger distance between 'neighbouring' atoms, Electrons from other atoms experience less electrostatic attraction to the nucleus of another atom. Therefore an atom in the same group has less electronegativity than an atom above it with less energy levels(Even though it has more nuclear charge)

Metals

- tend to have lower E.N.
- Lose electrons to form cations
- Usually have fewer electrons in valance shell than $\frac{1}{2}$ full

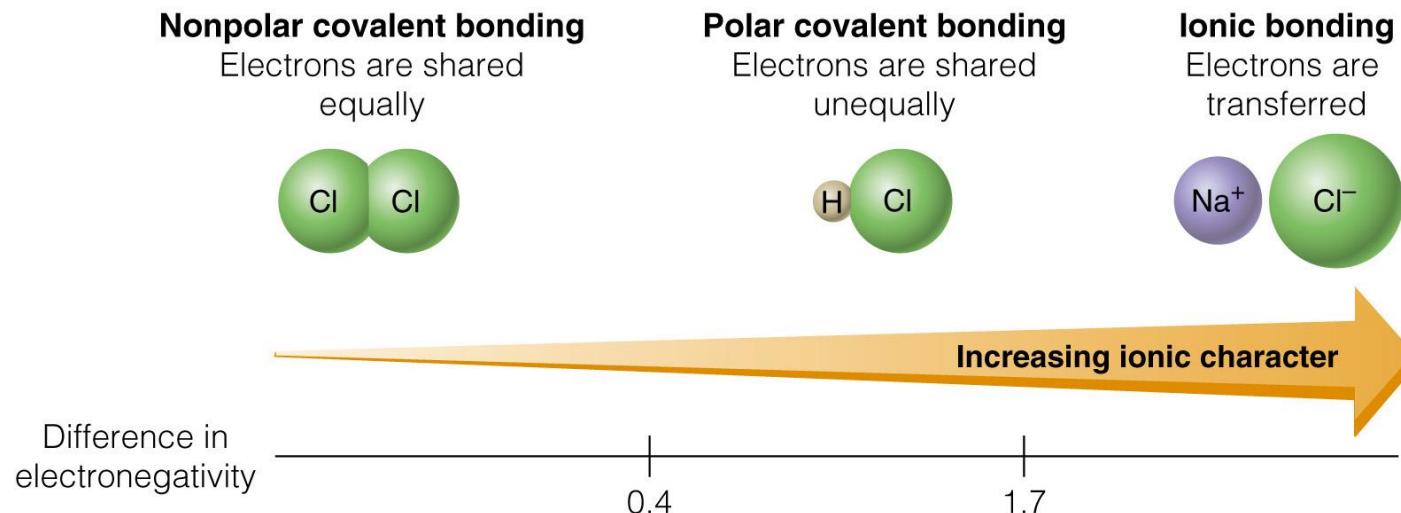
Non-Metals

- tend to have higher E.N.
- gain electrons to form anions
- Usually have more electrons in valance shell than $\frac{1}{2}$ full



Ionic – covalent bond continuum due to electronegativity

Bond types between atoms can depend on the **electronegativity** of the atoms. Rather than discrete categories, molecules fall along a continuum

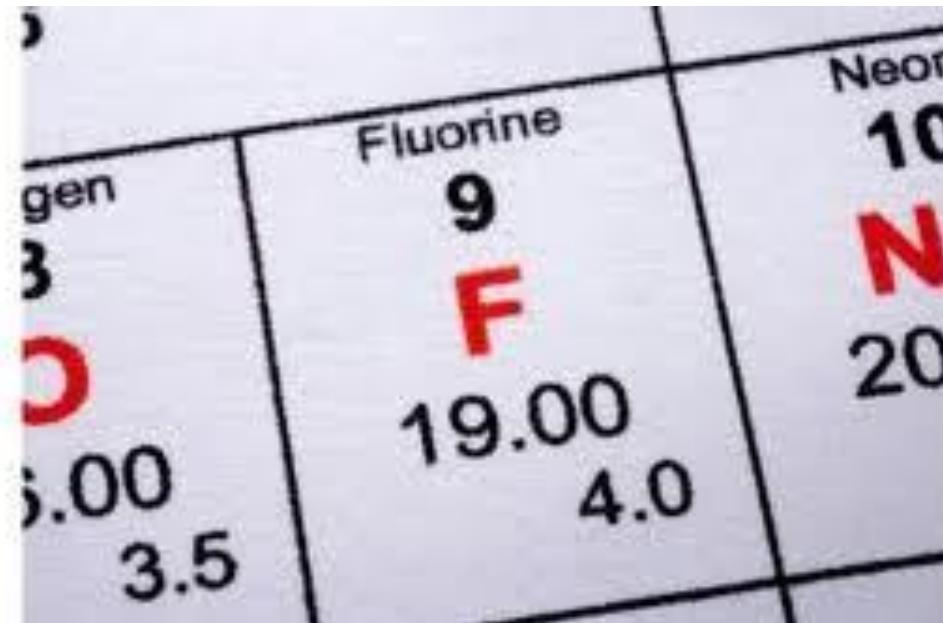


If there is little difference in electronegativity between two atoms then they tend to form a covalent bond with no polarity difference. A greater electronegativity difference creates a polar bond with uneven “sharing” of valence electrons. If the electronegativity is even greater then there will be a complete transfer of electron from one atom (Metal) to another atom (non-metal) and ions will form that are held together with an ionic bond.

Electronegativity trends

Across a Period the electronegativity **increases**

e.g. Li → Ne: The atoms have increased “pulling power” as the nuclear charge is increasing. Electrons are held tighter to the nucleus and there is a greater net electrostatic attraction. This allows another atom to be closer and it has a stronger attraction to electrons from that atom, so electronegativity increases.

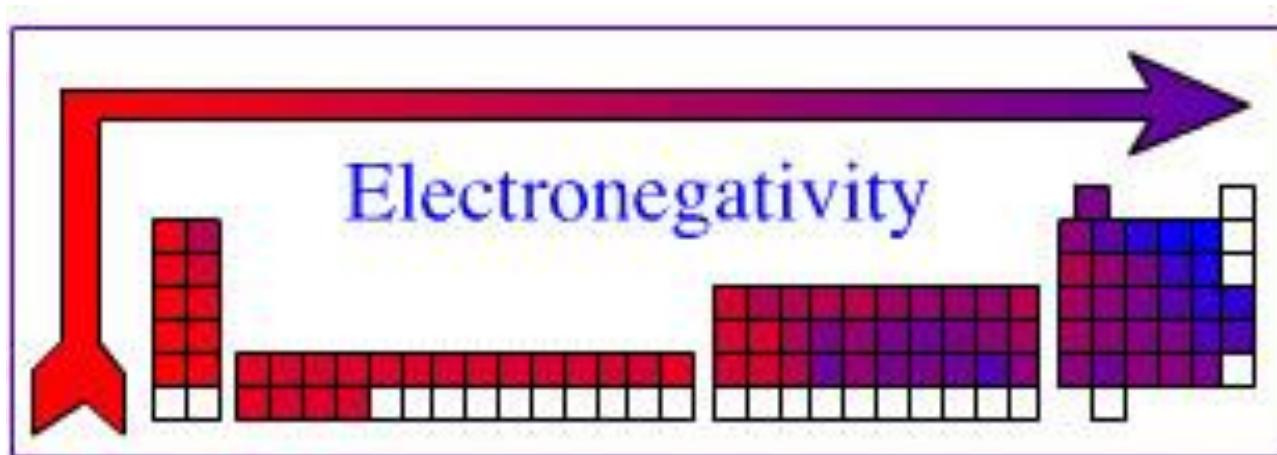


Electronegativity trends

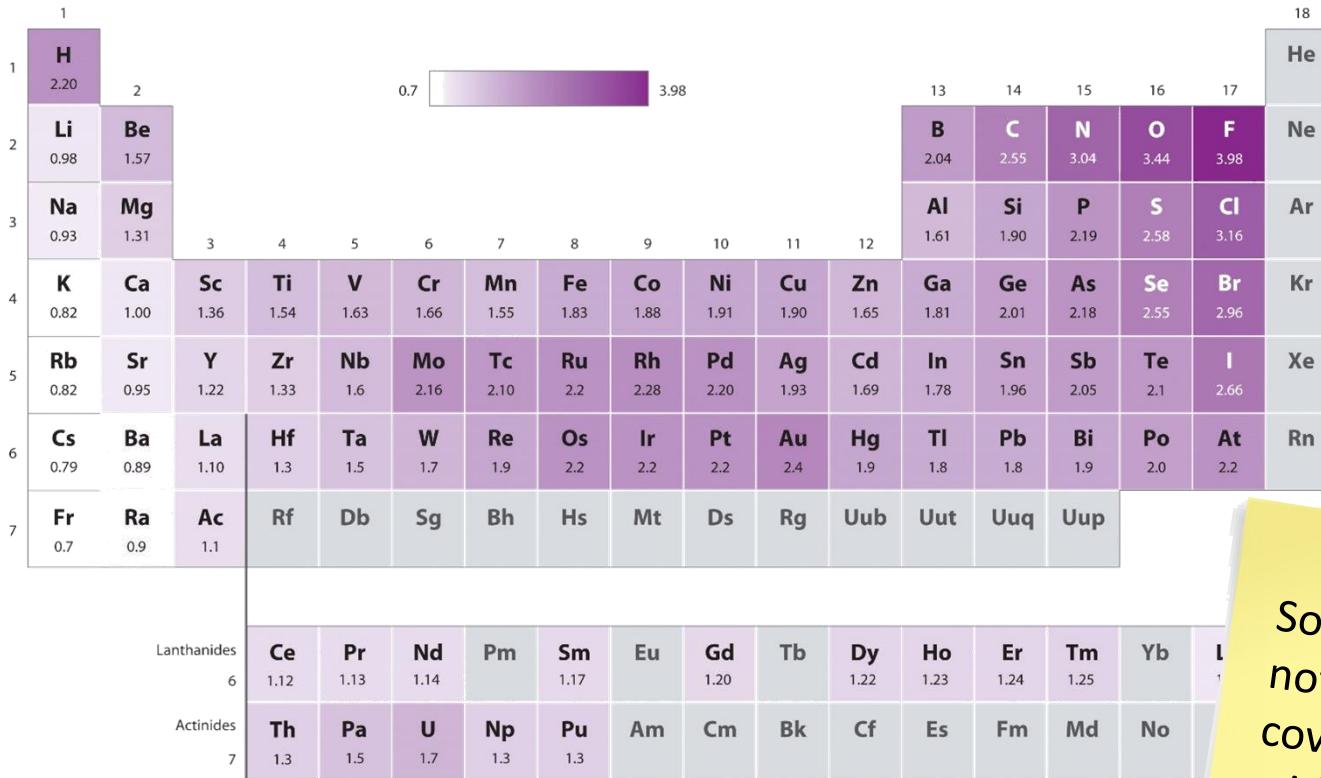
Down a group the electronegativity **decreases**

e.g. Li → Fr

Both nuclear attraction and electron repulsion increase in step, but with an overall decrease in Net electrostatic attraction. However, as successive shells increase atomic radii, then the electrostatic attraction of the nucleus to other atoms' electrons decreases, so atoms have less electronegativity as you move down a group.



Electronegativity – the Pauling Scale



Some elements do not form stable covalent compounds with other elements; so their electronegativities cannot be measured

Periodic trends Summary

	Electronegativity	1 st ionisation energy	Atomic radii
Across a Period	<p>The greater the nuclear charge, the easier it is to obtain more electrons from other atoms > more p+ to pull with</p> <p>INCREASES</p>	<p>As the nuclear charge is larger it requires more energy to remove an electron as they are held tighter (and closer) to the nucleus</p> <p>INCREASES</p>	<p>Across a period the energy level numbers stay the same but proton numbers increase pulling more at the valence electrons</p> <p>DECREASES</p>
Down a group	<p>The larger the number of energy levels the less net electrostatic attraction so the less ability an atom has to remove the valence electrons of another atom</p> <p>DECREASES</p>	<p>As the energy level numbers increase the easier it is to remove electrons as the valence electrons are further from the 'pull' of the protons and more electron repulsion by other electrons in inner energy levels</p> <p>DECREASES</p>	<p>Down a group the energy levels become further away from the nucleus therefore the valence electrons repel more, less effected by protons, taking up more space and increasing the size</p> <p>INCREASES</p>

Question 1b: Discuss the data for each of the following pairs of particles.

Atom	Electronegativity
O	3.44
Se	2.55

Se has more shells/electrons in energy levels further from the nucleus than O, with increased shielding from inner shells. This means there is a weaker electrostatic attraction between the nucleus and the bonded electrons, so Se has a lower electronegativity than O.

Cl^- has an extra electron in its outermost/same energy level. This causes increased repulsion between electrons in the valence shell, so the electrons move further apart. This makes Cl^- bigger than Cl. Both Cl and Cl^- have the same number of protons/attractive force of the nucleus remains the same.

Atom or ion	Radius / pm
Cl	99
Cl^-	181

Question 1b: Discuss the data for each of the following pairs of particles.

Atom	First ionisation energy/kJ mol ⁻¹
Li	526
Cl	1 257

Cl has more protons than Li. Therefore there is a greater attraction between the nucleus and outer electrons/electrons held more tightly so it is harder to remove an electron from Cl than Li.

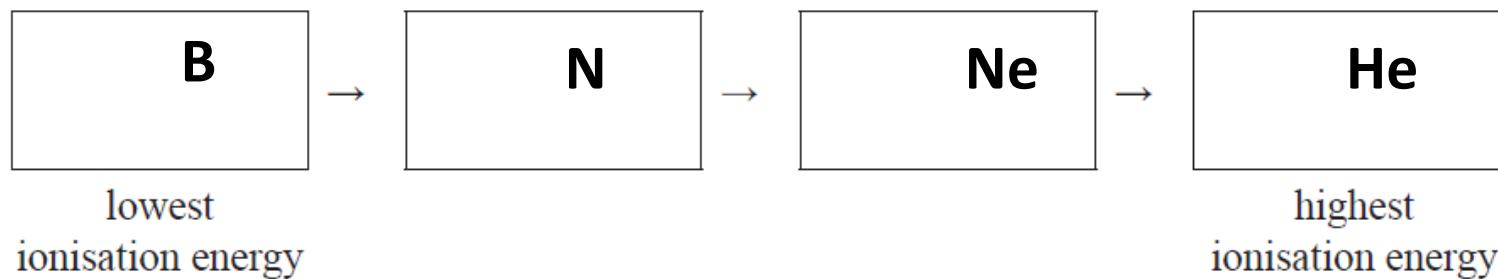
Even though the valence electrons of Cl are in the 3rd energy level/has an extra energy level the extra shielding is not as significant as the effect of the increased nuclear charge, so Cl has a higher first ionisation energy than Li.

NCEA 2014 Periodic trends

Question 1c: The following table shows the electron configurations of four atoms, He, B, N, and Ne. Arrange these atoms in order of increasing first ionisation energy by writing the symbol of the appropriate atom in the boxes below.

Atom	He	B	N	Ne
Electron configuration	$1s^2$	$1s^2 2s^2 2p^1$	$1s^2 2s^2 2p^3$	$1s^2 2s^2 2p^6$

Achieved
Question



NCEA 2015 Periodic Trends

Excellence Question

Question 1b: Define the terms electronegativity and first ionisation energy.

Answer 1b: Electronegativity is the ability of an atom in a compound to **attract electrons to itself**.

First ionisation energy is the minimum energy required to **remove one mole of electrons from one mole of gaseous atoms**.

It is well worth learning the definitions of the periodic trend well as these two correct together were worth an Excellence grade

NCEA 2014 Periodic Trends

Excellence Question

Question 1b: Explain the difference between the radii of the K atom and the K⁺ ion.

Answer 1b: The K⁺ ion has a smaller radius than the K atom, as the ion has lost an electron from the valence/outer energy level, and therefore has fewer shells. This results in greater attraction between the nucleus and the valence electrons, as the outer electrons are now closer to the nucleus. There is less repulsion between the remaining electrons. Both species have the same number of protons / amount of nuclear charge.

Question 1c: The following table shows the first ionisation energy values for elements in the third period of the periodic table. Justify the periodic trend of first ionisation energies shown by the data in the table above, and relate this to the expected trend in atomic radii across the third period.

Element	First ionisation energy / kJ mol ⁻¹
Na	502
Al	584
Si	793
Ar	1 527

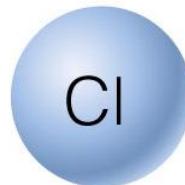
Both periodic trends are influenced by nuclear charge and the number of shells / distance, the ionisation energy increases while the atomic radii decrease.

The larger the ionisation energy the more strongly the valence electrons are held. Thus atomic radii across Period 3 decrease

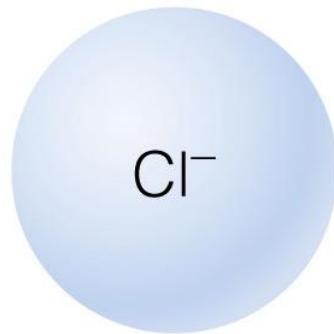
Answer 1c: First ionisation energy increases from 502 in Na to 1527 in Ar. There is an increase in the number of protons and thus the nuclear charge / attractive force of the nucleus. As the electrons are added to the same energy level, there is no increase in repulsion between energy levels. The nuclei with a greater number of protons have a stronger electrostatic attraction for the valence electrons in the third shell, thus the first ionisation energy increases across a period.

Question 1b (i) : Explain why the radius of the Cl atom and the radius of the Cl^- ion are different.

	Radius (pm)
Cl atom	99
Cl^- ion	181



Chlorine atom
17 protons
17 electrons
99 pm radius



Chloride ion
17 protons
18 electrons
181 pm radius

Answer 1b (i) : The Cl atom gains one electron to complete its valence shell to form the Cl^- ion, the nuclear charge remains the same. The increased inter-electron repulsion in the outer energy level causes the valence electrons to move further from the nucleus, so the Cl^- ion is larger than the Cl atom.

Question 1b (ii) : Explain the factors influencing the trends in electronegativity and first ionisation energy down a group of the periodic table.

In your answer you should:

- define both electronegativity and first ionisation energy
- explain the trend in both electronegativity and first ionisation energy down a group
- compare the trend in electronegativity and first ionisation energy down a group.

Electronegativity decreases down a group.

Electronegativity is a measure of how strongly an atom attracts bonding electrons. Although the nucleus will become increasingly positive down a group (number of protons increases), the atomic radius increases down a group as more energy levels are added and shielding / repulsion from inner shells increases. Therefore, the bonding electrons in the valence shell will be further from the positive nucleus, resulting in a weaker electrostatic attraction between the nucleus and the bonding electrons.

First ionisation energy is a measure of how easily the first mole of electrons is removed from one mole of gaseous atoms. It becomes easier to remove an electron down a group / first IE decreases down a group as the valence electrons are further from nucleus with greater repulsion / shielding from inner shells, so there is less electrostatic attraction between protons in the nucleus and valence electron to be removed.

For both EN and first IE, the attraction between the positive nucleus and bonding / valence electrons in the outer shell is decreasing down a group, so both EN and first IE decrease down a group.

Question 1b(i) : Define the terms electronegativity and first ionisation energy.

Answer 1b: Electronegativity is the ability of an atom in a compound to **attract a bonding pair of electrons to itself**.

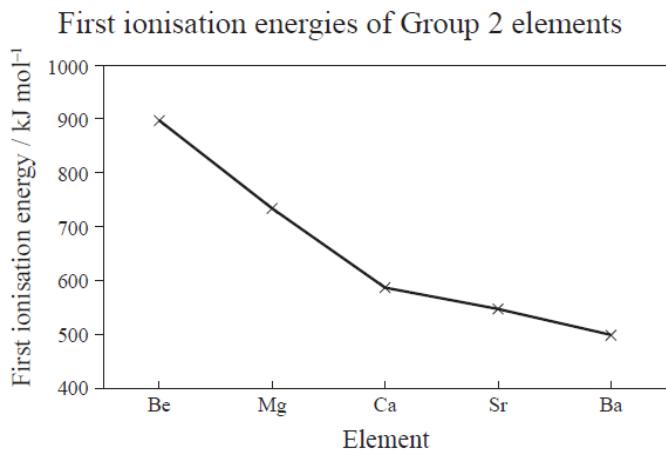
It is well worth learning the definitions of the periodic trend well as these two correct together were worth an Excellence grade

(ii) Explain why the electronegativity of chlorine is greater than that of phosphorus.

Answer 1b (ii): Electronegativity increases as you go across a period.

Both Cl and P are row 3 elements and have valence electrons in their 3rd shell. The electrons are in the same shell so experience the same shielding effect. Chlorine has more protons in its nucleus than phosphorus so its nuclear charge is greater. This means that chlorine will have more attraction for the bonding pair of electrons so its electronegativity is greater.

Question 1c: The following graph shows the first ionisation energies of the Group 2 elements from Be to Ba.



(i) Write an equation to show the first ionisation energy for the element calcium.



(ii) Explain the trend shown of first ionisation energies of the Group 2 elements.

The first ionisation energy is the energy required to remove one mole of the most loosely held electrons from one mole of gaseous atoms. The trend is that the ionisation energy decreases going down the group two elements. Although the nuclear charge increases due to more protons in the atoms going down a group, it is offset by the increasing distance of the outer electrons from the nucleus as the atomic radius increases due to more energy levels being added.

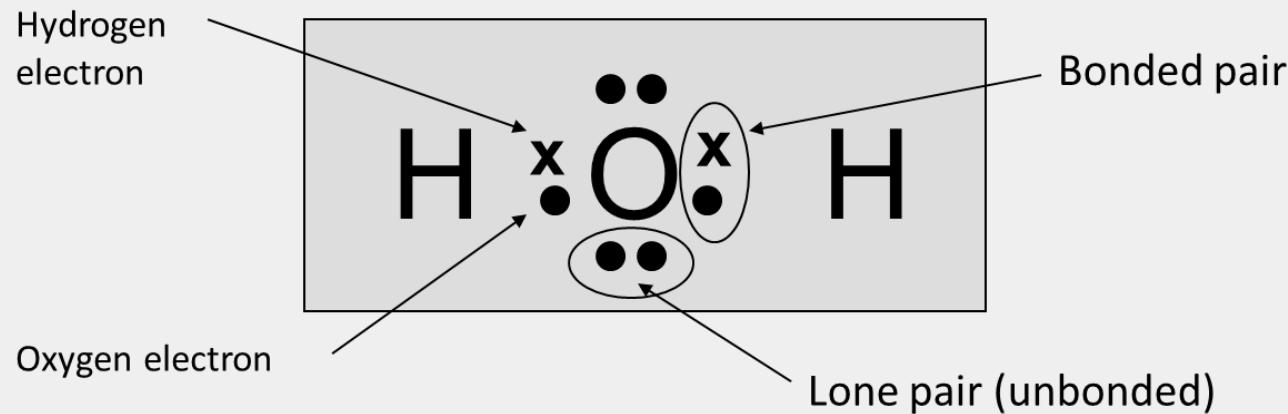
The full inner energy levels shield the outer electrons from the protons in the nucleus so the electrostatic attraction is less. Additional energy levels result in greater shielding / repulsion between energy levels. The further the outer electron is from the nucleus, the less energy needed to remove it.

Background Knowledge

Drawing Lewis Diagrams

G Lewis devised a system of drawing covalent molecules showing arrangement of atoms and valence electrons – both those involved in bonding and those that are not (called lone pairs). Electrons in inner shells are not involved in bonding. These diagrams are called **Lewis diagrams (or structures)**. The Lewis diagram is drawn so that each atom has eight electrons associated with it (except for hydrogen, which has two). This is the *octet rule*.

Lewis structure of H_2O (water)



Lewis Diagrams – Steps to drawing

1. Calculate valence electrons of all atoms. If the molecule is an ion then subtract the charge from the total electrons and place the charge outside of square brackets of the Lewis diagram at the end. *Example carbon dioxide.*

$\text{C} = 4$
$\text{O} = 6$
$\text{O} = 6$
16

CO₂

2. Write down number of pairs of electrons.

16 / 2 = 8 pairs

3. Place atom with least filled valence shell in the centre with the other atoms arranged around the out side (periphery)

O C O

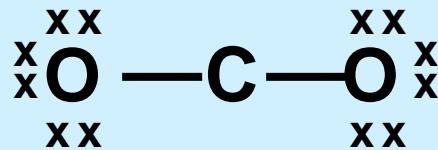
Lewis Diagrams - steps to drawing

4. Bond all atoms together (either x or — = one pair of electrons)



8 pairs – 2 pairs =
6 pairs remaining

5. Place remaining e- pairs around the periphery atoms so each has 4 pairs (including bond pair) around it.



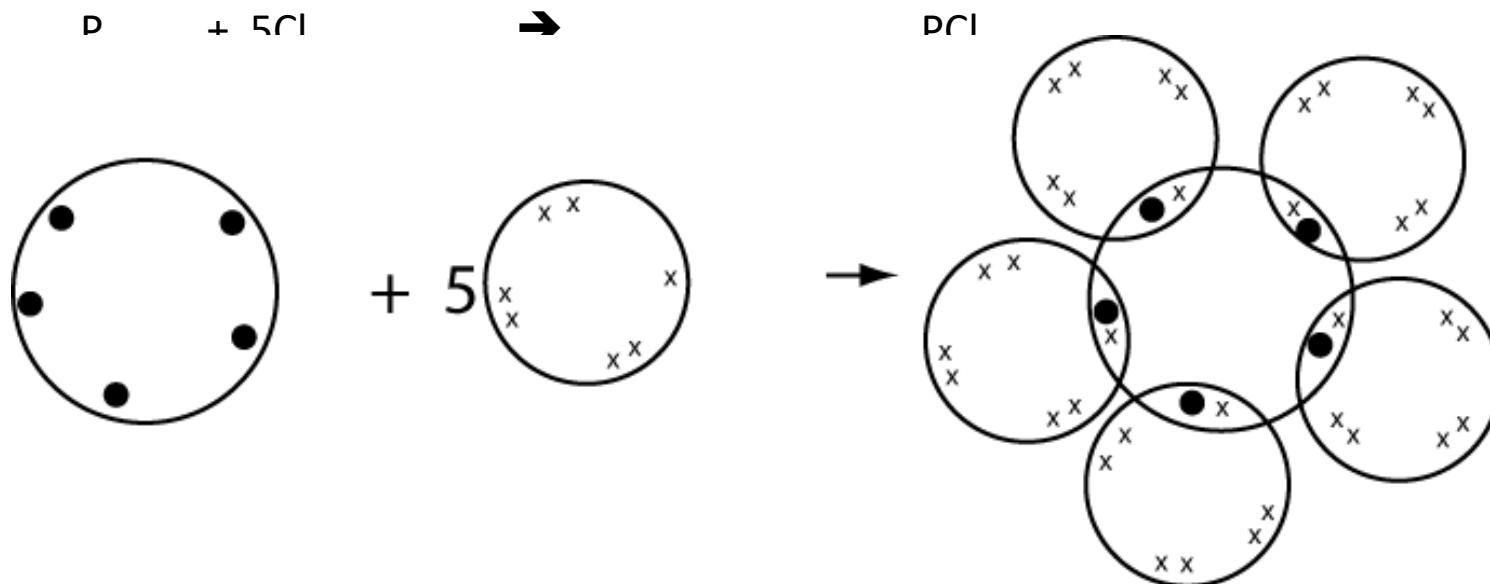
6 pairs – 6 pairs =
0 pairs remaining

6. If there are any remaining pairs place them around the outside of the central atom.
7. Rearrange non-bonded pairs into bonded pairs if the central atom does not have 4 pairs around it.

Expanded Octet

Third row elements (e.g., Al, Si, P, S, Cl) often have more than four valence shell orbitals filled with non-bonded Pairs and/or Bond Pairs; this is called "**expanded Octet**". Obviously, elements from the fourth and higher rows can also exhibit "expanded valence". **EXAMPLE** Phosphorus, electron configuration 2,8,5 can form up to 5 covalent bonds.

e.g. phosphorus pentachloride



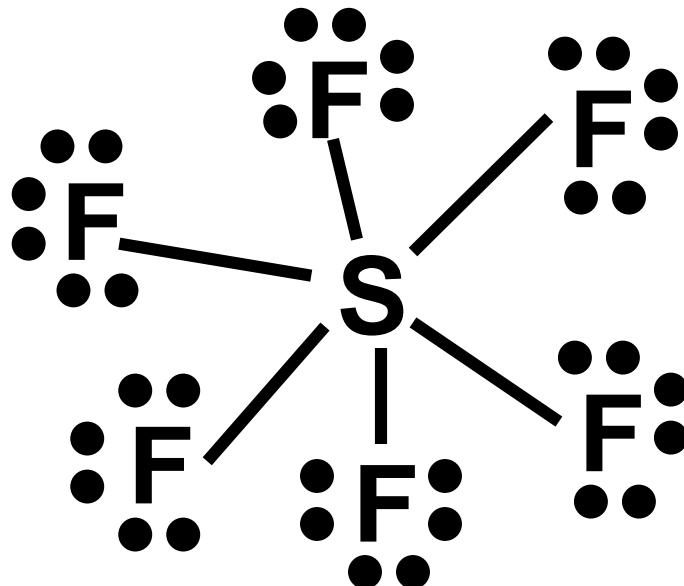
Expanded Octet - Rule of orbitals – exceptions to the rule

If there are extra non-bonded Pairs of electrons left after all of the periphery atoms are filled in accordance with the *octet rule* then they are placed around the central atom(s) according to the **Rule of Orbitals**. [extension] *The Rule of Orbitals*: the total number of non-bonded pairs and bonded pairs (NBP+BP) associated with an atom cannot exceed the number of Valence Shell Orbitals ($VSO = n^2$, where n is the row of the Periodic Table in which that atom resides).

$n = 1$ (H): maximum VSE pairs (NBP+BP) = VSO = 1;

$n = 2$ (B, C, N, O, F): maximum VSE pairs (NBP+BP) = VSO = 4 ("octet rule")

$n = 3$ ((Al, Si, P, S, Cl): maximum VSE pairs (NBP+BP) = VSO = 9 etc.



SF_6 creates a molecule that has 6 bonded F atoms around the central S atom.

Lewis Diagrams of ions

1. Calculate valence electrons of all atoms. If the molecule is an ion then subtract the charge from the total electrons and place the charge outside of square brackets of the Lewis diagram at the end. *Example carbon dioxide.*

C = 4
O = 6
O = 6
16

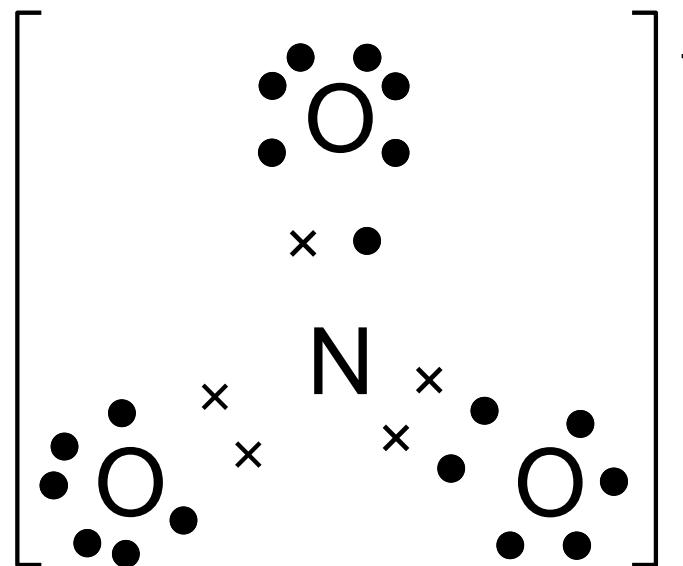
CO₂

In step 1. For negative ions, add extra e- to valence electrons

For positive ions remove e- from valence electrons

e.g. for nitrate NO₃⁻

Put bracket around ion and show charge.

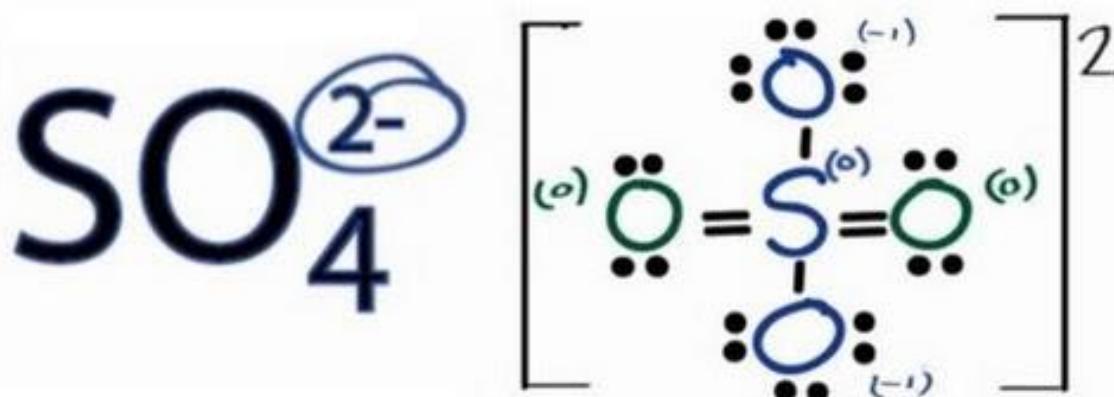


Lewis Diagrams of ions – Formal Charge



Use formal charge to identify stable canonical form

The Lewis diagram for SO_4^{2-} includes two double bonds rather than 4 single bonds because this arrangement has the lowest formal charge, FC, where $\text{FC} (= \text{no of valence e}^- \text{s} - [\text{no of non-bonded e}^- \text{s}] - (1/2 \text{ no of bonded e}^- \text{s}))$.



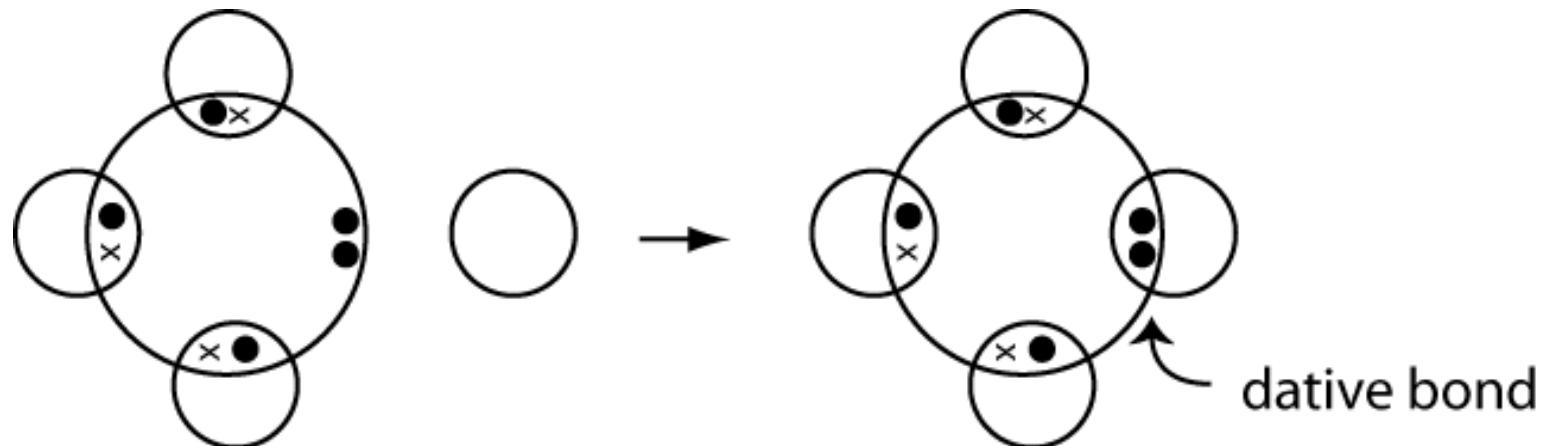
Charge Formal	=	Valence Electrons	-	NonBonding Val Electrons	-	Bonding Electrons	
S	=	6	-	0	-	$12/2$	= 0
O	=	6	-	4	-	$4/2$	= 0
O	=	6	-	6	-	$2/2$	= -1

Dative Bonds

e.g. an ammonium ion is made from an ammonia molecule plus a hydrogen ion.



A **dative bond** occurs when one atom donates both electrons to form a single covalent bond.



Bonding the atoms

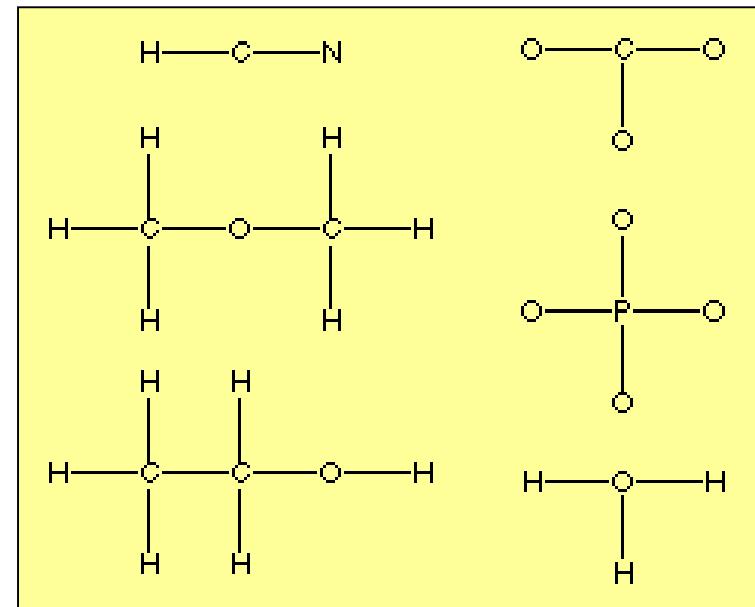
Otherwise, as a general rule, the least electronegative elements are central, the most electronegative elements are peripheral

Often, the formula is written to indicate connectivity.

For example: HCN = H bonded to C, C bonded to N, H and N are not bonded.

CH_3OCH_3 = three H bonded to C1, C1 bonded to O, O bonded to C2, C2 bonded to three H.

$\text{CH}_3\text{CH}_2\text{OH}$ = three H bonded to C1, C1 bonded to C2, C2 bonded to two H and O, O bonded to H.



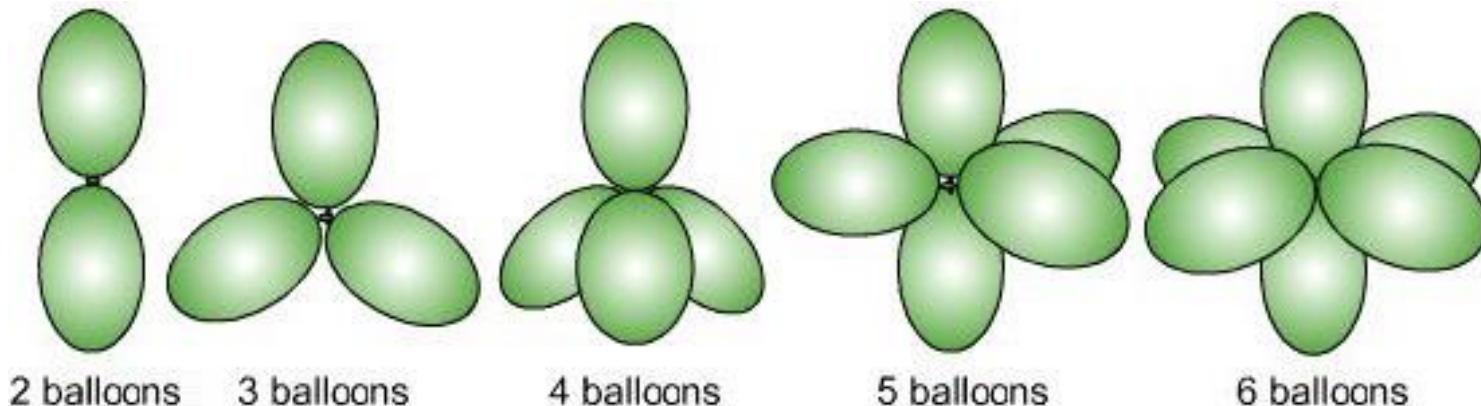
Determining Molecular Shapes

Valence Shell Electron Pair Repulsion Theory - electrons repel and therefore regions of negative charge move as far apart from each other as possible around a central atom. (used to predict molecular shape.)

1. Draw the electron dot diagram
2. Count the electron pairs (regions of negative charge) around the central atom. (Double and triple bonds may be considered as single charge regions)
3. Consider the shape the charge regions repel to.
4. Name the shape formed by the bonded atoms.

Repelling power of charge regions:

triple bond > double bond > lone pair > single bond

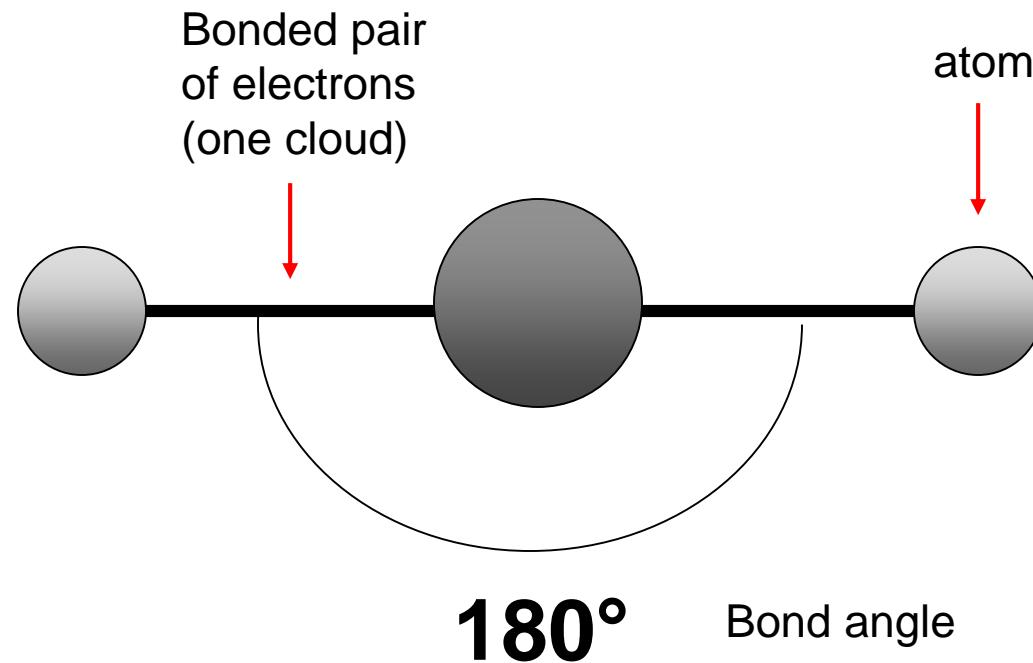


Molecular Shapes – two regions of charge

Since regions of electrons are negatively-charged, they repel each other as far apart as possible. Two regions arrange themselves on opposite sides of the central atom to form a linear shape.

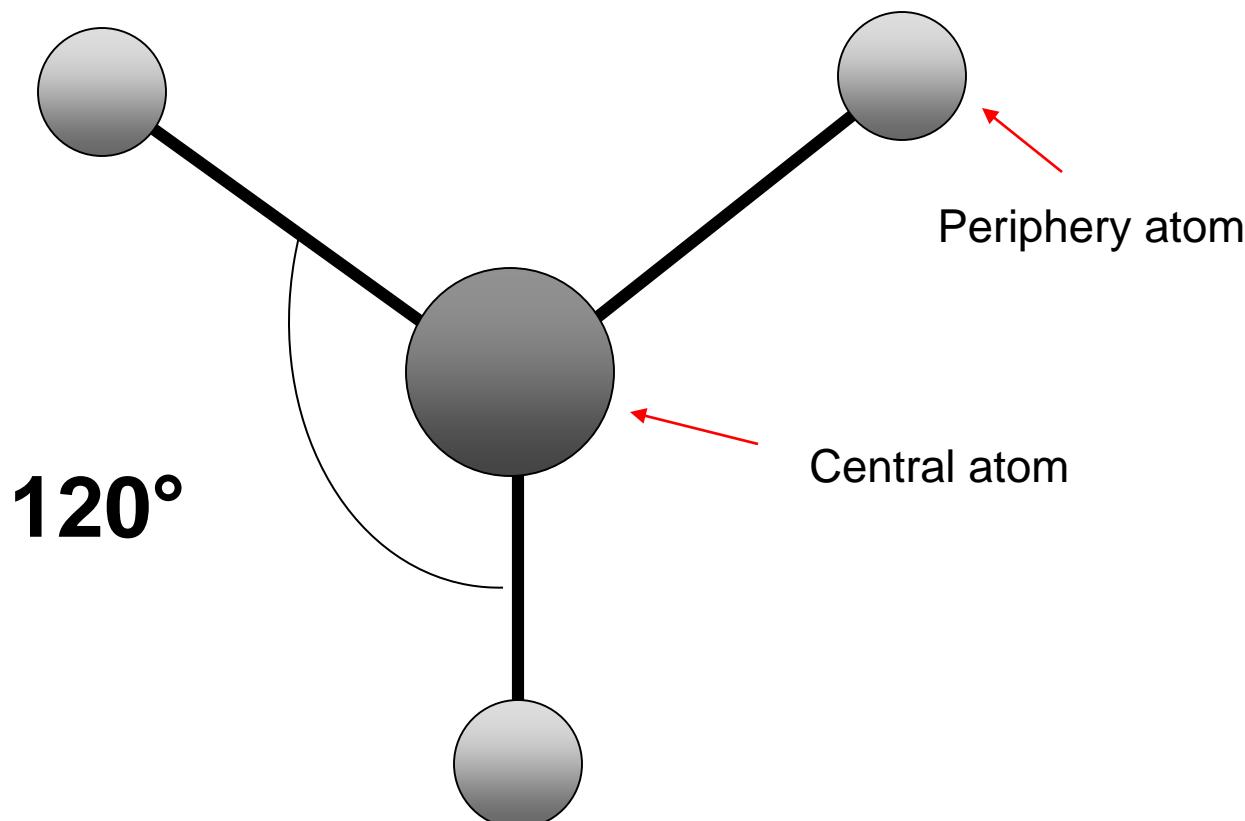
The bond angle will be 180° .

The bonded regions form a **linear shape**.



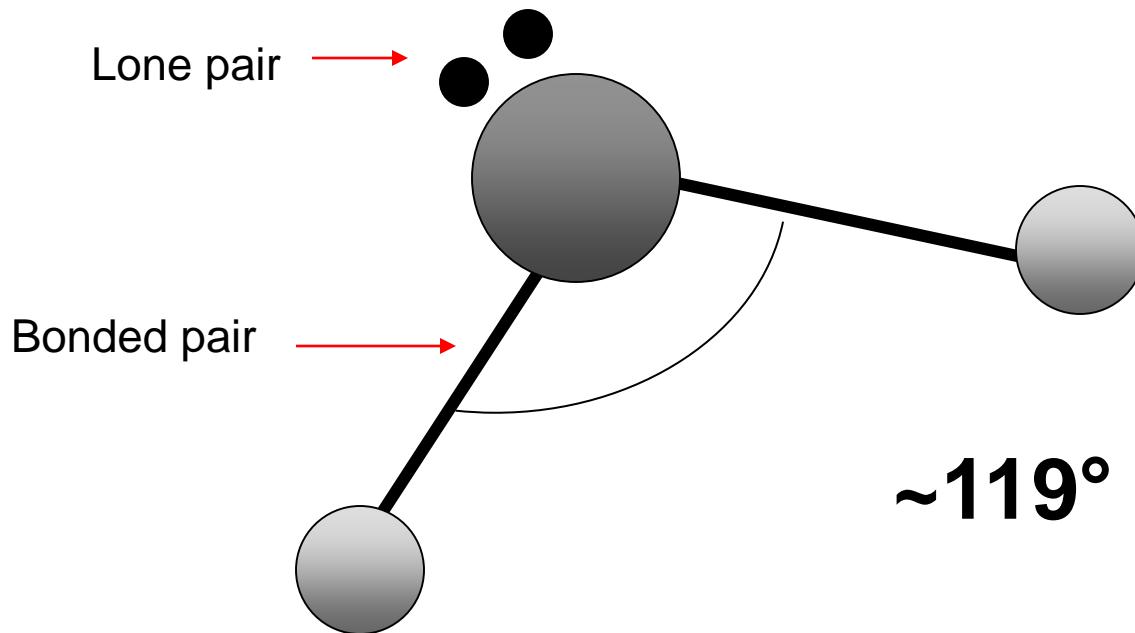
Molecular Shapes – three regions of charge (0 non-bonding pairs)

Three regions of negative charge will cause a bond angle of 120° as they repel each other. All the atoms still lie on a flat plane (like a sheet of paper) to form a trigonal planar shape. The bonded negative regions form a **trigonal planar shape**. (or triangular planar)



Molecular Shapes – three regions of charge (1 non-bonding pair)

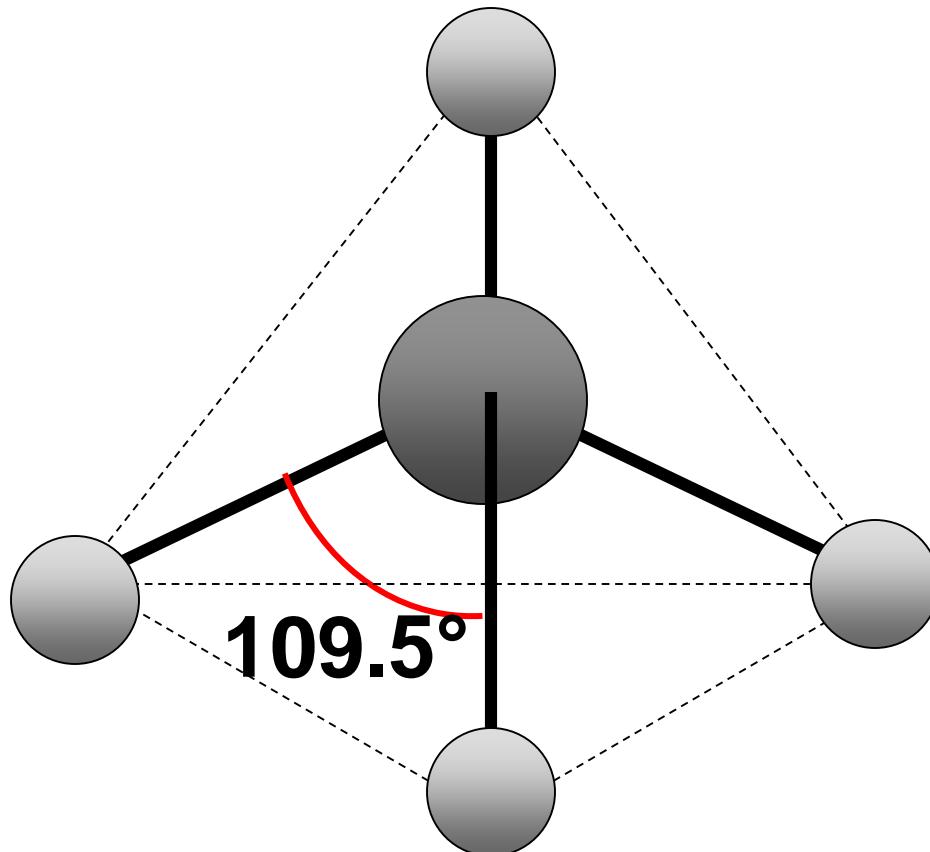
When one of the regions of electrons is a *non-bonding pair* it will have a slightly greater push to the bonded pairs. This is because the lone pair are only orbiting around one positive nucleus and their negative charge is less ‘neutralised’ than if they had another nucleus to orbit around. The regions of negative charge repel to a trigonal planar shape. The bond angle between the remaining pairs is approximately 120° (119°). The final shape formed by the atoms is called **bent**.



Molecular Shapes – four regions of charge (0 non-bonding pairs)

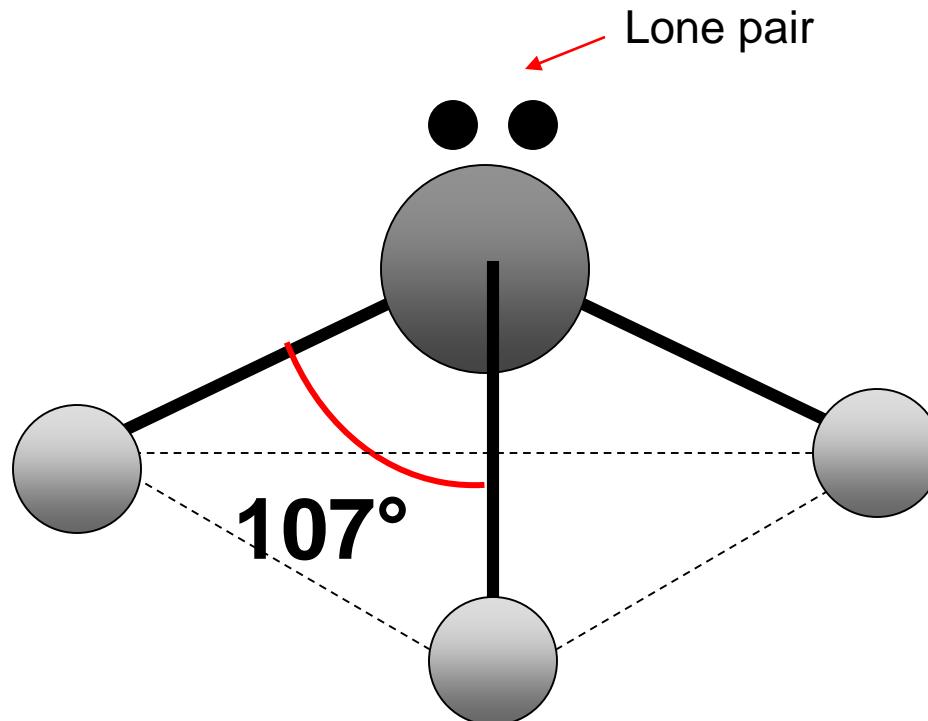
When four regions of negative charge are around a central atom they repel each other into a 3-dimensional shape. The bond angle is now 109.5° . This is because it is a sphere divided into 4 rather than a circle.

This shape formed is **tetrahedral**.



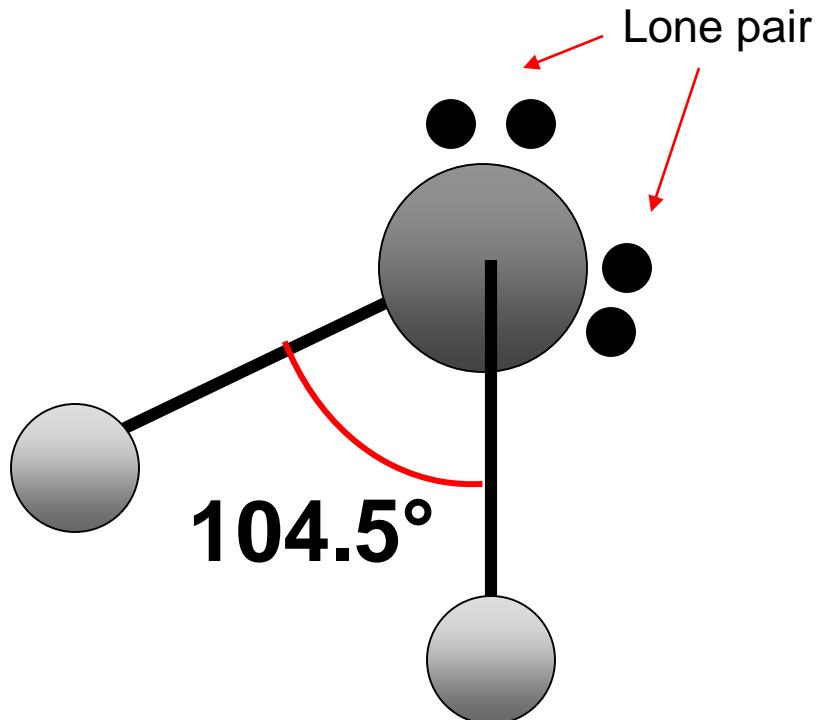
Molecular Shapes – four regions of charge (1 non-bonding pair)

The four regions of negative charge still occupy a 3-dimensional tetrahedral shape. (The non-bonding pair, however, exerts a stronger repulsion to the remaining bonded pairs). The bond angle is 109.5° . (107° actually because of the stronger non-bonded pair repulsion) The final shape the bonded atoms form is a **trigonal pyramid** (or a triangular pyramid)



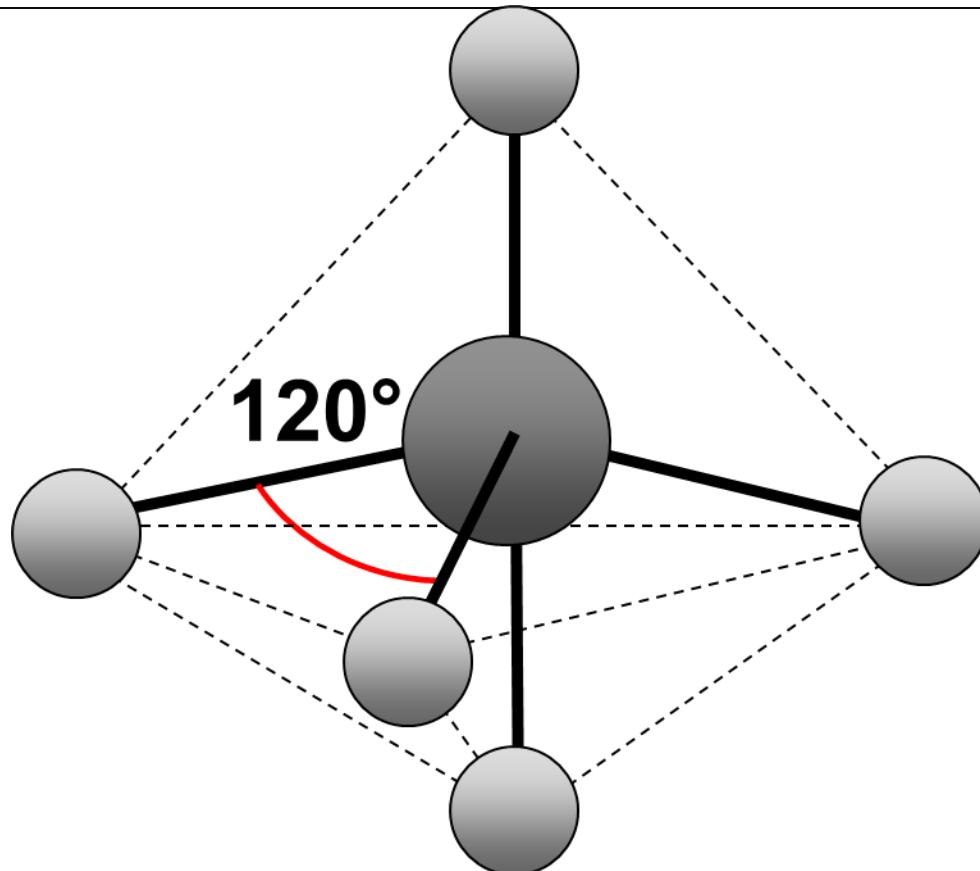
Molecular Shapes – four regions of charge (2 non-bonding pairs)

The 4 regions of negative charge repel each other to a (warped) tetrahedral shape. But The two non-bonding pairs create a much stronger repulsion than one lone pair and the bond angle between the remaining bonded pairs is smaller again at approximately 105° (compared to 119° of the bent shape with only 3 regions of negative charge). The final shape the bonded atoms form is called **Bent**.



Molecular Shapes – five regions of charge (0 non-bonding pairs)

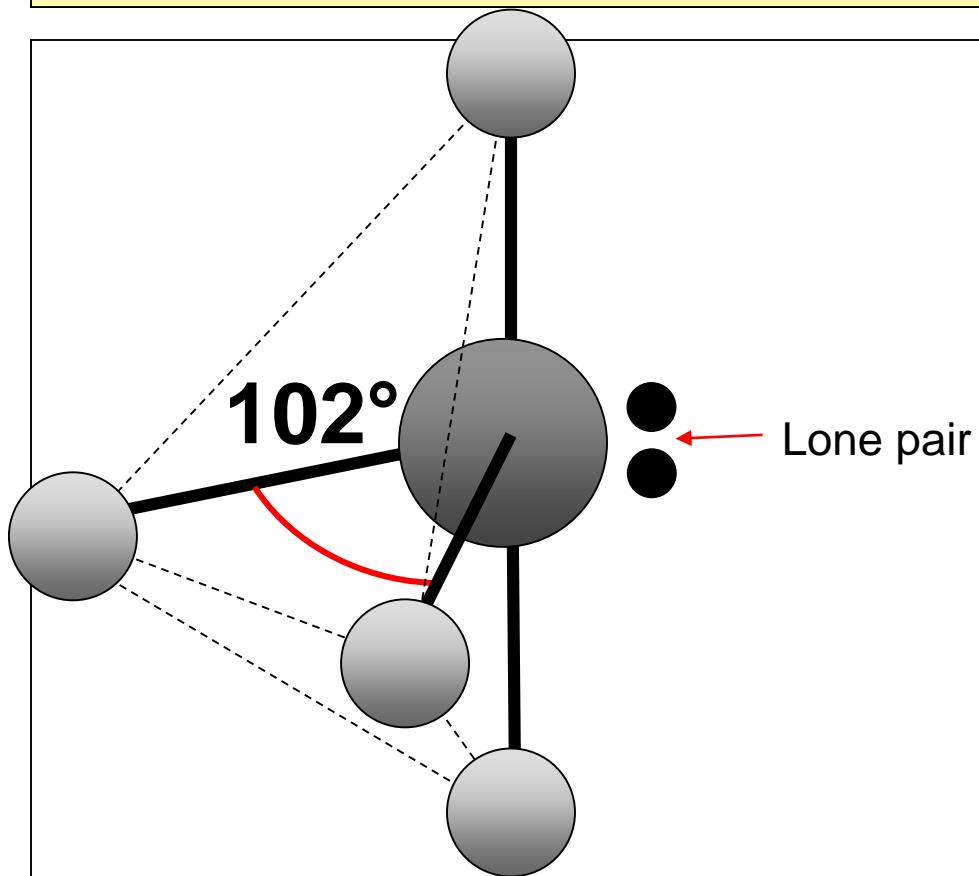
When five regions of negative charge are around a central atom they repel each other into a 3-dimensional shape. The bond angle is now 120° . The central atom has 3 central regions of negative charge that are 120° apart and 1 region above and below, 180° apart
This shape is **trigonal bipyramidal**.



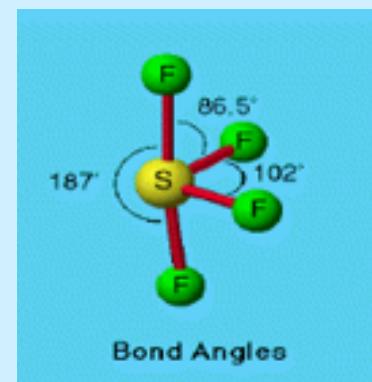
Molecular Shapes – five regions of charge (1 non-bonding pairs)

When five regions of negative charge are around a central atom they repel each other into a trigonal bi-pyramid shape. The bond angle is now 102° . One of the central regions is a non-bonding pair.

The overall shape formed from bonded regions is a **see-saw**.



EXAMPLE:
Sulfur Tetrafluoride
 SF_4 , S at the center with one lone electron pair and four fluoride atoms attached.



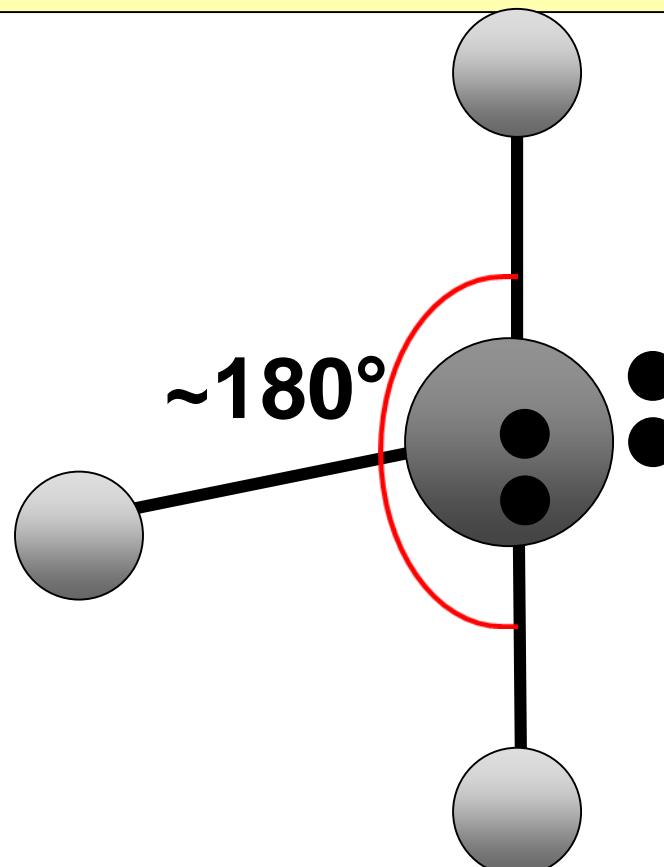
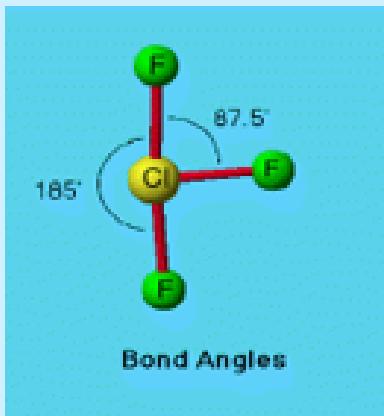
Molecular Shapes – five regions of charge (2 non-bonding pairs)

When five regions of negative charge are around a central atom they repel each other into a trigonal bi-pyramidal shape. The bond angle is slightly less than 180° between the 2 upright regions of negative charge. Two regions of negative charge in the form of non-bonding pairs exist around the central atom.

The final shape formed by bonded negative charge regions is **T-shaped**.

EXAMPLE: Chlorine Trifluoride

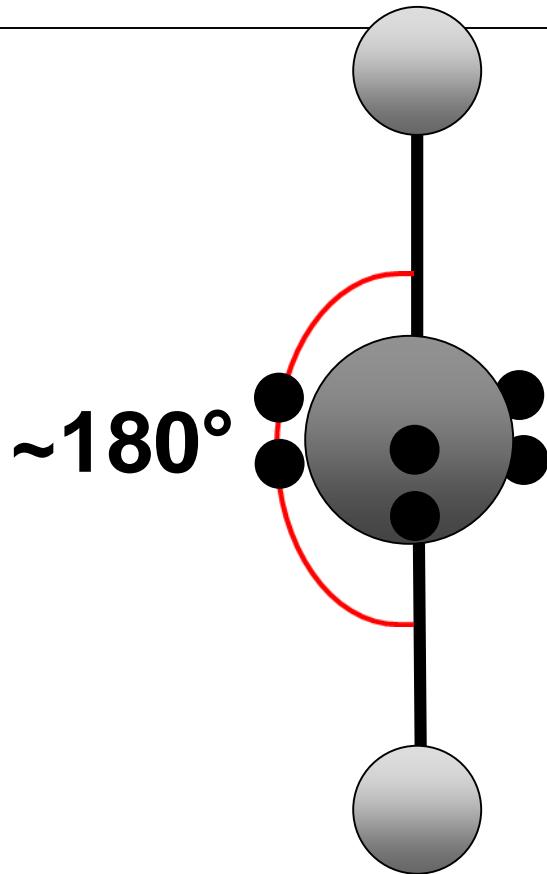
ClF_3 , chlorine at the center with three fluorine atoms attached and two lone electron pairs.



Molecular Shapes – five regions of charge (1 non-bonding pairs)

When five regions of negative charge are around a central atom they repel each other into a trigonal bi-pyramid shape. The bond angle is now slightly less than 180° . Three regions around the central atom are in the form of non-bonding pairs.

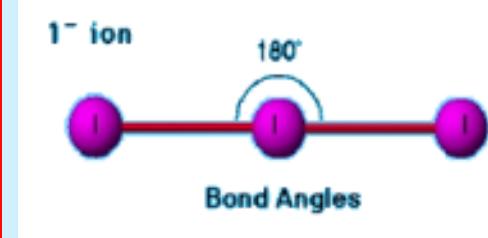
The final shape created by bonded regions of negative charge is **linear**.



EXAMPLE:

Triiodide Ion:

I_3^- , the I at the center with 3 lone electron pair and two other iodide atoms attached.



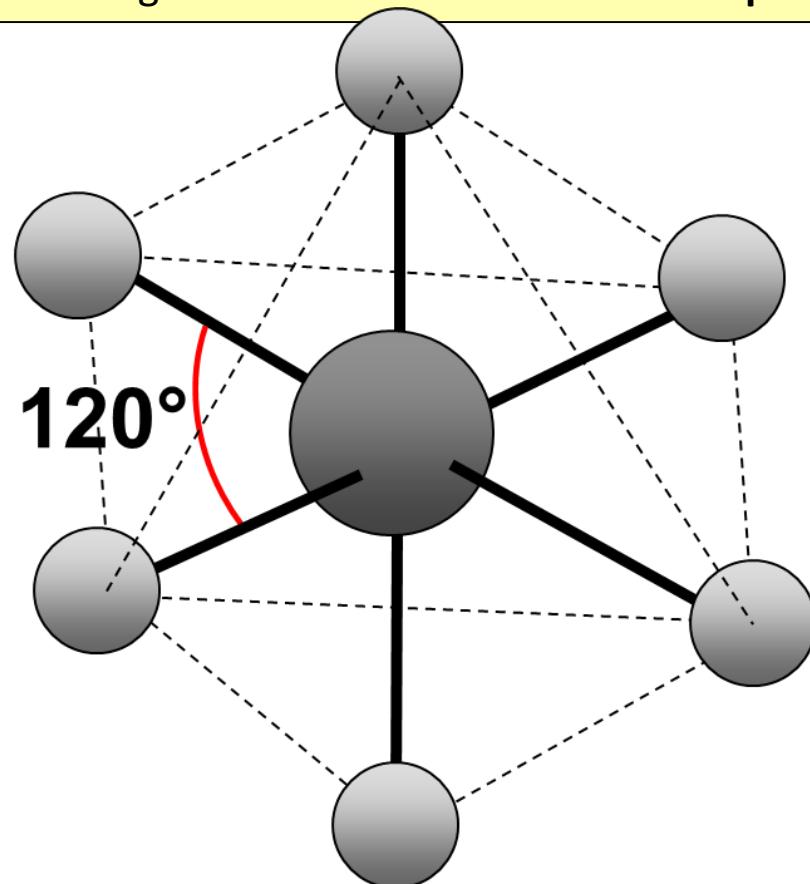
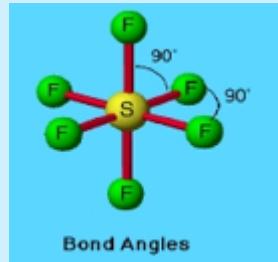
Molecular Shapes – six regions of charge (0 non-bonding pairs)

When six regions of negative charge are around a central atom, they repel each other into an octahedral shape. The bond angle is now 120° between the central regions of negative charge. Two regions of negative charge are vertical of the central atom at approximately 180° .

The shape the bonded regions of negative charge form is also an **octahedral shape**.

EXAMPLE: Sulfur hexafluoride:

An example of octahedral molecular geometry that results from six electron pair geometry is SF_6 . The sulfur atom has 6 valence electrons. However this is an example where six fluoride atoms are present and the octet is expanded.



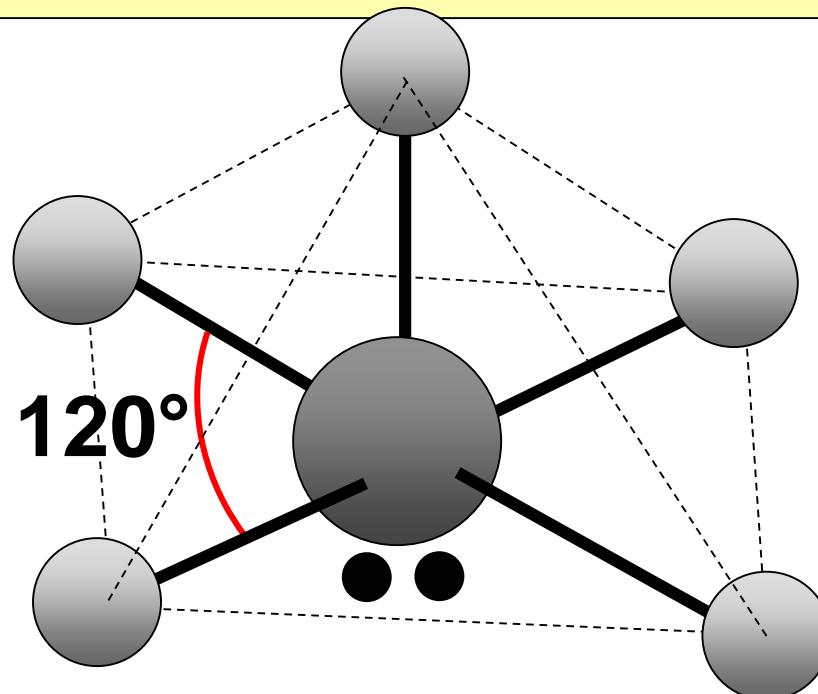
Molecular Shapes – six regions of charge (1 non-bonding pair)

When six regions of negative charge are around a central atom, they repel each other into an octahedral shape. The bond angle is now 120° between the central regions of negative charge. Unlike the 5-region of charge that loses the horizontal atoms first to non-bonding pairs, the 6 region shape loses its vertical atoms first to non-bonding pairs. The shape the remaining bonded regions of negative charge form is a **square pyramid shape**.

EXAMPLE:

Bromine pentafluoride:

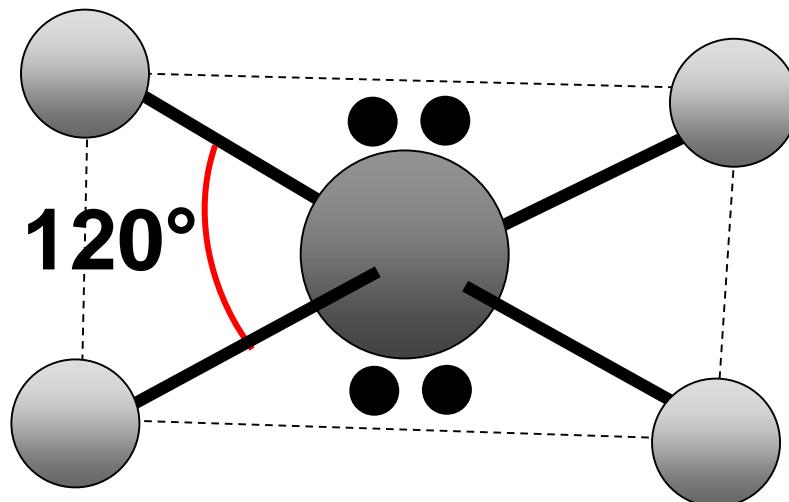
BrF_5 , the Lewis diagram shows Br at the center with one lone electron pair and five fluoride atoms attached.



Molecular Shapes – six regions of charge (2 non-bonding pairs)

When six regions of negative charge are around a central atom, they repel each other into an octahedral shape. The bond angle is now 120° between the central regions of negative charge. Unlike the 5-region of charge that loses the horizontal atoms first to non-bonding pairs, the 6-region shape loses its two vertical atoms which are replaced by non-bonding pairs.

The shape the remaining bonded regions of negative charge form is a **square planar shape**.

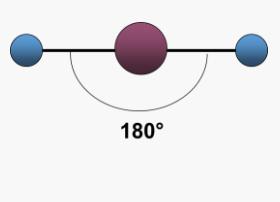


Determining Molecular Shapes

2 regions

No non-bonding pair

Linear



CO_2

180°

3 regions

No non-bonding pair

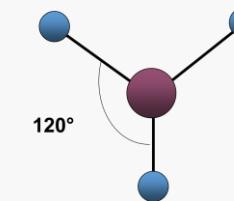
Trigonal Planar

120°

1 non-bonding pair

Bent

$\sim 119^\circ$



BF_3

120°

No non-bonding pair

Tetrahedral

109.5°

1 non-bonding pair

Trigonal Pyramid

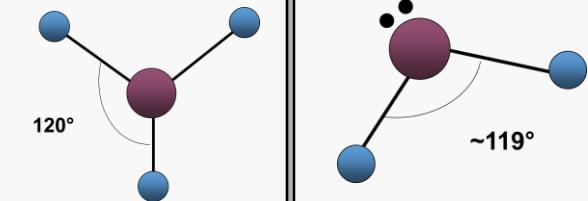
107°

2 non-bonding pairs

Bent

104.5°

2 non-bonding pairs



SO_2

119°

CH_4

109.5°

NH_3

107°

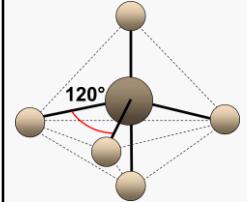
H_2O

105°

5 regions

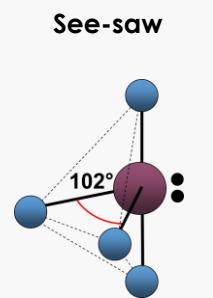
no non-bonding pairs

Trigonal bipyramidal



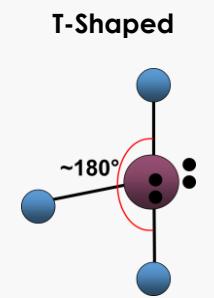
1 non-bonding pair

See-saw



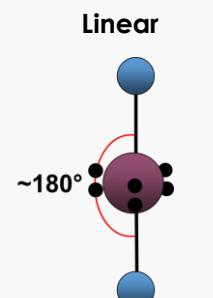
2 non-bonding pairs

T-Shaped



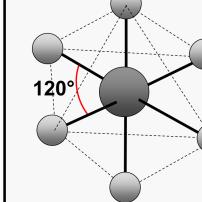
3 non-bonding pairs

Linear



no non-bonding pairs

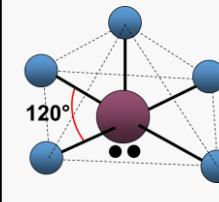
Octahedral



6 regions

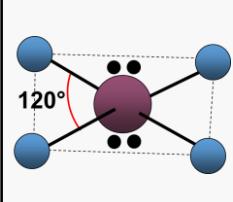
1 non-bonding pair

Square Pyramidal



2 non-bonding pairs

Square Planar



PCl_5

120°

SF_4

90°

ClF_3

102°

86.5°

I_3^-

185°

87.5°

SF_6

90°

BrF_5

90°

XeF_4

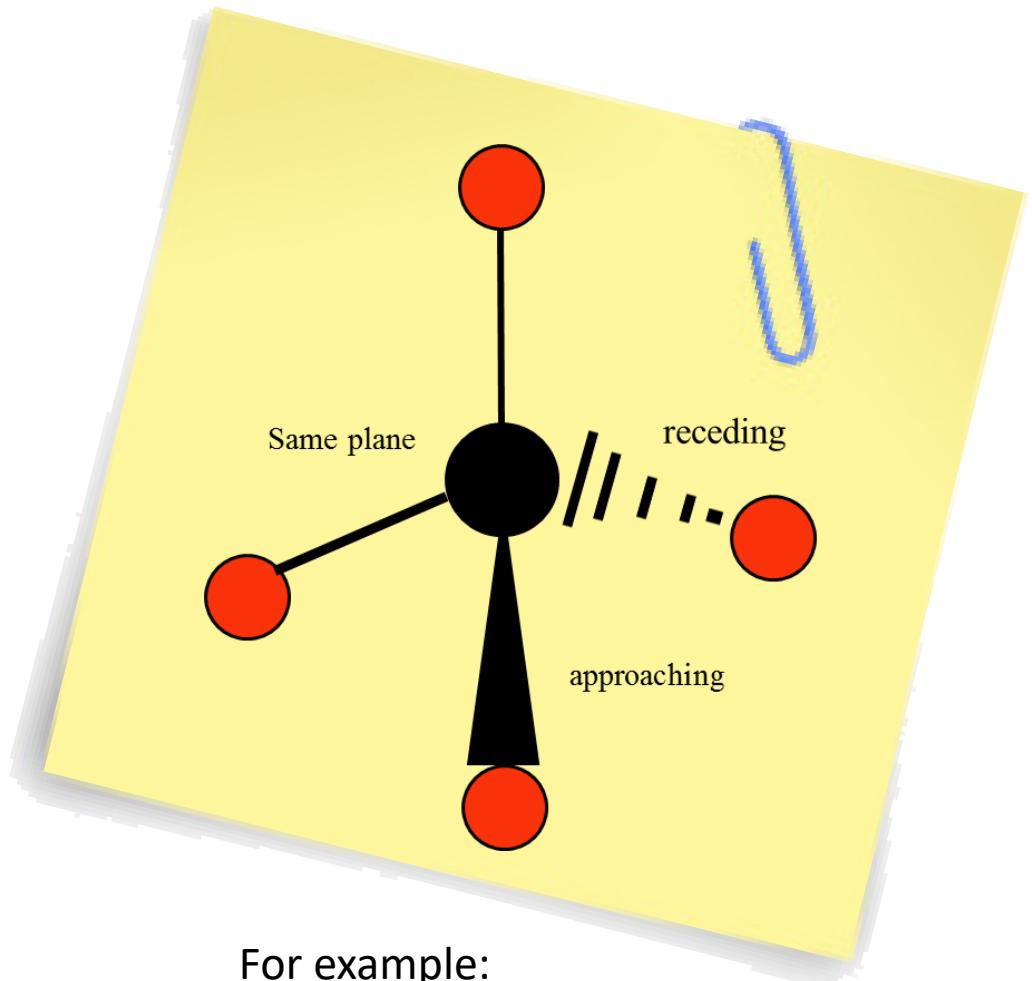
90°

horizontal

vertical

Drawing Shapes

1. Atom on **same plane** as central atom – straight solid line
2. Atom **receding** from central atom – lines starting large and getting smaller
3. Atom **approaching** from central atom – solid triangle starting small and getting larger

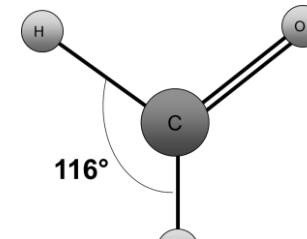


For example:
Tetrahedral shape

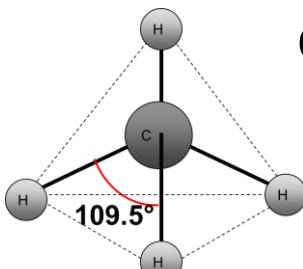
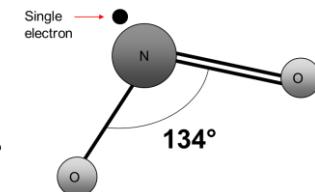
Minor variations in geometry of shapes



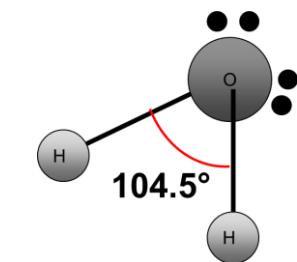
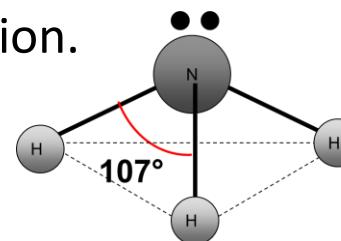
$\text{H}_2\text{C=O}$ is 116° because of greater repulsion from multiple bonds



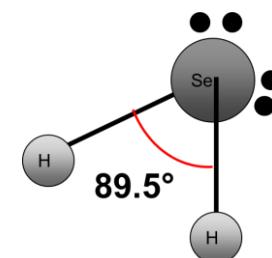
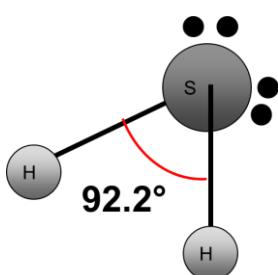
NO_2 is 134° because of smaller repulsion from unpaired electron.



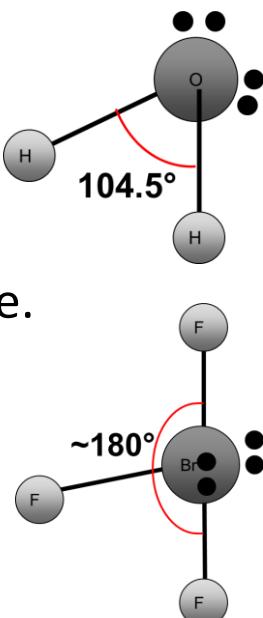
CH_4 is $109.5^\circ > \text{NH}_3$ is $107.3^\circ > \text{H}_2\text{O}$ is 104.5 because the lone pair repulsion > bonded pair repulsion.



BrF_3 is T-shaped rather than trigonal planar for same reason as above.



H_2O $104.5^\circ > \text{H}_2\text{S}$ $92.2^\circ > \text{H}_2\text{Se}$ 89.5° because of decreasing electronegativity of central atom.



Background Knowledge

Discussing shapes questions

Explain why the shape of the CO₂ molecule is linear but the shape of H₂O is bent?

1. The C (central atom) of CO₂ has 2 regions of negative charge around it in the form of double bonds connected to a O atom. (draw Lewis structure)
 2. Each of the regions of negative charge repel each other the furthest away from each other in 3 dimensional space into a linear shape.
 3. There are no lone pairs so the final CO₂ molecule therefore also forms a *linear shape*
-
1. The O molecule (central atom) of H₂O has 4 regions of negative charge around it in the form of two single bonds connected to a H atom and two lone pairs. (draw Lewis structure)
 2. Each of the regions of negative charge repel each other the furthest away from each other in 3 dimensional space and form a tetrahedral shape.
 3. However with only 2 of the regions bonded to atoms the final shape the H₂O molecule forms is a *bent shape*

2013 Lewis Diagrams and Shapes

Achieved
Question

Question 1c: (i) Complete the following table.

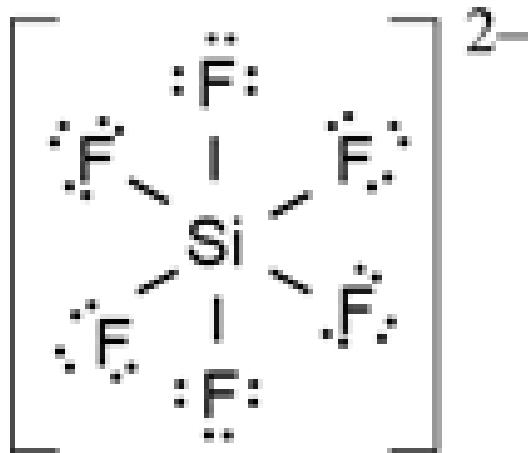
Molecule	BrF_3	PCl_6^-
Lewis diagram	$\begin{array}{c} \text{:} \ddot{\text{F}} \text{:} \\ \\ \text{:} \ddot{\text{F}} \text{--- Br} \text{:} \\ \\ \text{:} \ddot{\text{F}} \text{:} \end{array}$	$\left[\begin{array}{c} \text{:} \ddot{\text{Cl}} \text{:} \quad \text{:} \ddot{\text{Cl}} \text{:} \quad \text{:} \ddot{\text{Cl}} \text{:} \\ \diagdown \quad \diagup \quad \diagdown \\ \text{P} \\ \diagup \quad \diagdown \\ \text{:} \ddot{\text{Cl}} \text{:} \quad \text{:} \ddot{\text{Cl}} \text{:} \quad \text{:} \ddot{\text{Cl}} \text{:} \end{array} \right]^-$
Name of shape	T-shaped	Octahedral

NCEA 2014 Lewis Diagrams and Shapes

Merit
Question

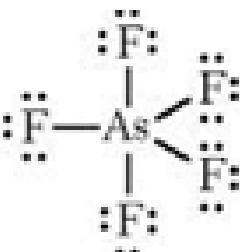
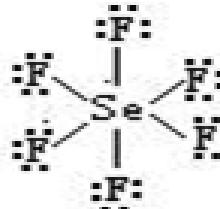
Question 3a: In New Zealand, fluoride for water treatment is supplied as sodium fluorosilicate, Na_2SiF_6 .

One of the ions formed in the solution from sodium fluorosilicate is SiF_6^{2-}
Complete the table below.

	SiF_6^{2-}
Lewis diagram	
Name of shape	Octahedral

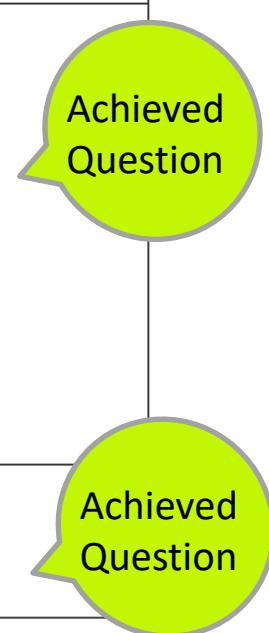
NCEA 2015 Lewis Diagrams and Shapes

Question 3a: Complete the following table

	AsF_5	SeF_6
Lewis diagram		
Name of shape	Trigonal bipyramidal	Octahedral

Only one of each correct required for the mark.

It is highly likely the Lewis structure will be an expanded Octet (more than 4 pairs around the central atom) so “L3” names can be used for shapes.



NCEA 2016 Lewis Diagrams and Shapes

Merit
Question

Question 1c (i) : Complete the following table

	ICl_4^-	ClF_3
Lewis diagram	$\left[\begin{array}{c} \text{:Cl:} \\ \\ \text{:Cl}-\text{I}-\text{Cl:} \\ \\ \text{:Cl:} \end{array} \right]^-$	$\begin{array}{c} \text{:F}-\text{Cl}-\text{F:} \\ \\ \text{:F:} \end{array}$
Name of shape	ICl_4^- : Square planar	ClF_3 : T-shaped

Only one name + diagram required for the mark.

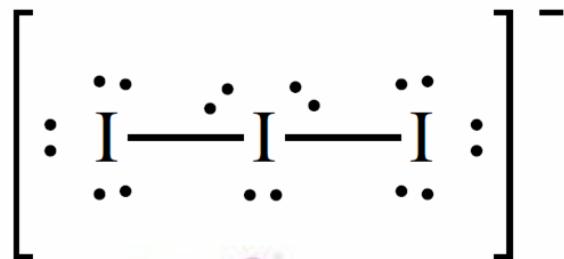
It is highly likely the Lewis structure will be an expanded Octet (more than 4 pairs around the central atom) so “L3” names can be used for shapes.

NCEA 2017 Lewis Diagrams and Shapes

MERIT
Question

Question 3c: Iodine forms a linear I^{3-} ion.

(i) Draw the Lewis structure for the I^{3-} ion below.



(ii) Explain why the I^{3-} ion has a linear shape.

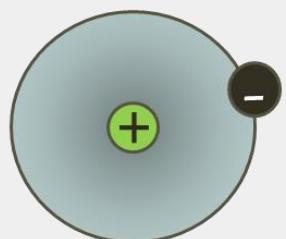
Arrangement of areas of electron density around the central I atom is trigonal bipyramidal due to five regions of negative charge. These areas all repel each other. As there are three non-bonding pairs (in the equatorial area) and two bonded atoms, the shape is linear.

Background Knowledge

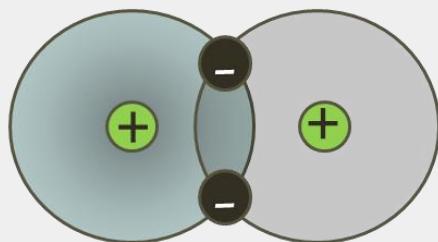
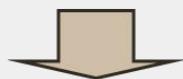
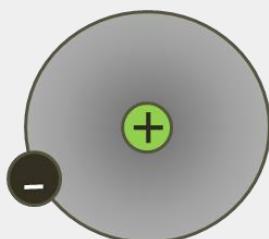
Covalent Bonding

Covalent Bonding occurs when electrons are shared between neighbouring atoms. No ions are formed and there is no transfer of electrons. The compound formed is neutral with no charge.

Non-Metal atom



Non-Metal atom



covalent bonding

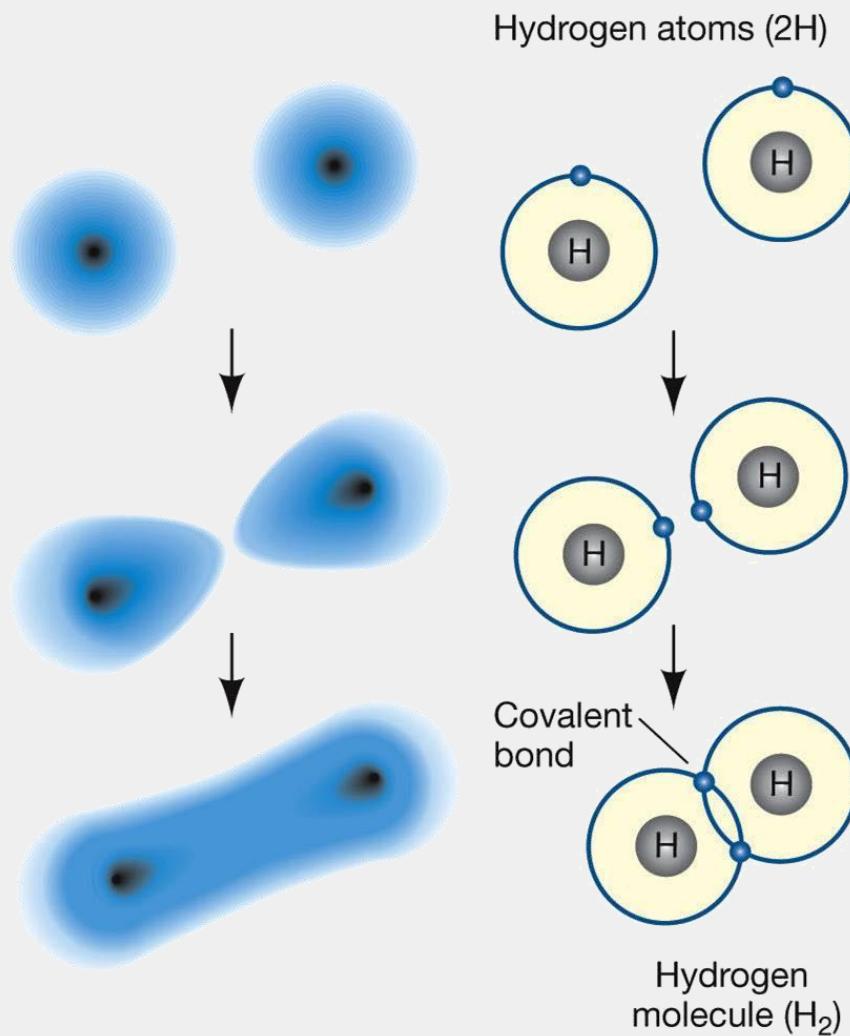
When the electronegativity is similar between atoms then the electrons will be shared evenly creating a **non-polar molecule**. If there is a significant electronegativity difference then dipoles will be created when the electrons orbit for a greater time around the more electronegative atom. This will create a **polar molecule**.

Background Knowledge

The valence electrons are involved in bonding. These electrons orbit in pairs. The negative charge of the electron pair will attract the positively charged nuclei of other atoms, and this holds the atoms together in a molecule.



Covalent Bonding



Background Knowledge

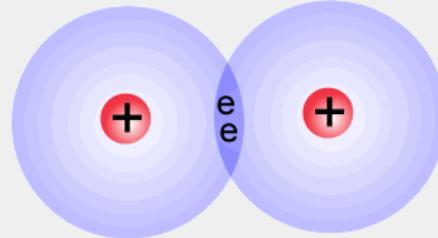
Covalent Bonding

The electron-pair must lie between the nuclei for the attraction to outweigh the repulsion of the two nuclei. This ‘sharing’ of electrons between atoms creates a covalent bond – giving both atoms the stability of a full outer shell.

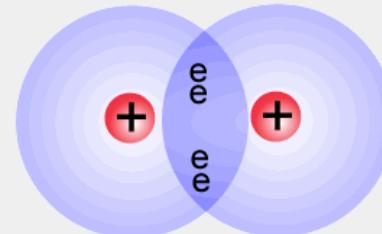
Covalent bonds are normally formed between pairs of non-metallic atoms.

Some covalent bonds involve only one pair of electrons and are known as single bonds. Other covalent bonds can involve two pairs of electrons; double bonds and three pairs of electrons; triple bonds.

Only one pair of electrons holding the nuclei together



Two pairs of electrons hold the nuclei tighter and closer

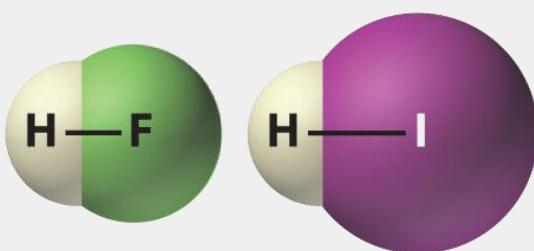


Background Knowledge

Covalent Bonding

All covalent bonds are strong. That is it requires a large amount of energy to ‘break’ the bond. However, some covalent bonds are stronger than others. The greater the overlap of valence orbitals (the area the valence electrons orbit the nucleus) the stronger the bond.

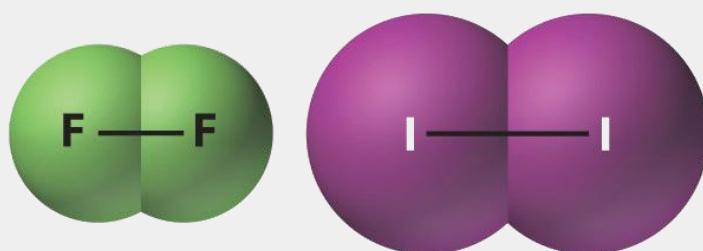
Bonding atoms



Overlap between valence orbitals



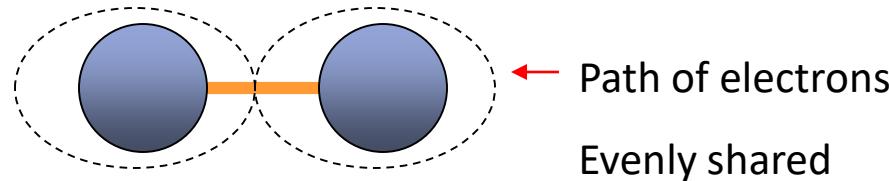
(a) H–F versus H–I



(b) F–F versus I–I

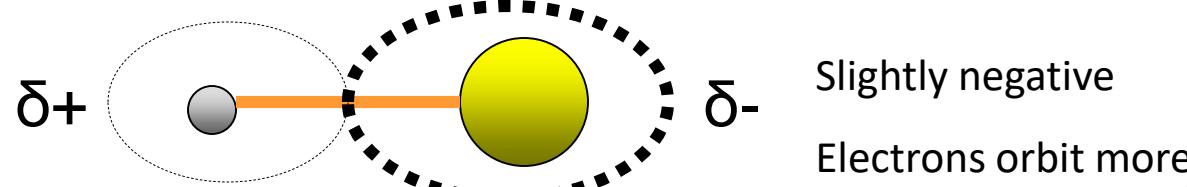
Polarity and dipoles

If two identical atoms are bonded together then they have exactly the same amount of attraction to the shared electrons in the bonded pair. This is because their electronegativity is the same. This becomes a **non-polar molecule with non-polar bonds**. Example - Iodine molecule I_2



If two different types of atoms are bonded together then they will exert different levels of attraction for the orbiting electrons. That is because they may have different numbers of electron shells and different numbers of protons in their nucleus. This will cause an electronegativity difference and a **dipole** will form. These bonds become **polar bonds**. Example – hydrochloric acid HCl

Slightly positive
Electrons orbit less

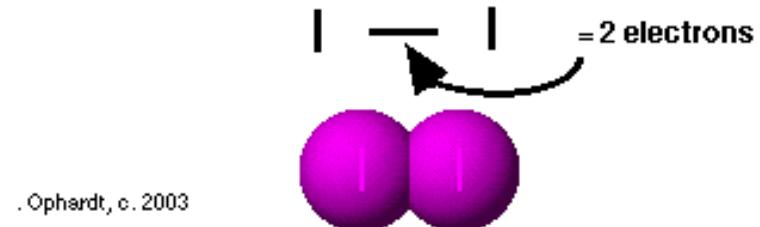


Polarity

If two bonded atoms are the same, the bond is said to be non-polar. i.e. I_2

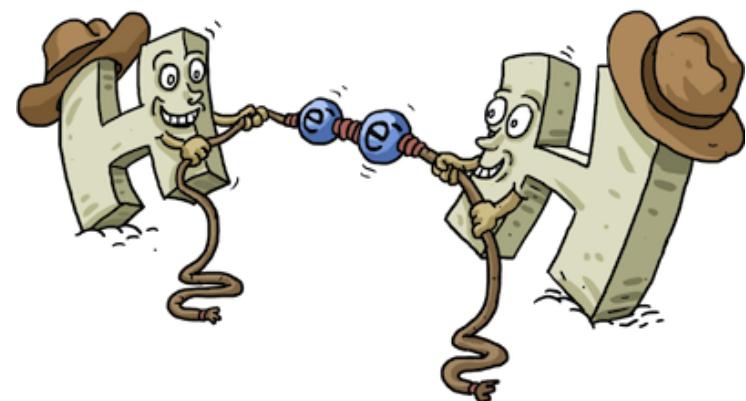
The whole molecule is also non-polar because there is no electronegativity difference and the valence electrons orbit each atom evenly. If two different atoms are bonded they form a polar bond, as there is an electronegativity difference and the valence electrons spend more time around the atom with the higher electronegativity value (that atom becomes slightly negative) The atom that the valence electrons spend less time around becomes slightly positive.

Equal Sharing of electrons between two identical non-metals.



.Ophardt, c. 2003

Non-Polar Covalent Bond

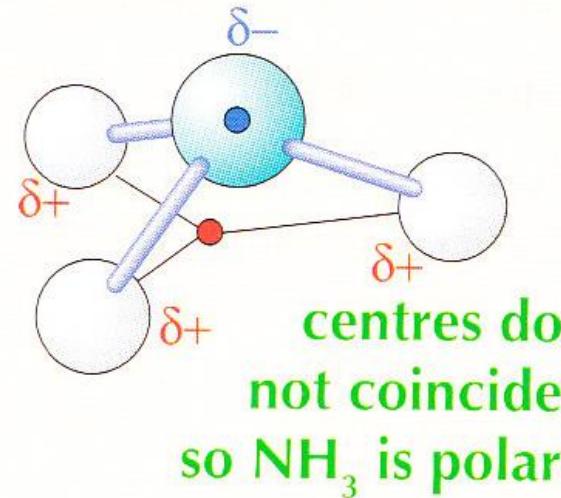
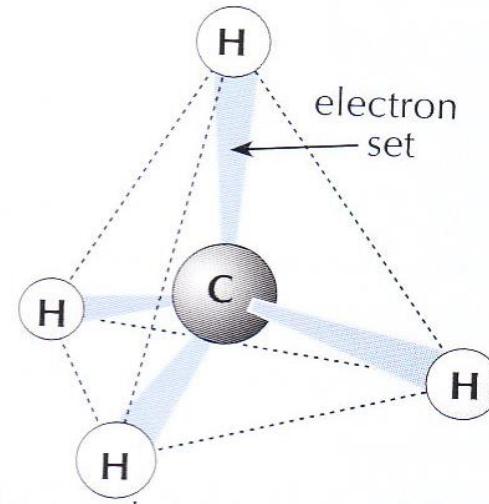


Symmetry and Polarity

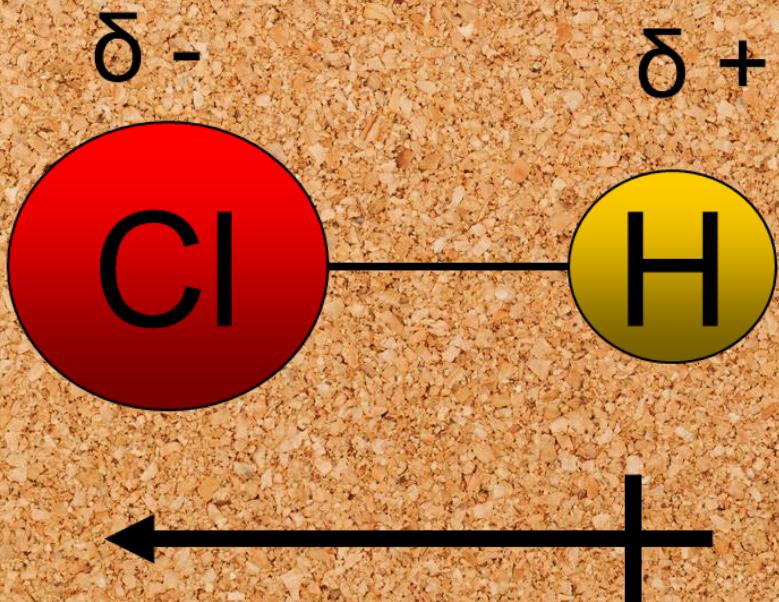
The polarity of a molecule with polar bonds depends upon whether the molecule is symmetrical or not.

A symmetrical molecule (one where the centres of peripheral atoms coincide) becomes a **non-polar molecule** – as the dipoles and thus the charges balance out

An unsymmetrical molecule (one where the centre of peripheral atoms do not coincide) is a **polar molecule**.



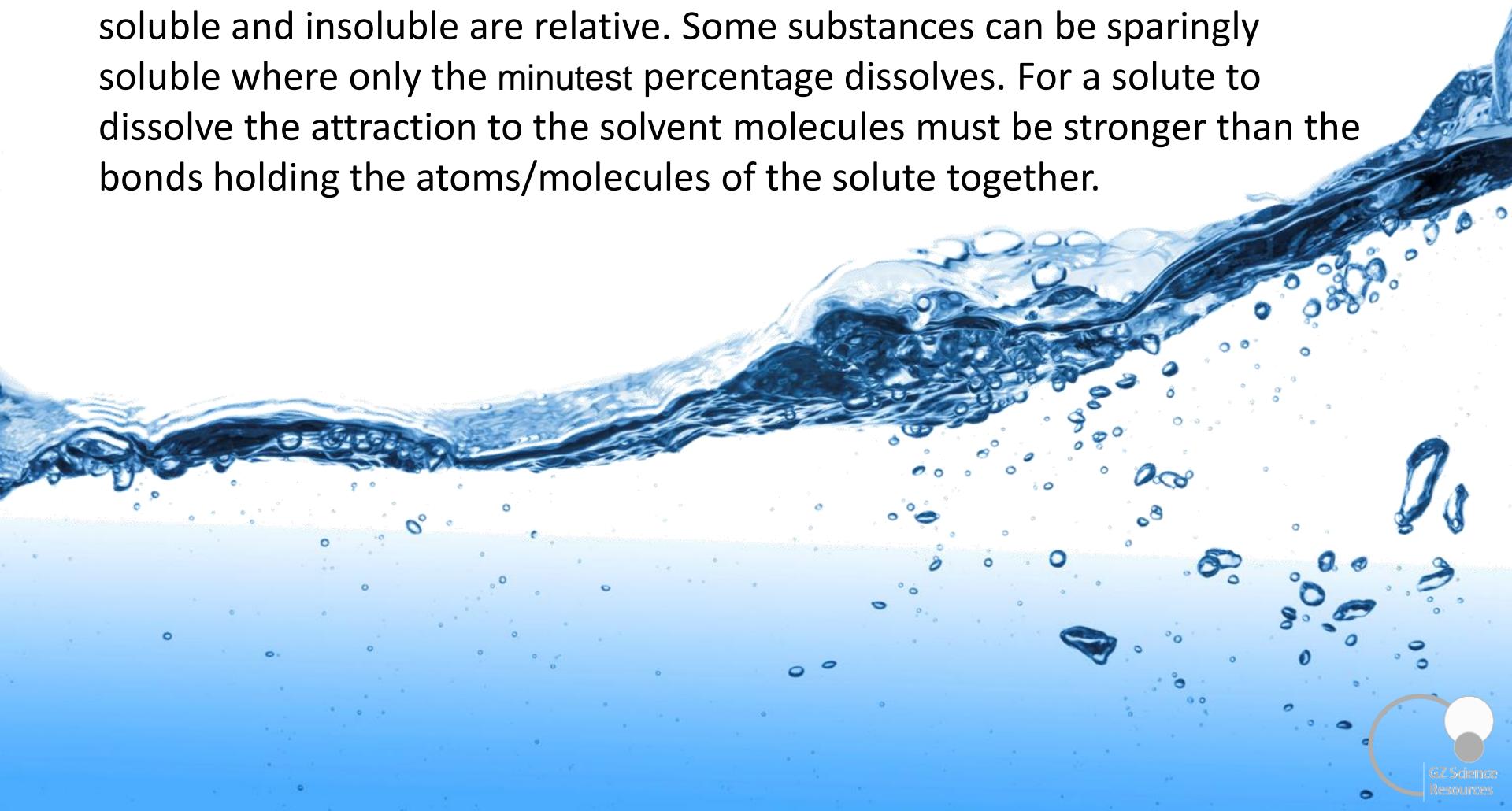
Polarity



Dipoles may also be shown as an arrow, with a cross, +ve, at the tail. The arrowhead is the -ve end. The more electronegative atom forms the negative end and the less electronegative atom forms the positive end.

Solubility

The solubility of a substance is the **amount** of that substance that will dissolve in a given amount of solvent. Solubility is a quantitative term. Solubility's vary depending on the solvent and the solute. The terms soluble and insoluble are relative. Some substances can be sparingly soluble where only the minutest percentage dissolves. For a solute to dissolve the attraction to the solvent molecules must be stronger than the bonds holding the atoms/molecules of the solute together.



Dissolving and Polarity

Polar substances dissolve polar substances.

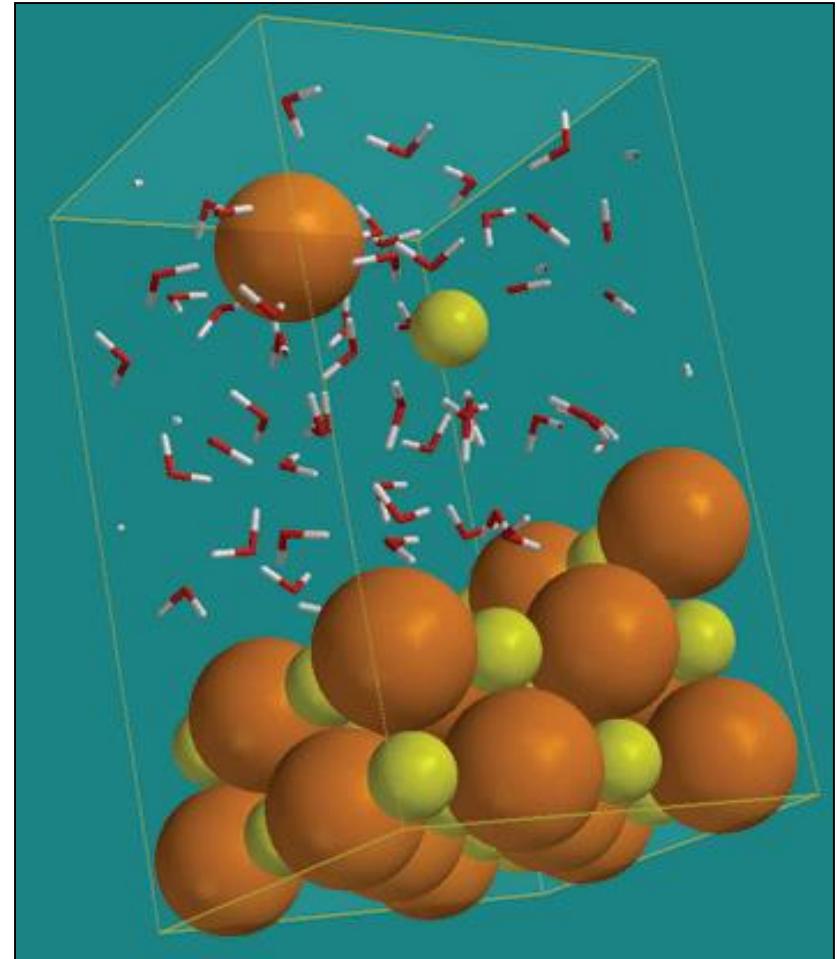
e.g. Water, being polar attracts the molecules of other polar substances (e.g. HCl) and will dissolve them.

Polar substances will not dissolve non-polar substances.

e.g. Water, (polar) has a stronger attraction to itself than to non-polar molecules (e.g. cyclohexane) and will not dissolve them.

Non-polar substances dissolve non-polar substances.

e.g. Non polar solvents (like cyclohexane) attract non-polar solutes (like napthalene) by the same weak Van der Waals forces they attract themselves by and so will dissolve non-polar solutes.



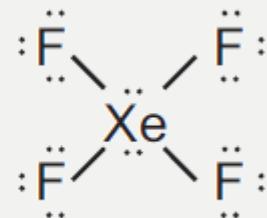
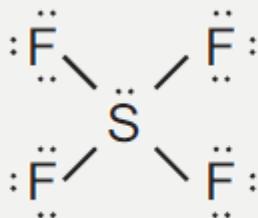
Ionic solid dissolving in water

Answering Polarity Questions

Explain why molecules x (CCl_4) and y (NCl_3) are polar and non-polar?

Polar molecule	Non-polar molecule
<ol style="list-style-type: none">1. molecule (NCl_3) is polar (state which one)2. (NCl_3) contains polar bonds due to electronegativity difference of N and Cl.3. over the whole molecule the atoms are not distributed symmetrically in 3 dimensions therefore...4. polar bonds do not cancel each other out and the whole molecule is polar.	<ol style="list-style-type: none">1. molecule (CCl_4) is non-polar (state which one)2. (CCl_4) contains polar bonds due to electronegativity difference of C and Cl. Cl attracts more electrons than C because it has a bigger atomic number than C but with the same number of shells3. over the whole molecule the atoms are distributed symmetrically in 3 dimensions therefore...4. polar bonds cancel each other out and the whole molecule is non-polar.

Question 1c: (ii) The Lewis diagrams for SF_4 and XeF_4 are shown below. Compare and contrast the polarities and shapes of these two molecules.



There is a difference in electronegativity between S and F, so the S-F bonds are polar covalent. SF_4 has a see-saw shape (distorted tetrahedron) due to the repulsions between four bonding regions and one non-bonding region of charge, which is asymmetric therefore the polarities/dipoles do not cancel. As a result, SF_4 is a polar molecule.

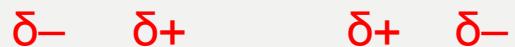
There is a difference in electronegativity between Xe and F, so the Xe-F bonds are polar covalent. XeF_4 has a square planar shape, due to the repulsions between four bonding regions and two non-bonding regions of charge; therefore the polarities/dipoles do cancel. As a result, XeF_4 is a non-polar molecule.

Question 1d: The halogens make up Group 17 of the periodic table.

(i) The polarity of the HBr molecule is shown below.



Using this as an example, indicate the polarity of the following bonds by indicating any dipoles present.



1. F — Cl 2. At — Cl

(ii) Using your knowledge of trends in the periodic table, circle the atom below that has the greater electronegativity value. Br I

Justify your answer.

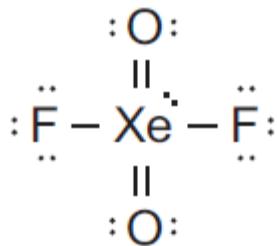
Answer 1d: Lower electronegativity means less attraction of a bonded atom for a bonding pair of electrons.

The lower value for iodine indicates that the attraction for the bonding pair in compounds is less than the attraction for bonding pairs in compounds of bromine. As the radii of atoms increase, electronegativity decreases, despite the increased nuclear charge. This is due to more energy levels being added.

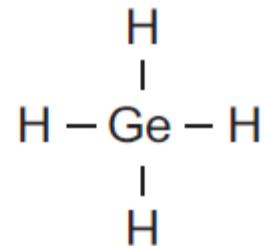
Iodine has a greater number of shells (5th row) than bromine (4th row). This factor outweighs the increased nuclear charge (53 protons) of the iodine atom, as compared to the bromine atom (35 protons).

NCEA 2015 Polarity

Question 3b: The Lewis diagrams and shapes for XeO_2F_2 and GeH_4 are shown below. Compare and contrast the polarities and shapes of these two molecules.



see-saw



tetrahedral

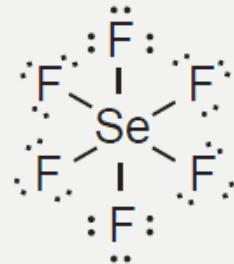
Answer 3b: XeO_2F_2 is polar. It has 5 areas of electron density around the central Xe atom, one of which is a lone pair. Maximum separation for minimum repulsion means that the shape is based on a trigonal bipyramidal structure, but the final shape is actually see-saw. The Xe=O bonds are polar, due to the greater electronegativity of O, and the Xe-F bonds even more polar, due to the F atom having the highest electronegativity on the periodic table. The molecule is **not symmetrical**, and so the dipole moments cannot cancel, making the **molecule polar**.

GeH_4 is non-polar. It has 4 areas of electron density around the central Ge atom, all of which are bonded. Maximum separation for minimum repulsion means that the shape is tetrahedral. This is a **symmetrical** structure, thus the bond dipole moments cancel, and therefore the **molecule is non-polar**.

NCEA 2016 Polarity

Excellence Question

Question 1c (ii): The Lewis diagram for SeF_6 is shown beside. Would you expect SeF_6 to be soluble in water? Explain your answer in terms of the shape and polarity of SeF_6 .



Answer 1c (ii): No. There is an electronegativity difference between Se and F, so the Se-F bonds are polar covalent. The six bond pairs around the central Se atom arrange themselves as far apart as possible to minimise repulsion, so SeF_6 has an octahedral shape. Since this is a symmetrical shape, the bond dipoles cancel out, so SeF_6 is a non-polar molecule.



Water is a polar solvent. Non-polar molecules like SeF_6 are not attracted to polar molecules like water, i.e. the intermolecular attraction between the water molecules and the SeF_6 molecules is insufficient to overcome the attraction between the water molecules. Therefore, SeF_6 is insoluble in water.

Question 3c (iii): IF_5 has a square pyramidal shape.

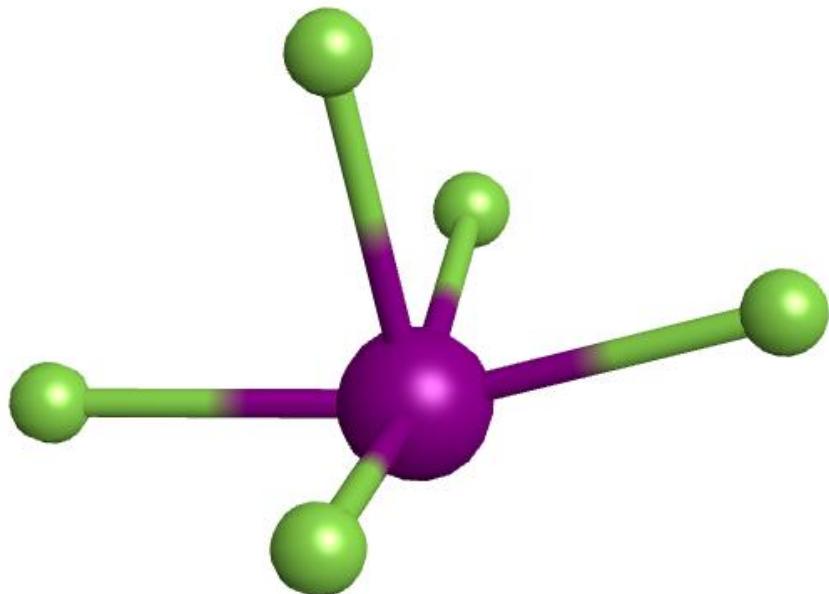
Indicate whether the molecule IF_5 is polar or non-polar.

Justify your choice.

Polar.

The I-F bond is polar due to a difference in electronegativity.

There are six regions of negative charge giving IF_5 an octahedral geometry. The five bonded and one lone pair around the central iodine atom gives it the square pyramid shape. This means the molecule is asymmetric so the bond polarities don't cancel causing the molecule to be polar.



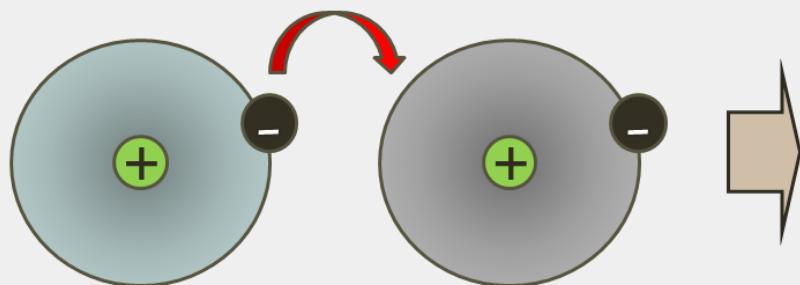
Background Knowledge

Ionic Bonding

Ionic Bonding is where one atom completely takes valence electrons from another to form ions and the resulting negative and positive ions hold together with electrostatic attraction. This type of bonding occurs when a **metal** and **non-metal** react and there is a **transfer of electrons** to form ions.

The ions then combine in a set ratio to form a neutral compound with negative and positive charges balanced out.

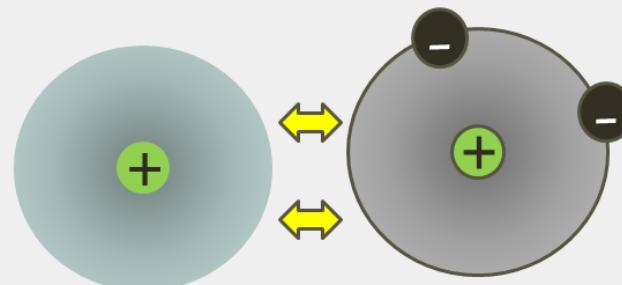
Electron transfer



Metal atom

Non-Metal atom

Ionic bonding



Positive ion

Negative ion

Background Knowledge

Strength of Ionic Bonds

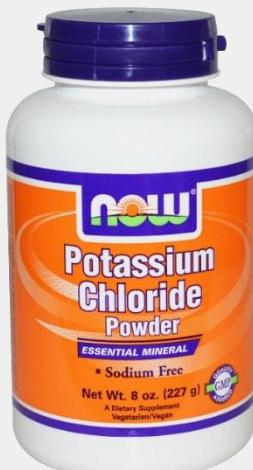
Two factors are involved with determining the strength of ionic bonds.

The first is the charge of the ions. A 2+ and 2- (e.g. MgO) bond will be much stronger than a + and - (e.g. KCl) ionic bond.

Secondarily is the distance between the ions. The closer the ions, the stronger the electrostatic bond.



MgO
Melting point 2,852 °C

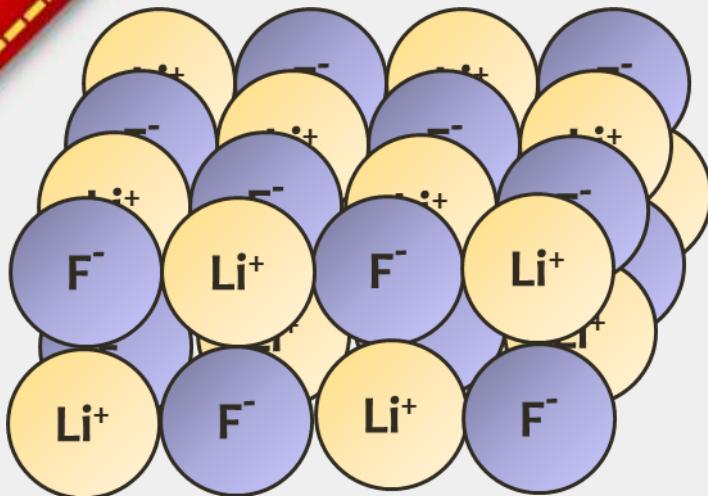


KCl
Melting point 770 °C

Background Knowledge

Ionic compounds are the product of chemical reactions between metal and non-metal ions

Some compounds are ionic compounds, since they are made up of cations and anions.



The Anion (F) takes the electrons off the Cation (Li) so their outer energy levels have a stable 8 electrons each.

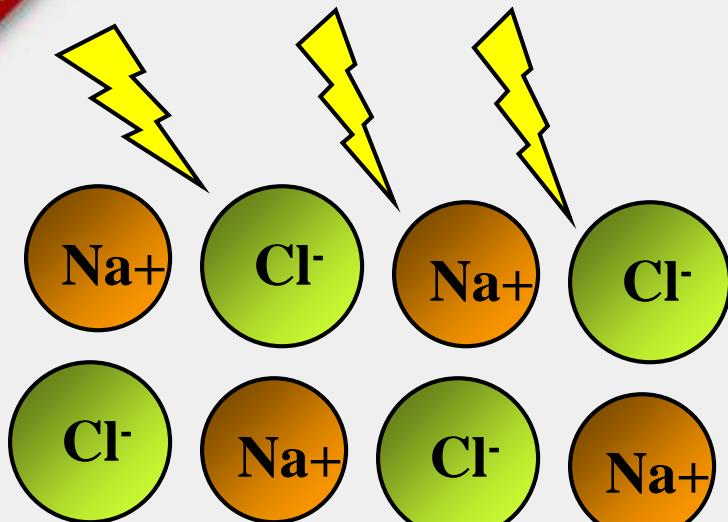
Anions and Cations have a strong electrostatic attraction for each other so they bond together as a compound.

Compounds are neutral substances. For ionic compounds, the charges of the positive ions are balanced by the charges of the negative ions.

Background Knowledge

Ionic Solids – Melting Point

An ionic solid is made up of ions held together by strong electrostatic attractions between +ve and -ve ions in a 3-dimensional lattice. Because these strong bonds require a large amount of energy to break the ionic solids have a high melting point.



By adding heat energy to the ionic solid this is then transformed into kinetic energy. When the kinetic energy is high enough and the electrostatic bonds are broken then melting point has been reached.

Ionic compounds with double charged ions ($2+$ and $2-$) will have a higher melting point as the bonds require more energy to break.

Background Knowledge

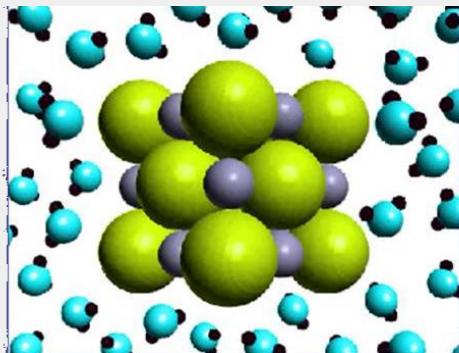
Ionic Solids - Solubility

In order for substance to dissolve in water (a polar liquid) the attraction between the particles in a substance must be less than the attraction towards water molecules

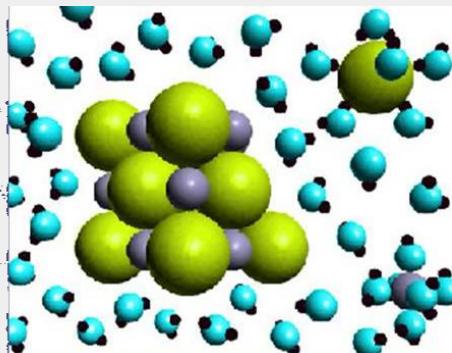
For example:

1. Sodium chloride (NaCl) is an ionic solid
2. Sodium chloride is made up of ions held together by strong electrostatic attractions between +ve and –ve ions in a lattice
3. the electrostatic attractions of water molecules have sufficient strength to pull the ions apart however
4. therefore the solid will dissolve and is soluble

NaCl first place in water



Na⁺ and Cl⁻ ions breaking apart

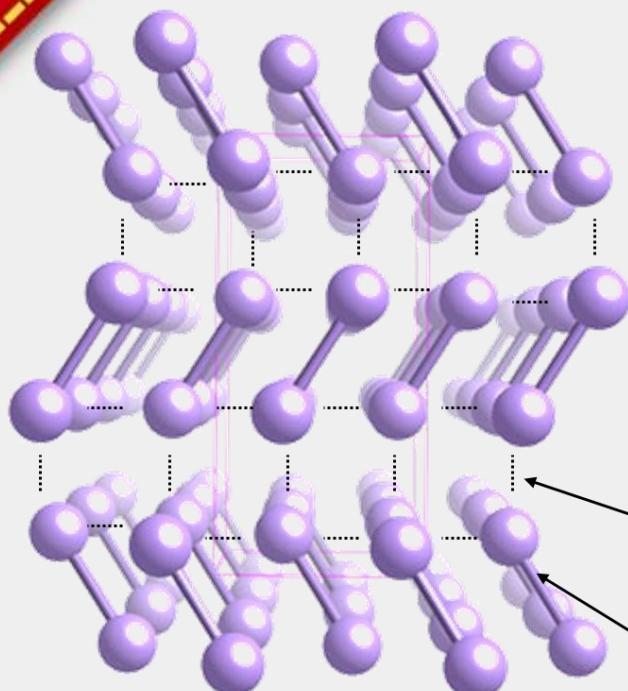


The positive hydrogen end of water is attracted to the anions and the negative oxygen end of water is attracted to the cations

Background Knowledge

Molecular solids

non-metal + non-metal



Non-polar molecules held together by intermolecular forces caused by temporary dipoles induced by electrons randomly spending more time around one nucleus than the other.

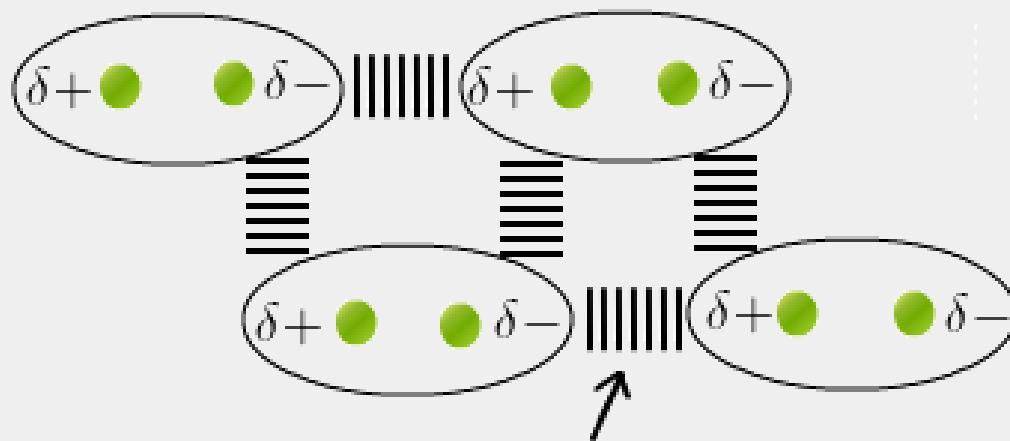
Weak intermolecular bond

Strong covalent bond

Background Knowledge

Molecular solids

Polar molecules held together by **weak intermolecular forces** caused by permanent dipoles induced by electrons spending more time around one nucleus in the molecule that has greater electronegativity than the other. The $\delta -ve$ end of one molecule is attracted to the $\delta +ve$ end of another.



Intermolecular Force between dipoles

Background Knowledge

Solids Summary

Name of solid substance	Type of particle in solid	Attractive force broken when solid melts	Attractive force between particle –weak or strong	Relative melting point	solubility
molecular	molecules	Weak intermolecular van der waals	weak	low	Yes if polar No if non-polar
metal	atoms	Metallic bonding	strong	high	no
ionic	ions	Ionic bonding	strong	high	yes
covalent	atoms	Covalent bonding	strong	high	no



Weak Intermolecular Force



Weak intermolecular forces of attraction occur between molecular solids

3 types of forces:

Instantaneous dipole (ID) – temporary dipole – all molecules have this type

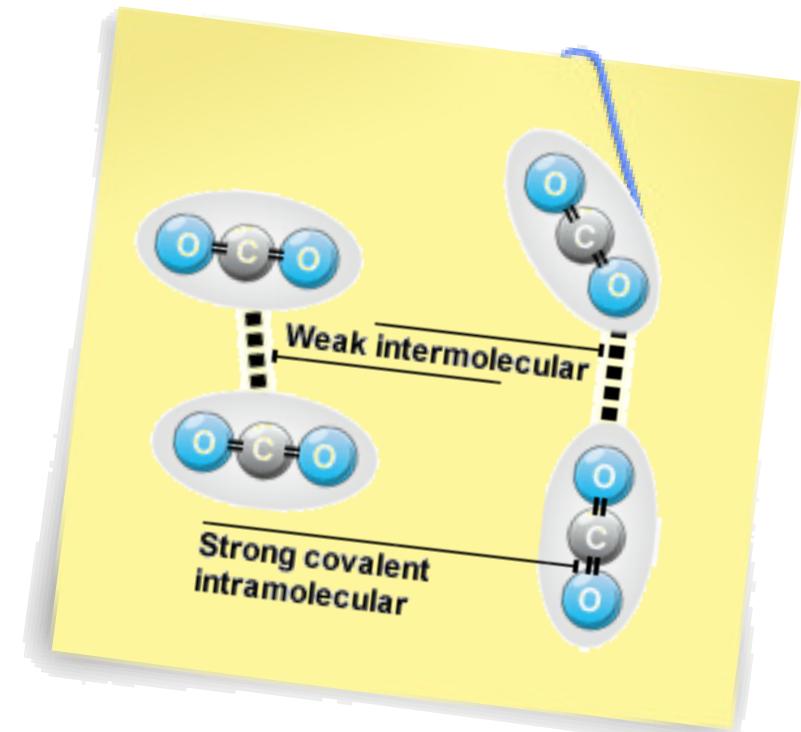
Permanent dipole (PD) – permanent dipole – only polar molecules have this type **in addition** to ID-ID

Hydrogen bonding (HB) – permanent dipole – molecules with H bonded to O, N or F have this type of bonding

Note the distinction:

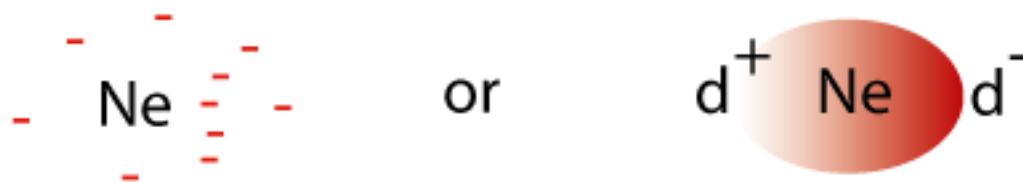
Intra-molecular Forces: the strong bonding forces within a molecule. i.e. the covalent bonds holding the molecule together.

Inter-molecular Forces: the weak bonding forces between molecules due to the attractions between partial charges.

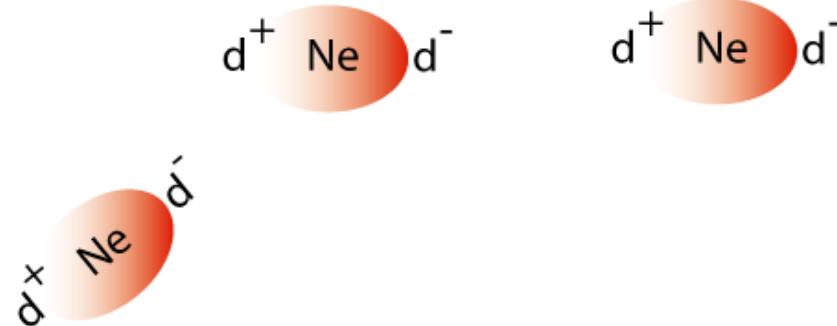


Instantaneous/temporary Dipole

In any monatomic element or molecule, the electrons are moving rapidly. At any one instant, the arrangement of electrons about the nucleus will not be symmetric. This creates an instantaneous dipole (ID).



An atom with an ID will attract electrons in a neighbouring atom. This causes an induced dipole in this atom. The instantaneous dipole atom then attracts the induced dipole atom.



Instantaneous dipole (ID – ID) Attractions

The inert gases (group 18) are monatomic, and must be non-polar, yet the atoms attract together to form liquids and freeze to form solids. Likewise, non-polar molecules like cyclohexane condense and freeze. This suggests that some kind of bonding force operates between **non-polar** monatomic elements or **non-polar** molecules.

Gp 18	M.P. /°C	Gp 17	M.P. /°C	Misc.	M.P. /°C
He	-272	F ₂	-220	O ₂	-219
Ne	-249	Cl ₂	-101	N ₂	-210
Ar	-189	Br ₂	-7	S ₈	113
Kr	-157	I ₂	114	C ₆ H ₁₂	6.6
Xe	-108			polythene	85 - 110

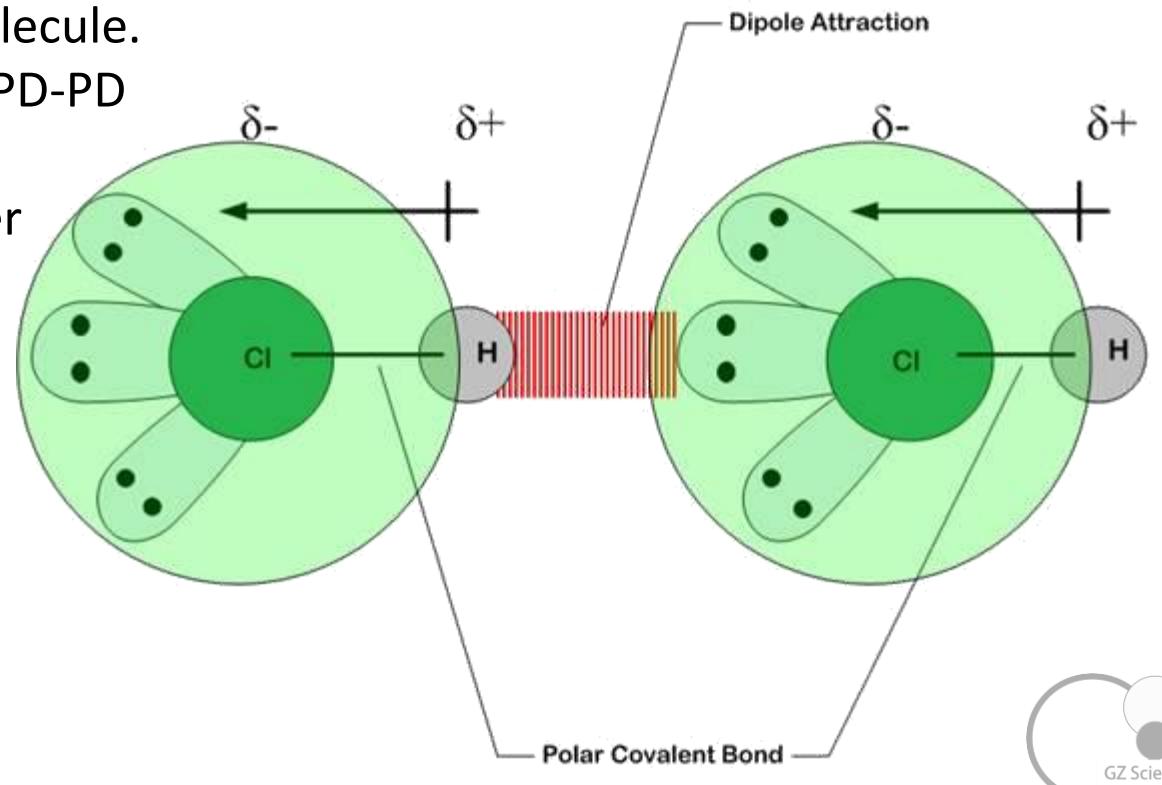
Permanent Dipole

Permanent dipole (PD – PD) Attractions

Polar molecules have an imbalance of charge caused by an electronegativity difference between its constituent atoms. The weak molecular force always involves instantaneous dipole but in small molecules permanent dipole will play a larger part in the bonding.

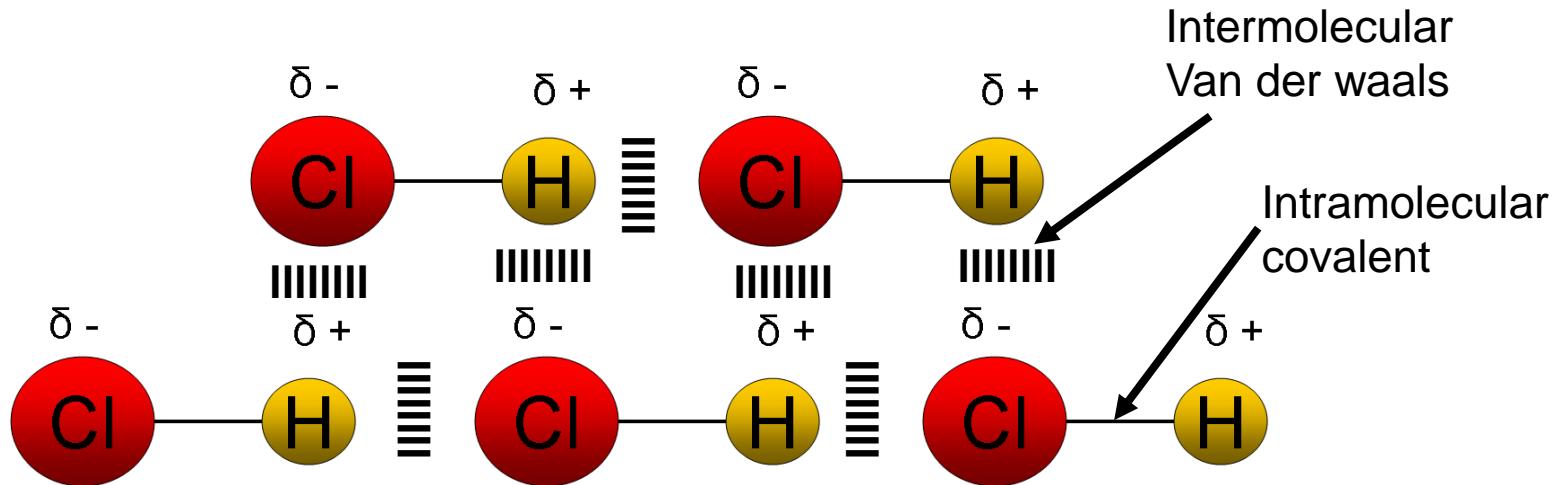
The slightly negative end of one molecule will be attracted to the slightly positive end of another molecule.

The higher strength of the PD-PD bonding means that polar molecules will have a higher boiling/melting point to non-polar molecules (with only ID-ID bonding) of similar molar mass.



Permanent Dipole (PD – PD) Attractions

e.g. Bonding in solid HCl



The weakness of PD – PD bonding is revealed by the low melting points of PD molecular solids, by comparison with other types of solids.

e.g. hydrogen chloride (PD – PD)
acetone (PD – PD)
NaCl (ionic)
copper (metallic)

-114 °C
-95 °C
801 °C
1085 °C

Molecules that have side chains do not “pack” together so well as single chain molecules so cannot get as close to other molecules – all things being equal **straight chained** versions of molecules tend to have **higher MP and BP**

Strength of ID-ID attractions compared with PD-PD

ID – ID attractions increase in strength as the number of electrons in the atom or molecule increase. See trend He – Xe. Increasing MPs show increasing force of intermolecular bonds.

Small molecules that have ‘ID-ID only’ have lower MPs than small molecules with both PD-PD and ID-ID, indicating that ‘ID-ID only’ is a weaker bond than ‘PD-PD + ID-ID’. e.g.

	Type	Num e-	MP (°C)
F_2	ID-ID	18	-220
HCl	ID-ID + PD-PD	18	-114

Strength of ID-ID attractions compared with PD-PD

When both ID-ID and PD-PD are present in a series of compounds, which has the greater influence on MP?

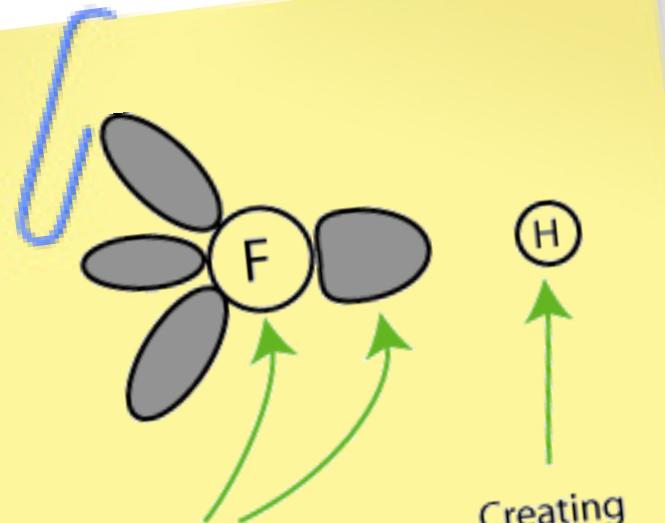
	Ne	MP (°C)
HCl	18	-114
HBr	36	-87
HI	54	-51

ID-ID increase down this series due to increasing number of e- per molecule. But PD-PD increase going up series due to increasing electronegativity difference between the atoms in the molecules.

As MPs increase going down the series it seems that increasing ID-ID is making the stronger contribution to inter-molecular forces. For polar molecules with higher numbers of electrons such as HI, ID-ID makes a stronger contribution to intermolecular forces than PD-PD.

Hydrogen Bonding

This is a special type of PD – PD bonding. It occurs when hydrogen is bonded to N, O or F. Since these are the three most electronegative elements and since they have very small atoms, (which concentrates their charge), they have a strong polarising effect on the covalent bond with hydrogen. Hydrogen, having no inner electron shells, is left as an exposed proton.



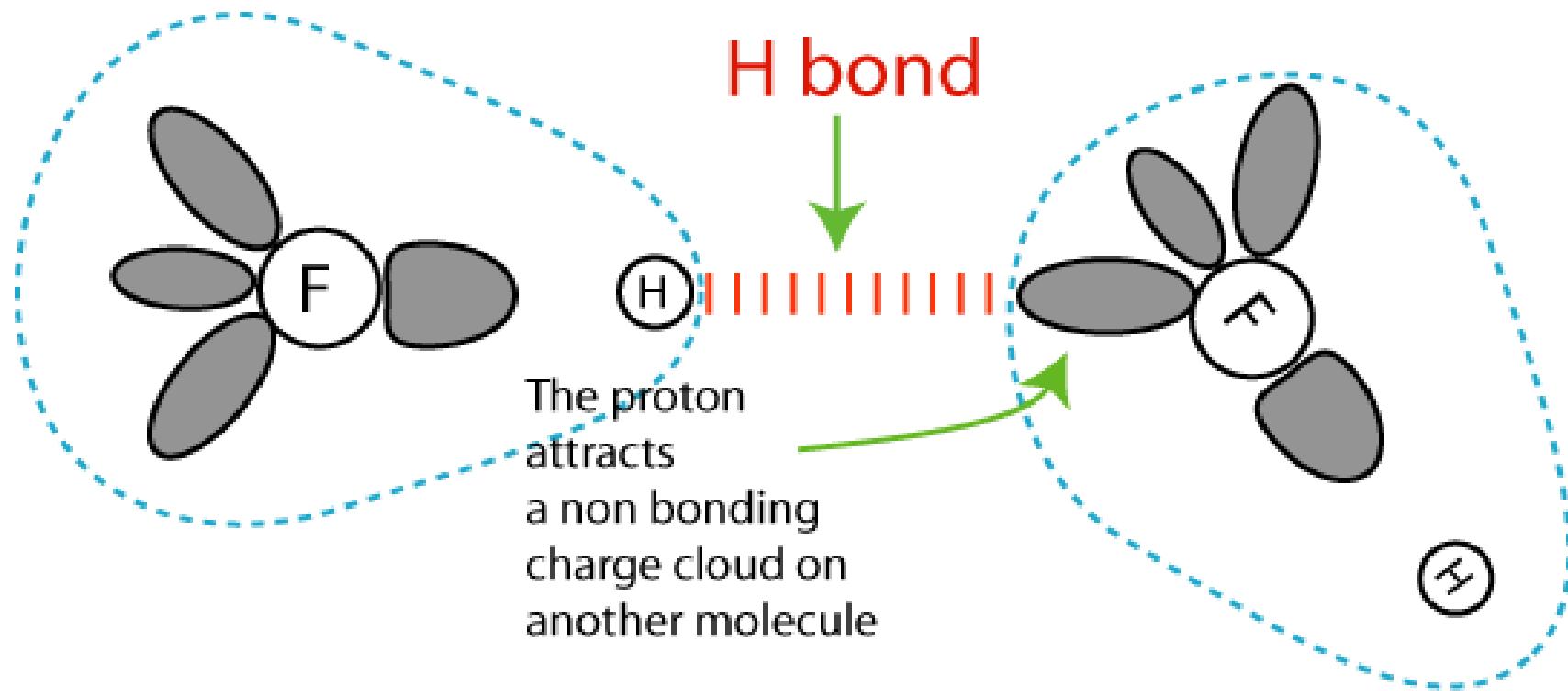
Creating exposed H nucleus (a proton)

F atom
strongly
attracts
bonding e-

This proton, being very small indeed, exerts a strong attraction to a non-bonding pair of e- on a neighbouring molecule.

Hydrogen Bonding

The hydrogen bond is around 10% of the strength of a covalent bond, and is the strongest of the three types of intermolecular attraction.



Hydrogen Bonding

Boiling points of ammonia, water and hydrogen fluoride.

On average:

Ammonia can form two H-bonds per molecule.

(1 for the three H and 1 for the non-bonding pair of e-)

Water can form four H-bonds per molecule.

(2 per H and 2 per non-bonding pair of e-).

Hydrogen fluoride can form two H-bonds per molecule.

(1 for the three non-bonding pair of e- and 1 for the H)

	Ne	MP (°C)			Ne	MP (°C)			Ne	MP (°C)
NH ₃	17	-33	H ₂ O	10	0		HF	10	-83	
			H ₂ S	18	-86		HCl	18	-114	
			H ₂ Se	36	-64		HBr	36	-87	
			H ₂ Te	54	-49		HI	54	-51	

This accounts for the anomalously high M.P.s for NH₃, H₂O and HF when considered alongside the other hydrogen compounds of their groups.

Hydrogen Bonding of Water

The high surface tension of water is explained by the presence of a hydrogen-bonded network of water molecules at the surface. This network is sufficiently strong to enable a needle to be floated on the surface of the water.

H bonding gives ice a network tetrahedral structure (like diamond). When ice melts, this partially collapses, and molecules move closer together so water is denser.

(density-water = 1.0 g cm^{-3} density-ice = 0.92 g cm^{-3})

In contrast most molecular solids expand on melting.



Answering Intermolecular Questions

Non-Polar Temporary (Instantaneous) dipole ID - ID	Polar Permanent dipole + Instantaneous dipole PD – PD + ID - ID	Polar (H-O, H-N, H-F) Hydrogen Bonding + Instantaneous dipole HB – HB + ID - ID
<p>The (.....) molecular solid is non-polar and so the only intermolecular forces would be due to temporary dipole interactions.</p> <p>This type of intermolecular bonding is the weakest of the three so these molecular solids will have the lowest boiling point.</p> <p>Generally as the molar mass increases there are more electrons and more instantaneous dipole-dipole interactions so all things being equal, the boiling points would increase.</p>	<p>The (....) molecular solid is polar and contains both Permanent dipole and instantaneous dipole interactions.</p> <p>The permanent dipole is generally the stronger force and will be the dominant force found in the molecular solid and therefore these substances tend to have a higher boiling point than the non-polar substances.</p> <p>The instantaneous dipole forces will become more significant if the molar mass of the molecule becomes greater.</p>	<p>The (.....) molecular solid has the highest boiling point of the three. This is because it has hydrogen bonds which are very strong intermolecular forces.</p> <p>The electronegativity difference between the H-.... Bond creates a very polar molecule which takes a lot of energy to break the intermolecular bond between molecules hence a high boiling point.</p> <p>These molecular substances also contain instantaneous dipoles which only become significant when the molar mass is large.</p>

Question 3a: Use the information in the table above to compare and contrast the boiling points of hydrazine, fluoromethane, and decane in terms of the relative strengths of the attractive forces between the particles involved.

Molecule	Boiling point / °C
Hydrazine, N_2H_4	114
Fluoromethane, CH_3F	-78.4
Decane, $\text{C}_{10}\text{H}_{22}$	174

N_2H_4 is a polar molecule. (Due to the presence of the highly polar N-H bonds), there is hydrogen bonding between N_2H_4 molecules.

CH_3F is also a polar molecule. (Due to the presence of the C-F bond), there are permanent dipole attractions between the CH_3F molecules.

The attractive forces due to permanent dipoles in CH_3F must be weaker than the attractive forces due to hydrogen bonding in N_2H_4 , because CH_3F boils at a lower temperature and they are similar masses so temporary dipole attractions are similar.

$\text{C}_{10}\text{H}_{22}$ is a non-polar molecule. The only attractive forces between the $\text{C}_{10}\text{H}_{22}$ molecules are due to temporary dipoles. However, since $\text{C}_{10}\text{H}_{22}$ is a significantly larger molecule than N_2H_4 , and CH_3F , it is more polarisable / has more electrons / greater molar mass, so its temporary dipole attractions are even stronger than the hydrogen bonds in N_2H_4 . As a result, $\text{C}_{10}\text{H}_{22}$ requires the most heat energy to break its intermolecular forces and therefore has the highest boiling point.

NCEA 2014 Intermolecular Forces

Question 2a: The boiling points of ammonia, NH₃, fluorine, F₂, and hydrogen chloride, HCl, are given in the table below.

Complete the table to identify the attractive forces between the molecules in their liquid state.

Molecule	Boiling point/°C	Attractive forces
Ammonia, NH ₃	–33	Hydrogen bonds, instantaneous dipoles
Fluorine, F ₂	–188	Instantaneous dipoles
Hydrogen chloride, HCl	–85	Permanent dipoles, instantaneous dipoles

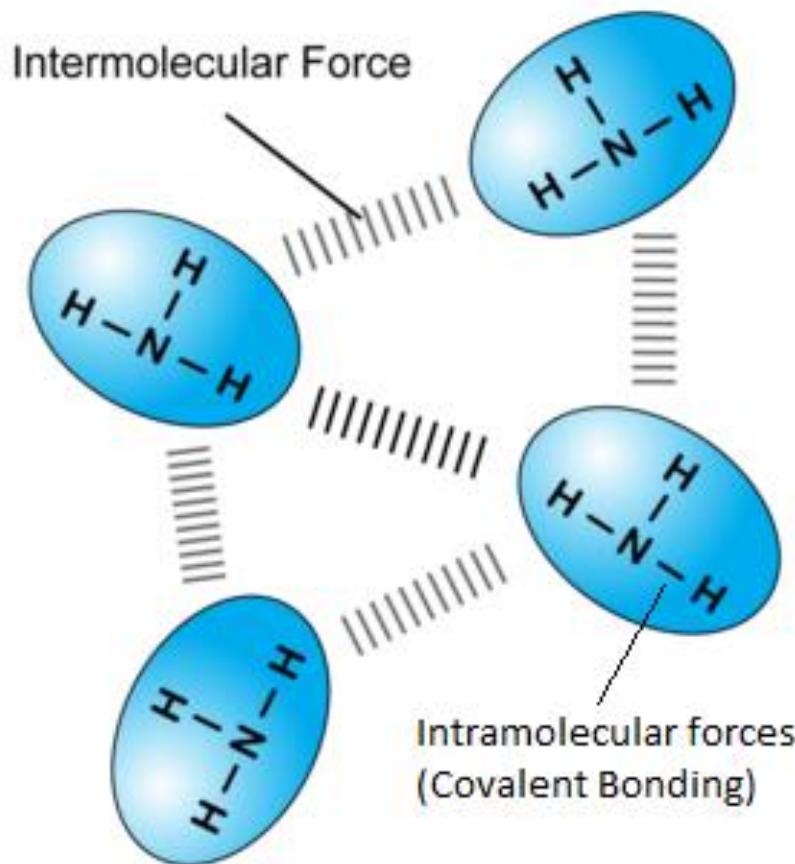
In answering the question don't forget that all molecules have instantaneous dipoles, plus PD if they are polar or HD if they have H-O, H-N, or H-F bonds

NCEA 2014 Intermolecular Forces

Question 2b: Discuss the differences between the boiling points of NH_3 and HCl , in terms of the strength of the attractive forces between the particles involved. Then describe why F_2 has the lowest boiling point.

Answer 2b: NH_3 and HCl both have temporary and permanent dipoles, as they are polar molecules. However, NH_3 has H-bonding, which means the boiling point is higher due to these stronger forces of attraction. HCl has a permanent dipole, but not H-bonding.

F_2 has the lowest boiling point, due to having only temporary dipoles. This type of intermolecular bonding is the weakest of the three so these molecular solids will have the lowest boiling point.



NCEA 2015 Intermolecular Forces

Question 3c: The two molecules below have the same molecular formula ($C_5H_{12}O$) but have different boiling points.

- List all the forces of attraction between these molecules in each of their liquid states.
- Use the information above to explain the difference in the boiling points of pentan-1-ol and dimethylpropan-1-ol by comparing and contrasting the relative strengths of the attractive forces between the molecules involved.

Name	Pentan-1-ol	Dimethylpropan-1-ol
Structure	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	$\begin{array}{c} CH_3 \\ \\ CH_3-C-CH_2-OH \\ \\ CH_3 \end{array}$
Boiling point	$138^\circ C$	$113^\circ C$

In answering the question cross off all of those factors that are the same (Molar mass, HB and PD bonding) and look for differences – side chains and no side chains – How does this effect bonding [the closer, the stronger the bond]

NCEA 2015 Intermolecular Forces

Name	Pentan-1-ol	Dimethylpropan-1-ol
Structure	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{OH} \\ \\ \text{CH}_3 \end{array}$
Boiling point	138°C	113°C

Answer 3c: (i) FORCES

- hydrogen bonding
- permanent dipoles
- instantaneous dipoles.

(ii) The attractive forces due to the **hydrogen bonding and permanent dipoles are similar** between the molecules in both liquids, as they both have one OH group, which causes the molecule to be polar and take part in hydrogen bonding.

The **two molecules have the same mass**, and so the same number of electrons involved in the weak instantaneous dipoles.

However, the **pentan-1-ol molecule has no side chains** and so the main chains can get closer to each other (less steric hindrance, greater surface area), thus the instantaneous dipoles are stronger / greater in pentan-1-ol, and therefore the boiling point is higher.

NCEA 2016 Intermolecular Forces

Question 2a: Identify all the attractive forces between particles of the following compounds in their liquid state.

Compound	$\Delta_{\text{vap}}H^\circ / \text{kJ mol}^{-1}$	Attractive forces
NaCl	194	NaCl: Ionic bonds.
HCl	16.0	HCl: Permanent dipole-dipole attractions, temporary dipole-dipole attractions.
CH ₃ Cl	22.0	CH ₃ Cl: Permanent dipole-dipole attractions, temporary dipole-dipole attractions.

This year they also included an example of a molecule with ionic bonds – **Watch for this**

NCEA 2016 Intermolecular Forces

Question 2b (i) : The standard enthalpy of vaporisation, $\Delta_{\text{vap}}H^\circ$, of sodium chloride, NaCl, hydrogen chloride, HCl, and chloromethane, CH_3Cl , are given in the table below. Explain why $\Delta_{\text{vap}}H^\circ(\text{NaCl})$ is significantly higher than both $\Delta_{\text{vap}}H^\circ(\text{HCl})$ and $\Delta_{\text{vap}}H^\circ(\text{CH}_3\text{Cl})$.

Compound	$\Delta_{\text{vap}}H^\circ / \text{kJ mol}^{-1}$
NaCl	194
HCl	16.0
CH_3Cl	22.0

Answer 2b: (i) Much more heat energy is required to overcome the attraction between its particles and convert NaCl from a liquid to a gas than HCl and CH_3Cl , because NaCl has strong ionic bonding between its ions compared to weak intermolecular bonding between the HCl and CH_3Cl molecules.

Question 2b:(ii) Explain why $\Delta_{\text{vap}}H^\circ(\text{CH}_3\text{Cl})$ is greater than $\Delta_{\text{vap}}H^\circ(\text{HCl})$.

Answer 2b: (ii) Both HCl and CH_3Cl are polar molecules and therefore have permanent dipole-dipole attractions and temporary dipole-dipole attractions between their molecules. However, CH_3Cl has a larger molar mass and therefore more electrons, so its temporary dipole-dipole attractions are stronger than between the HCl molecules. This means more heat energy is required to overcome the attractions between liquid CH_3Cl molecules, so it has a higher $\Delta_{\text{vap}}H^\circ$.

NCEA 2017 Intermolecular Forces

Molecule	Boiling Point / °C	M / g mol ⁻¹
Hydrazine, N ₂ H ₄	114	32
Iodomethane, CH ₃ I	42.4	142
Decane, C ₁₀ H ₂₂	174	142

Question 2a: Use the information in the table above to compare and contrast the boiling points of the substances below.

In your answers, you should:

- list the types of intermolecular forces present for each substance
- explain the relative strength between the particles involved.

(a) (i) Hydrazine and iodomethane.

Hydrazine (N₂H₄) hydrogen bonding, (permanent dipole attractions) temporary dipole attractions.

For **iodomethane (CH₃I)** permanent and temporary dipole attractions.

The hydrogen bonds between N₂H₄ molecules are stronger than the permanent dipole forces between CH₃I molecules therefore require more energy to break resulting in a higher boiling point.

The presence of hydrogen bonding outweighs the expected higher temporary dipole in CH₃I due to the greater molar mass.

NCEA 2017 Intermolecular Forces

Molecule	Boiling Point / °C	M / g mol ⁻¹
Hydrazine, N ₂ H ₄	114	32
Iodomethane, CH ₃ I	42.4	142
Decane, C ₁₀ H ₂₂	174	142

Question 2a: Use the information in the table above to compare and contrast the boiling points of the substances below.

(a)(ii) Iodomethane and decane.

Iodomethane (CH₃I) has permanent and temporary dipole attractions.

Decane (C₁₀H₂₂) has temporary dipole attractions.

Despite the molecules having the same molar mass, decane C₁₀H₂₂ has stronger intermolecular attractions. Decane is a longer molecule, when compared to the spherical shape of iodomethane CH₃I, so it has a greater surface area / electron cloud / number of electrons meaning stronger temporary dipole attractions.

Therefore, more energy is needed to break these attractions, resulting in a higher boiling point.

NCEA 2017 Intermolecular Forces

Molecule	Boiling Point / °C	M / g mol ⁻¹
Hydrazine, N ₂ H ₄	114	32
Iodomethane, CH ₃ I	42.4	142
Decane, C ₁₀ H ₂₂	174	142

Question 2b: Explain why the solubility of hydrazine in water is greater than that of decane in water.

Hydrazine is a polar molecule. Decane is non-polar. As water is a polar solvent, the hydrazine will be more soluble than the decane.

The attractive forces between the molecules of hydrazine are less than the attractive forces between the hydrazine and water molecules, and therefore it is more soluble than decane, where the attractive forces between the decane molecules are greater than the attractive forces between the decane and water molecules.

NCEA 2017 Intermolecular Forces

Question 3a: Chlorine, Cl_2 , bromine, Br_2 , and iodine, I_2 , are all halogens.

Bromine is a liquid at room temperature.

(i) In the box below, tick the type(s) of intermolecular attractions in liquid bromine.

Intermolecular attraction	Tick (✓)
Temporary dipole-dipole attractions	✓
Permanent dipole-dipole attractions	
Hydrogen bonding	

(ii) Explain why bromine is a liquid at room temperature, whereas chlorine is a gas.

Bromine is a larger molecule than chlorine so the temporary dipole intermolecular attractions are greater. Thus, more energy is required to separate the molecules and so Br_2 has a higher boiling point and is a liquid at room temperature



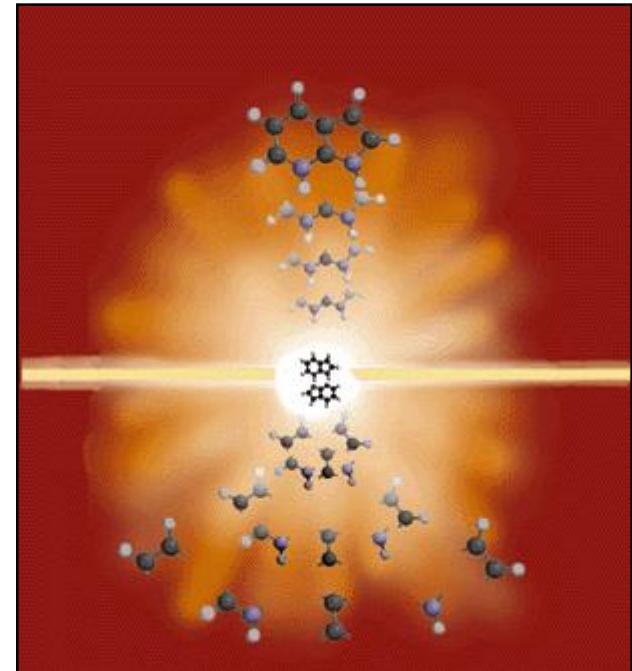
Enthalpy

Enthalpy and Enthalpy Change ΔH

Enthalpy (or Heat Content) is the energy in a substance due to kinetic energy of particles and potential energy in chemical bonds

Enthalpy change ΔH is the difference in enthalpy of products H_p and reactants H_R

$$\Delta H = H_p - H_R$$

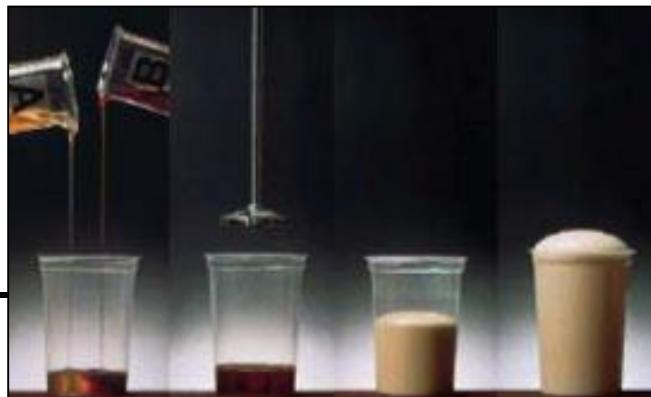


Enthalpy Changes

H_p (products) and H_r (reactants) cannot be measured.

We can measure Enthalpy change (ΔH) by measuring energy;

Released to surroundings
(Exothermic Reactions)



Absorbed from surroundings
(Endothermic Reactions)

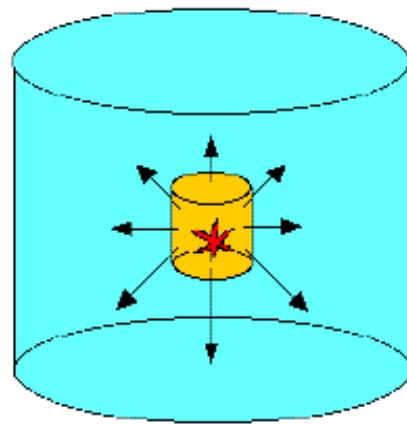


Endothermic and Exothermic

Exothermic Reactions

These are reactions where **heat energy** is **released** into the surroundings.

Surroundings gain heat energy. (increase in temperature)



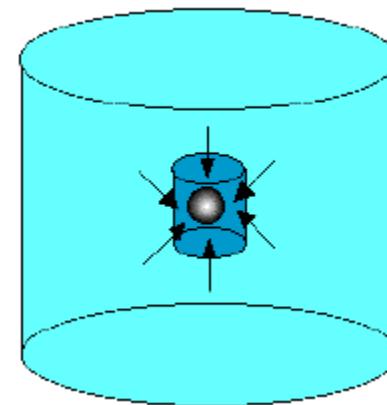
Products will have less energy than reactants.

△ H is NEGATIVE (-)

Endothermic Reactions

These are reactions where **heat energy** is **absorbed** from the surroundings.

Surroundings lose heat energy. (Decrease in temperature)



Products will have more energy than reactants.

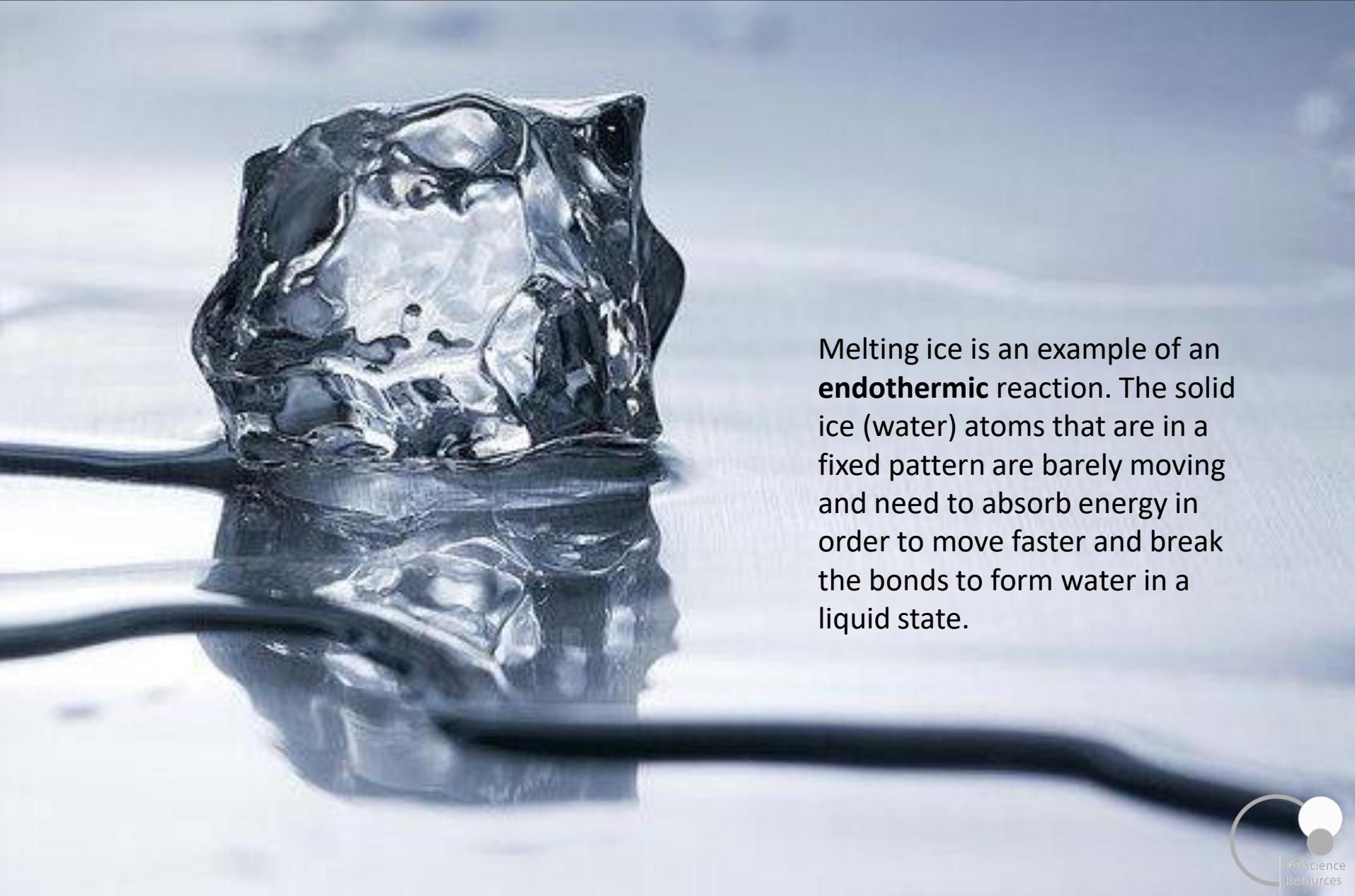
△ H is POSITIVE (+)

Exothermic reactions

Any combustion reaction is **exothermic**. The bonds holding the atoms of fuel molecules together (usually consisting of carbon and hydrogen atoms) release a lot of energy in the form of light and heat when they are broken. The total energy holding the bonds together in the products are less than the total energy in the reactants and the difference is released.



Endothermic reactions



Melting ice is an example of an **endothermic** reaction. The solid ice (water) atoms that are in a fixed pattern are barely moving and need to absorb energy in order to move faster and break the bonds to form water in a liquid state.

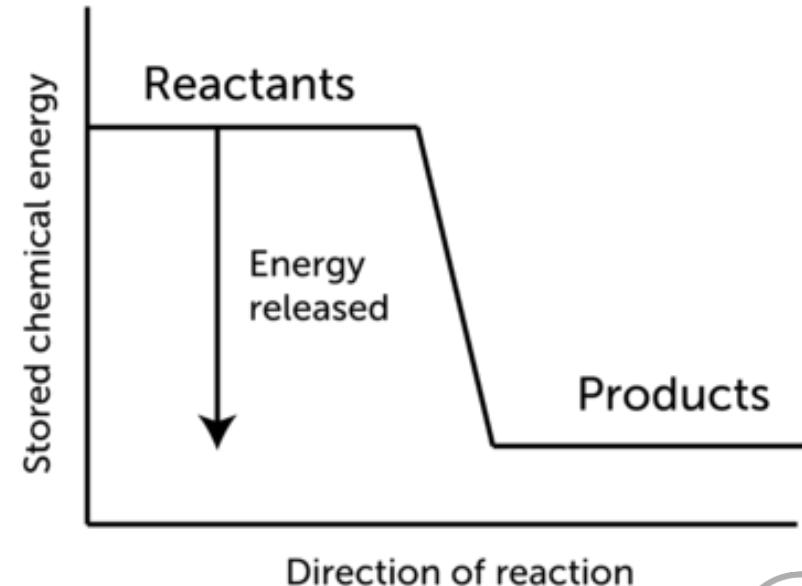
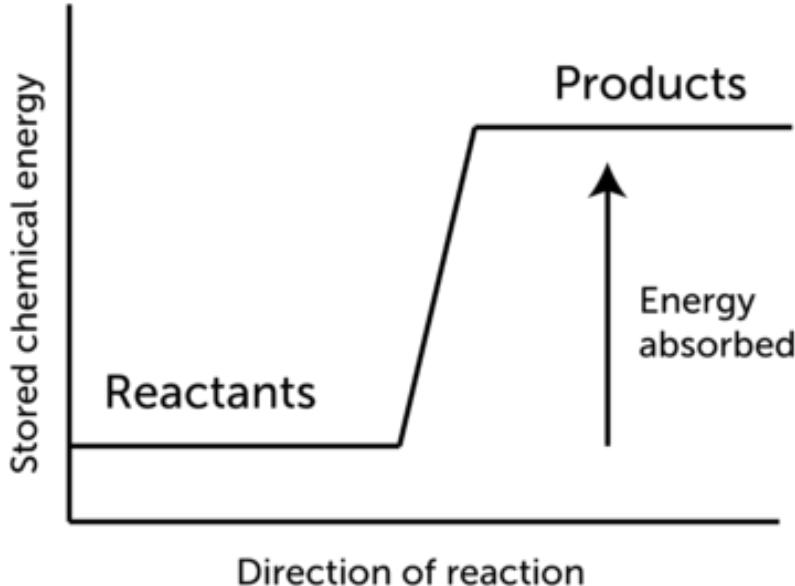
Enthalpy Diagrams

Endothermic Reactions

e.g. Reacting methane with steam at high pressure and temp. Energy is absorbed

Exothermic Reactions

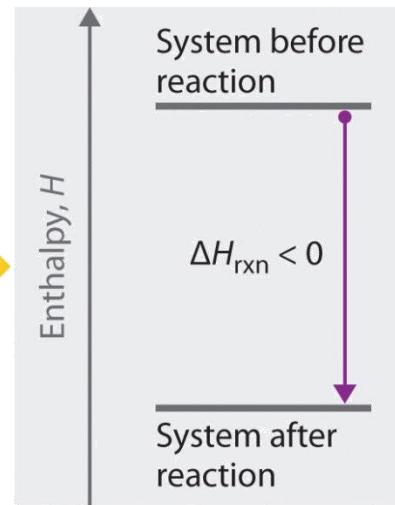
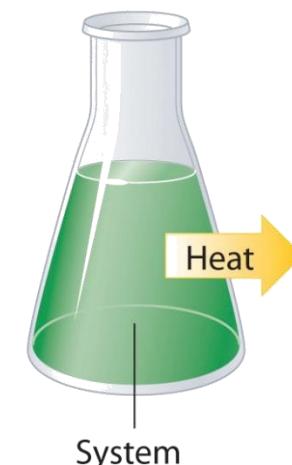
e.g. Burning of methane in air. Energy is released



Enthalpy Change

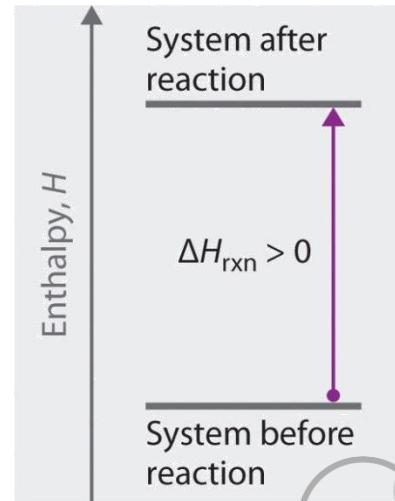
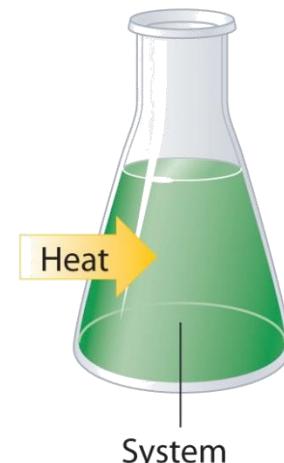
An exothermic reaction will release energy and the products will be at a lower enthalpy level than the reactants.

The reaction system will feel hot to the touch as the energy is released as heat energy.



(a) Exothermic reaction

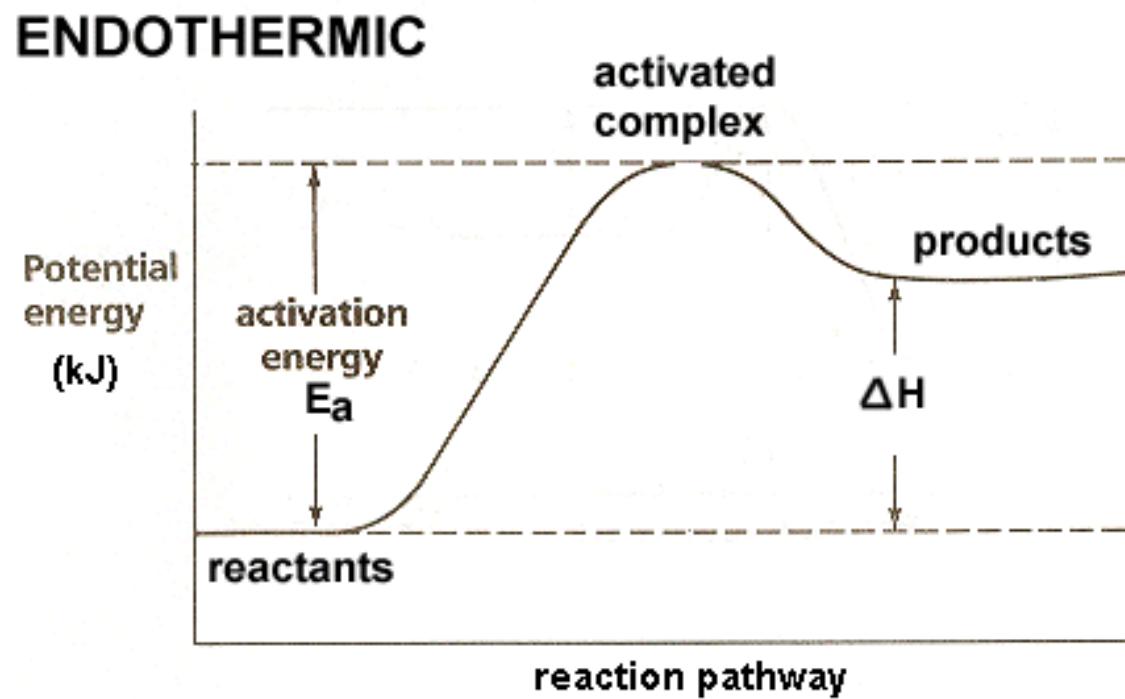
An endothermic reaction will absorb energy and the products will be at a higher enthalpy than the reactants. The reaction system will feel cool to the touch as heat energy is taken from the surroundings, including your skin, and used to break bonds in the molecules.



(b) Endothermic reaction

Energy Diagrams

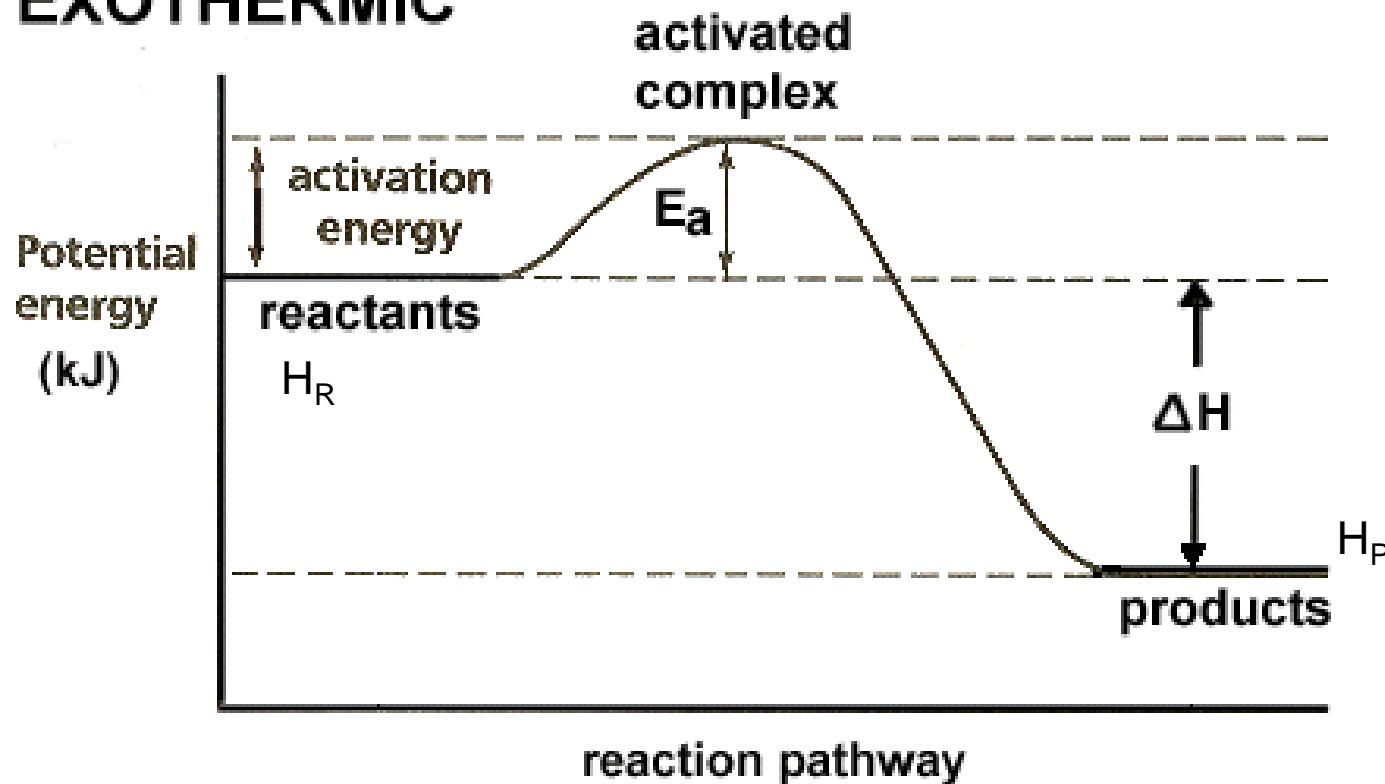
Endothermic Reaction e.g. Reacting methane with steam at high pressure and temp.
Energy is absorbed



Energy Diagrams

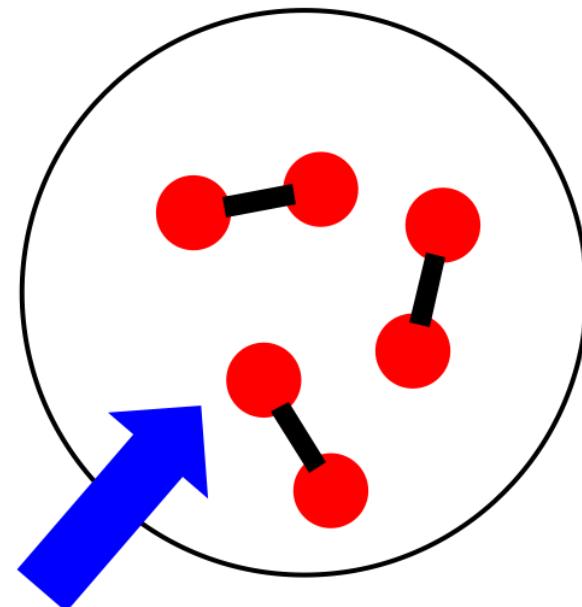
Exothermic Reaction e.g. concentrated Hydrochloric acid reacting with zinc metal

EXOTHERMIC

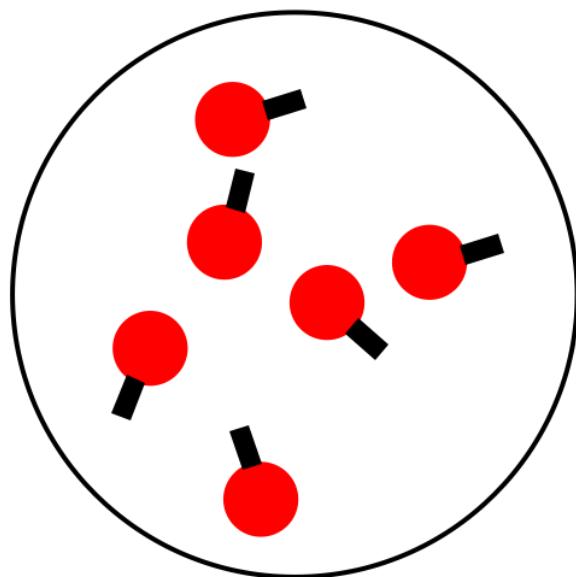


Breaking Bonds - endothermic

Bonds holding atoms and molecules together require the input of energy in order to break them apart therefore breaking of bonds is an endothermic reaction. The input of energy (usually light or heat energy) cause the atoms and molecules to move faster and 'pull away' from each other. Each type of bond has its own specific amount of energy, called bond energy measured in kJ, required to break its bond.



heat energy in



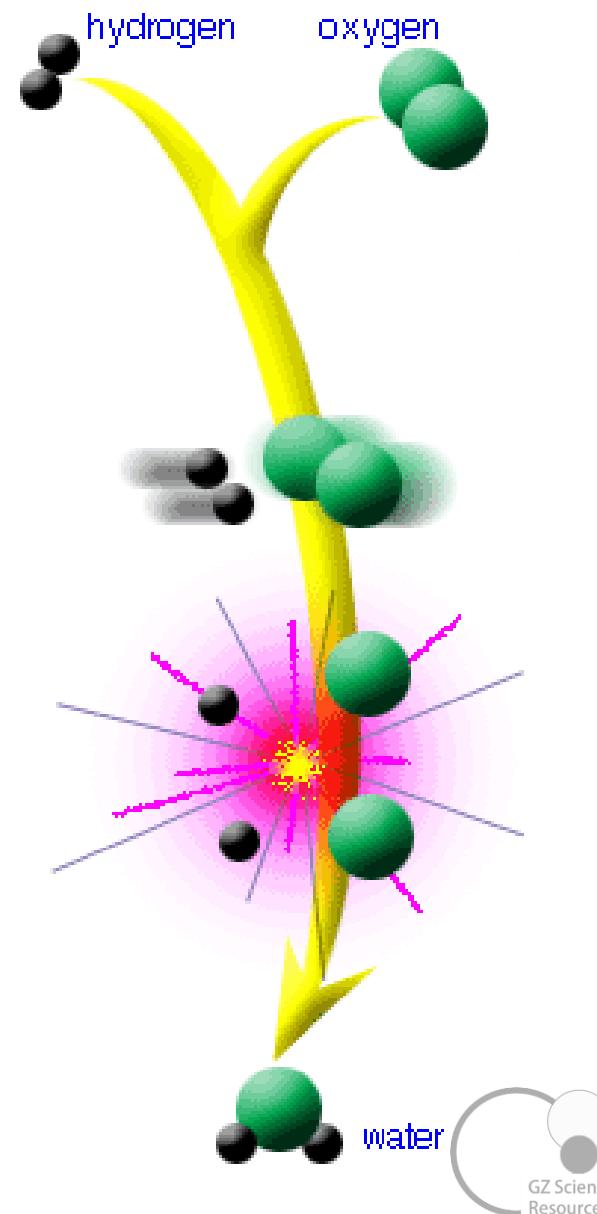
bond-breaking

Forming Bonds - exothermic

Bonds forming between atoms and molecules release energy therefore bond forming is an exothermic reaction. Bonds are formed to form a stable molecule.

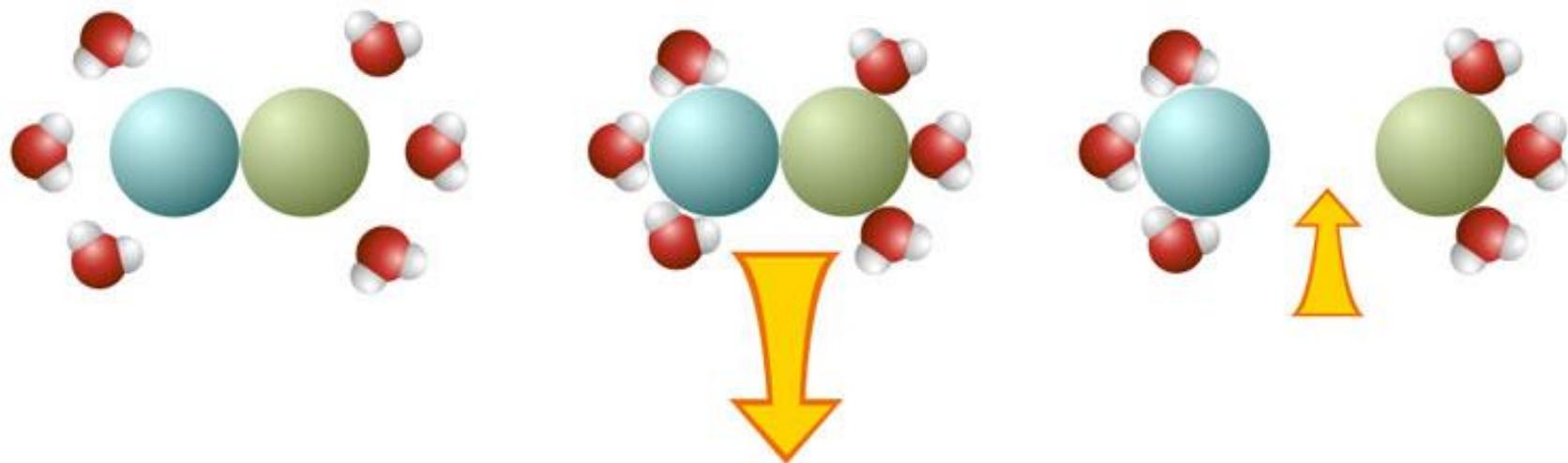
If more energy is required to break the bonds of the reactants than released when the bonds of the products are formed then the overall reaction is **endothermic**.

If less energy is required to break the bonds than is released when the bonds of the products are formed then the overall reaction is **exothermic**.

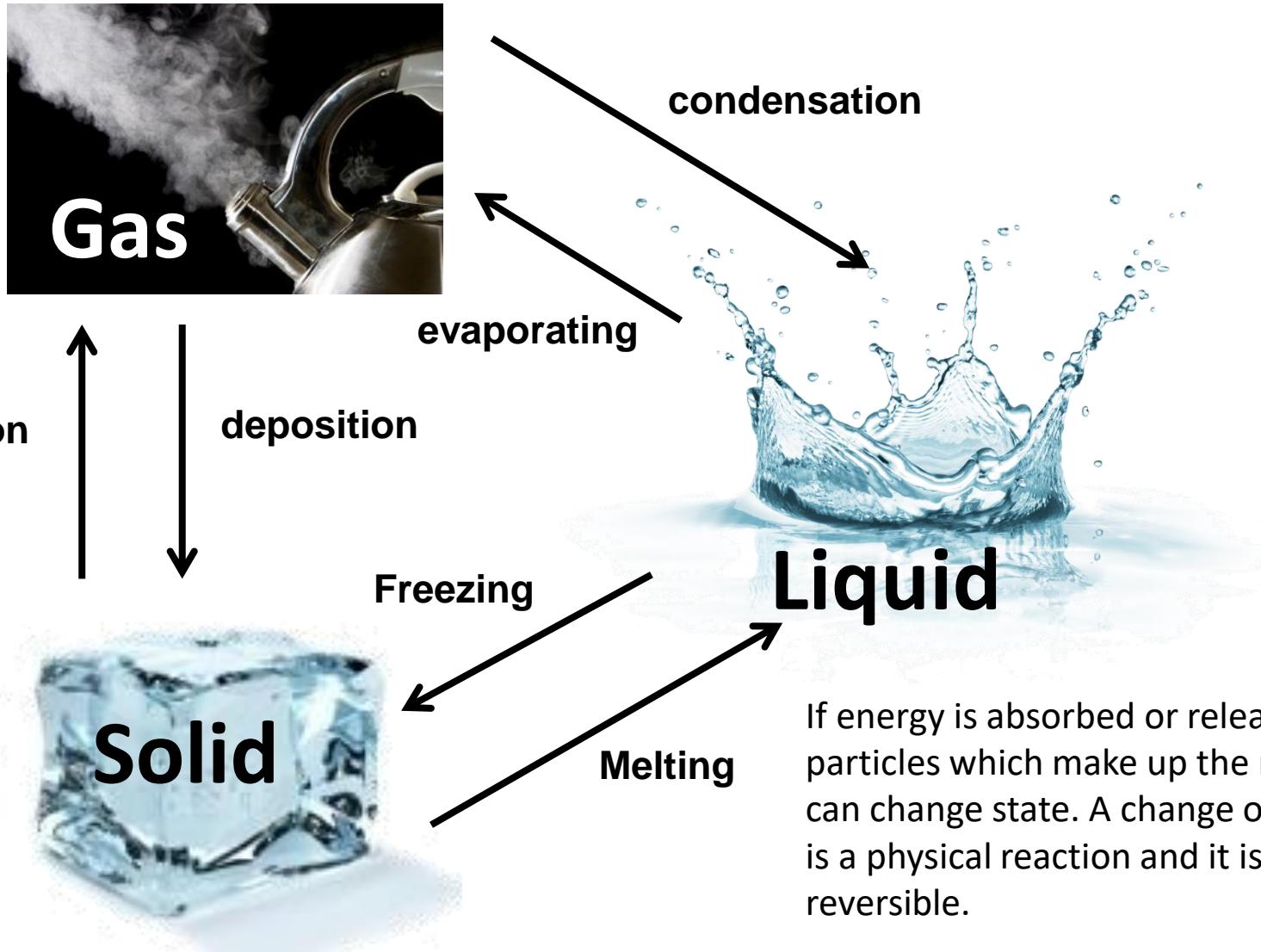


Enthalpy in Dissolving

If more energy is released when water bonds to the solute than it takes to separate the solute, the dissolving is exothermic and the temperature increases. An example is adding a strong acid (such as sulfuric acid) or base (such as sodium hydroxide)



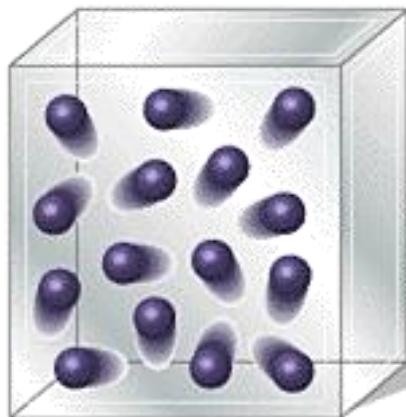
Enthalpy in Changes of State



Enthalpy in Changes of State

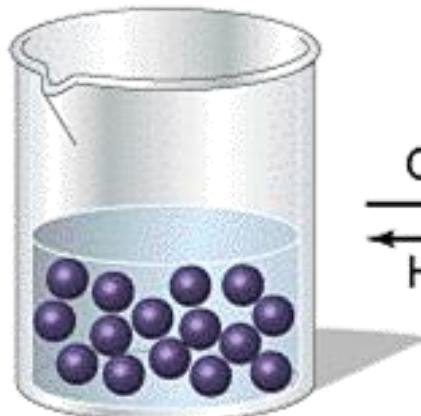
Solid particles are packed closely and only vibrate in a fixed position. **Liquid particles** are also packed closely but the particles move around more. **Gas particles** have a lot of space between them and move around quickly.

Gas



Cool or
compress
↔
Heat or
reduce
pressure

Liquid



Cool
↔
Heat

Solid



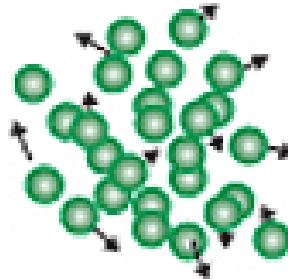
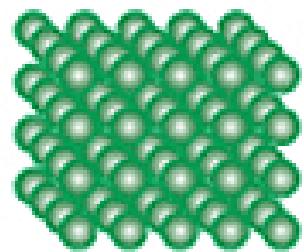
Total disorder; much empty space; particles have complete freedom of motion; particles far apart.

Disorder; particles or clusters of particles are free to move relative to each other; particles close together.

Ordered arrangement; particles are essentially in fixed positions; particles close together.

Particles of different states have different kinetic energy levels

Kinetic energy causes particles to move. The more kinetic energy a particle has the faster it moves. Kinetic energy can be added to a particle by adding heat energy (and heats up). The heat energy is then **transformed** into the kinetic energy. Kinetic energy can also be lost from a particle, which slows it down, when it changes back into heat energy and is lost (and cools).

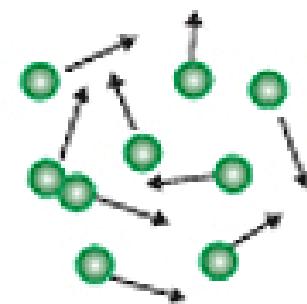


The first state: Solid
(i.e. Ice)

Maintains formation with
a little vibration only

The second state: Liquid
(i.e. water)

Movement of molecules or
atoms become free and
disorderly



The third state: Gas
(i.e. vapor)

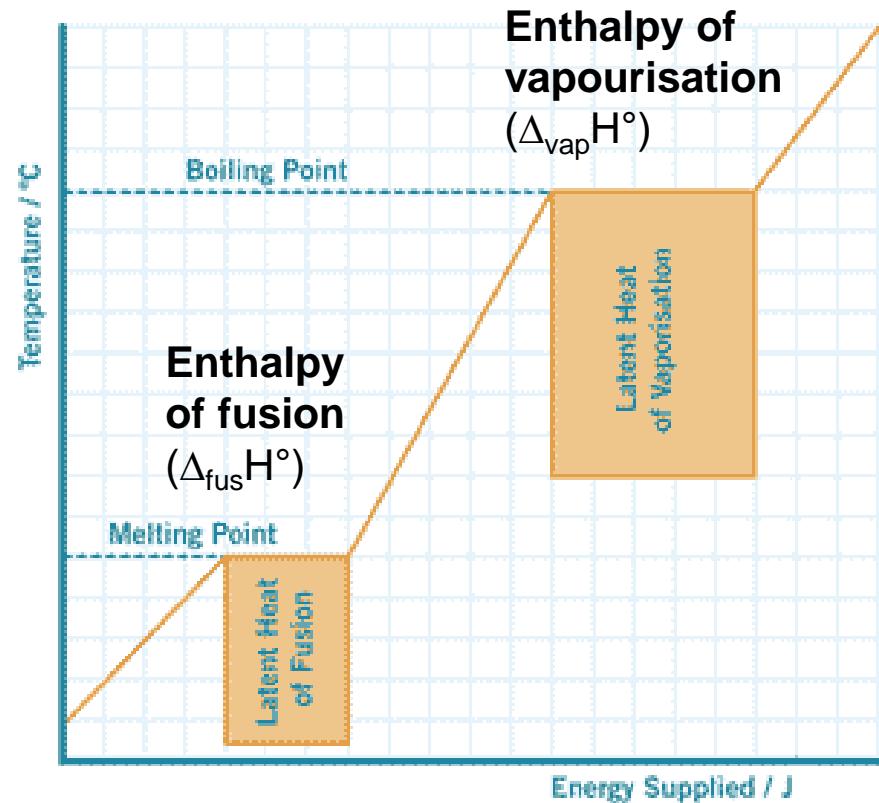
Movement of molecules
and electrons become
further freer

Enthalpy in State Change

When heat energy is added to a solid substance at a particular temperature called the melting point, it will change state into a liquid.

Prior to this point a rise in heat energy will also show a rise in temperature. At the melting point the heat energy will be used to break the bonds in a solid – an **endothermic** reaction called **latent heat of fusion** - rather than show a temperature increase.

The same occurs at the boiling point from a liquid to a gas – an endothermic reaction called **latent heat of vaporisation**.



Enthalpy Changes

Standard Enthalpy of combustion ($\Delta_c H^\circ$) 1 mol of substance combusted completely in oxygen

Standard Enthalpy of formation ($\Delta_f H^\circ$) 1 mol of substance formed from constituent elements

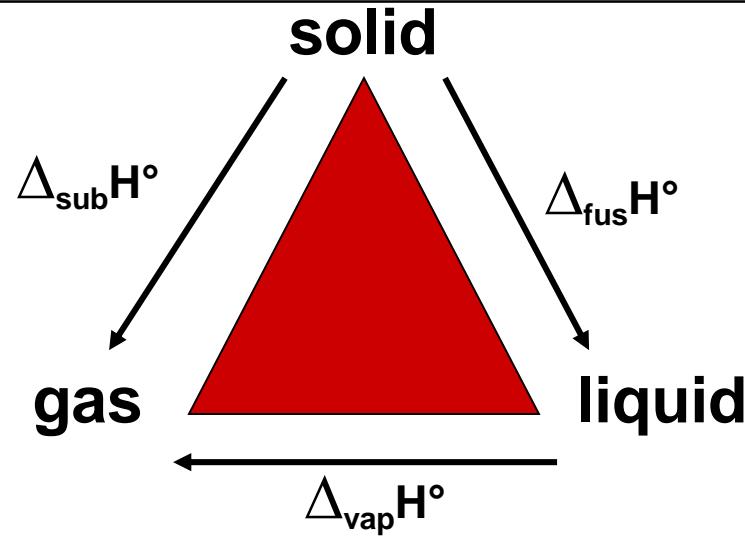
Enthalpy of reaction ($\Delta_r H$) for any given reaction

Standard conditions ($\Delta_r H^\circ$) 1 atmosphere of pressure, 25°C

Enthalpy of fusion ($\Delta_{fus} H^\circ$) 1 mol solid to liquid state

Enthalpy of vapourisation ($\Delta_{vap} H^\circ$) 1 mol liquid to gas state

Enthalpy of sublimination ($\Delta_{sub} H^\circ$) 1 mol solid to gas state



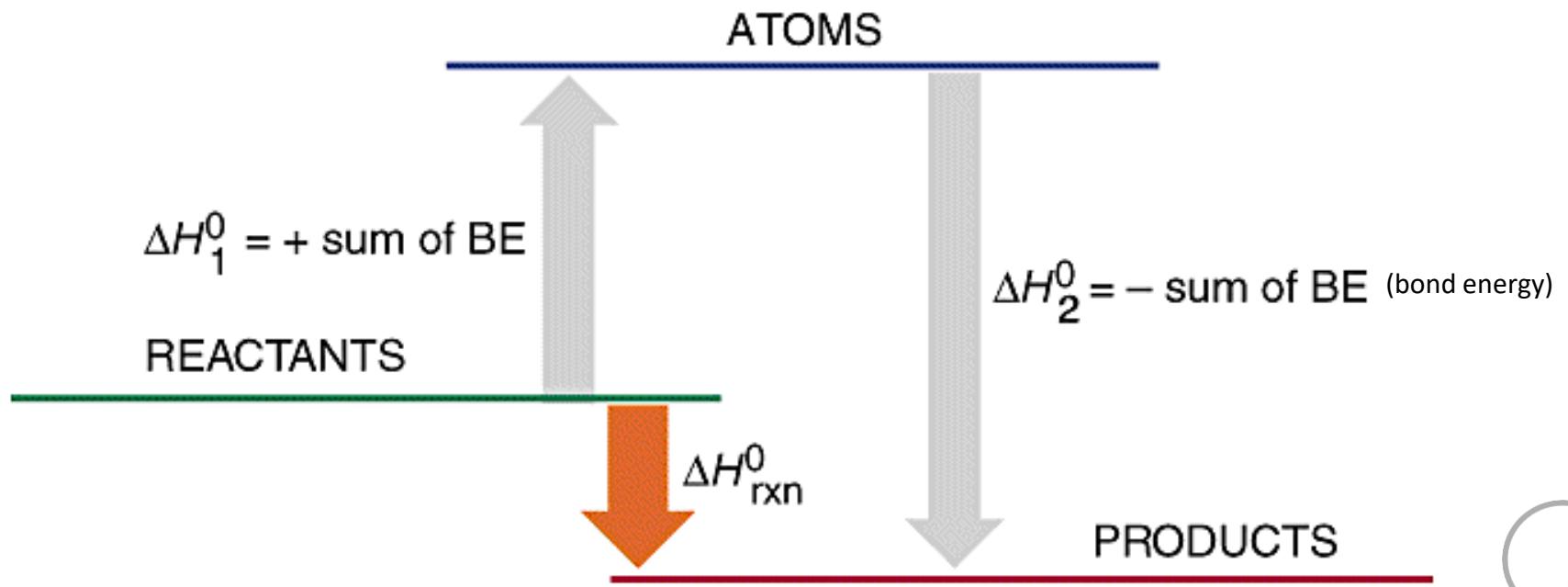
Enthalpy of Reaction

Exothermic - energy released ΔH negative

Endothermic - energy absorbed ΔH positive

Standard Enthalpy of Reaction $\Delta_r H^\ominus$

“The enthalpy change when products are formed from their constituent reactants under standard conditions.”



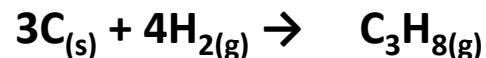
Enthalpy of Formation

Exothermic - energy released ΔH negative

Endothermic - energy absorbed ΔH positive

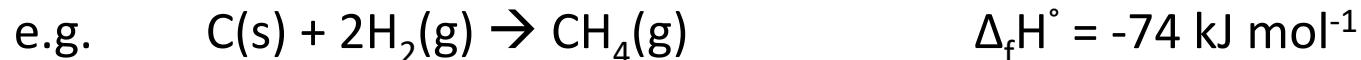
Standard Enthalpy of formation ($\Delta_f H^\circ$) - 1 mol of substance formed from constituent elements

Example: $C_3H_{8(g)}$ ($\Delta_f H^\circ$)



Standard Enthalpy of Formation $\Delta_f H^\ominus$

“The enthalpy change when one mole of a substance is formed from its constituent elements under standard conditions.”



Enthalpy of Combustion

Exothermic - energy released ΔH negative

Endothermic - energy absorbed ΔH positive

Standard Enthalpy of combustion ($\Delta_c H^\circ$) – 1 mol of substance combusted completely in oxygen

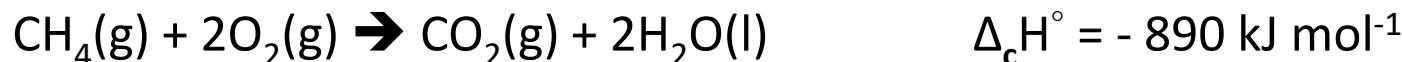
Example: $C_3H_{8(g)}$ ($\Delta_c H^\circ$)



Standard Enthalpy of Combustion $\Delta_c H^\ominus$

“The enthalpy change when one mole of an element or compound reacts completely with oxygen under standard conditions.”

e.g.



Standard conditions



Measurements depend on conditions

When measuring a enthalpy change you will get different values under different conditions. For example, the enthalpy change of a particular reaction will be different at different temperatures, different pressures or different concentrations of reactants. The values for enthalpy are given for standard conditions, indicated by the superscript θ

Standard conditions include:

Temperature of 25°C

Atmospheric pressure conditions of
1ATM

Concentration of 1mol per Litre

Question 2a: (i) Explain what is meant by the term $\Delta_{\text{vap}}H - (\text{H}_2\text{O}_{(\ell)})$.

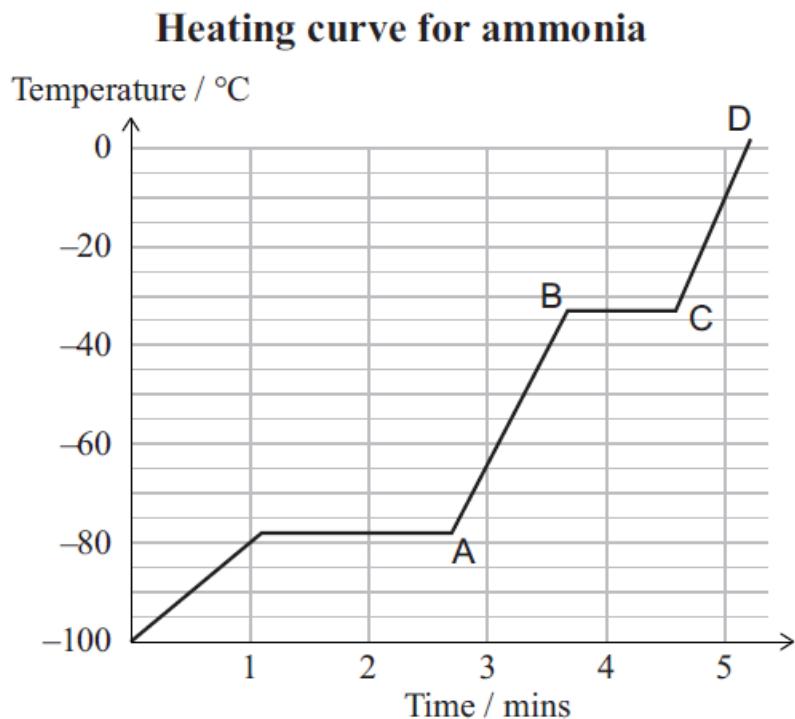
Answer 2a: (i) The enthalpy change when one mole of liquid water is converted to gaseous water under standard conditions. OR $\text{H}_2\text{O}_{(\ell)} \rightarrow \text{H}_2\text{O}_{(g)}$

Merit
Question

Question 2a:(iii) Explain why the temperature of liquid water does not change when it is heated at 100°C.

Answer 2a: (iii) At 100°C, energy is used to change liquid water to water vapour. At its boiling point, the heat energy is used to break the intermolecular forces /hydrogen bonds between the H_2O molecules

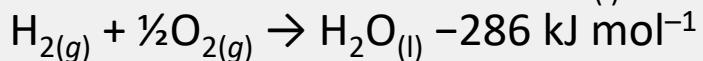
Question 2d: The following graph shows the change in temperature over a five-minute period for a sample of ammonia, where a constant amount of heat was applied per minute. Using the graph below, justify the physical changes occurring to ammonia between points A and D, in terms of the energy of the particles and the intermolecular forces of attraction.



Answer 2d: Between A and B, molecules of ammonia are gaining kinetic energy, and hence the temperature increases. Between B and C, molecules of ammonia change from liquid to gas. Energy supplied is used to overcome the intermolecular forces rather than increase the kinetic energy of the particles; thus the temperature does not increase until all the NH_3 is in the gas phase. Between C and D, the molecules of ammonia gas are again gaining kinetic energy, and so the temperature increases.

Question 2a (i):

The equation for $\Delta_f H^\circ$ of $H_2O_{(l)}$ is:



(a) (i) Write the equation for $\Delta_c H^\circ (H_{2(g)})$.

Answer 2a (i): $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$

Must have states to get correct

Question 2a(ii) : Using the equations above, explain why $\Delta_c H^\circ (H_2)$ and $\Delta_f H^\circ (H_2O)$ have the same value of -286 kJ mol^{-1} .

Achieved
Question

Answer 2a (ii): The equation for the combustion of hydrogen is the same as the equation for the heat of formation of water..

Standard Enthalpy of combustion ($\Delta_c H^\circ$) 1 mol of substance combusted completely in oxygen

Standard Enthalpy of formation ($\Delta_f H^\circ$) 1 mol of substance formed from constituent elements

Question 2b:

The enthalpy of formation would change if the water was formed as a gas rather than a liquid.

(i) Circle the correct phrase to complete the sentence below.

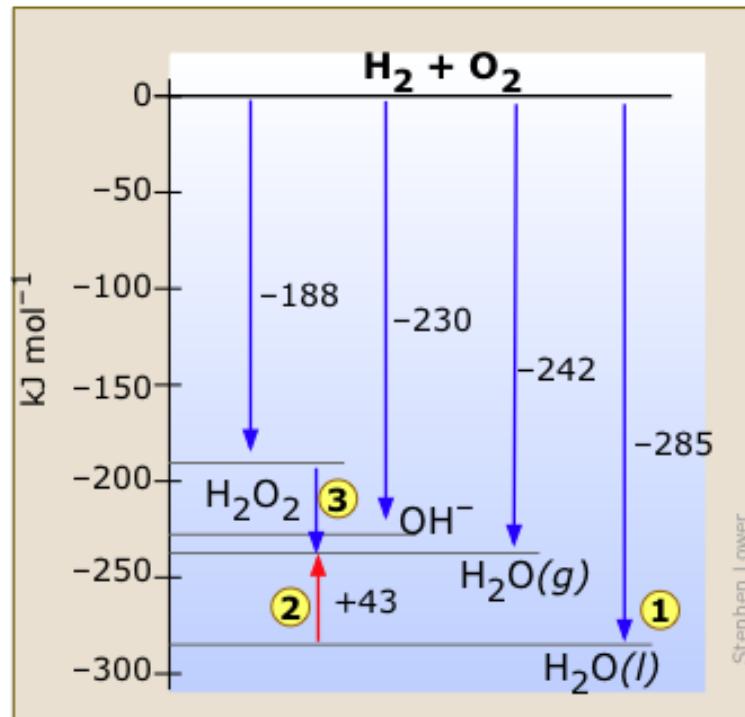
$\Delta_f H^\circ (H_2O_{(g)})$ is:

less negative than / the same as / more negative than $\Delta_f H^\circ (H_2O_{(l)})$.

(ii) Justify your choice.

Answer 2a (ii): The $\Delta_f H^\circ (H_2O_{(g)})$ will be **less negative** than $\Delta_f H^\circ (H_2O_{(l)})$.

Making bonds releases energy. As less bonding is present in water as a gas than a liquid then less energy will be released when gaseous water is formed thus the $\Delta_f H^\circ (H_2O_{(g)})$ will be less negative.



NCEA 2016 Enthalpy

Question 2c (i) : Define $\Delta_{\text{fus}}H^\circ(\text{NaCl})$.

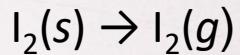
Enthalpy of fusion is the energy required to change 1 mol of a substance (NaCl) from a solid to a liquid.

Question 2c (ii) : Why is $\Delta_{\text{vap}}H^\circ(\text{NaCl})$ greater than $\Delta_{\text{fus}}H^\circ(\text{NaCl})$?

Fusion of NaCl only requires sufficient heat energy to break / overcome some of the ionic bonds, whereas vaporisation requires much more heat energy to overcome all the ionic bonds, therefore the $\Delta_{\text{vap}}H^\circ$ of NaCl is much greater than its $\Delta_{\text{fus}}H^\circ$.

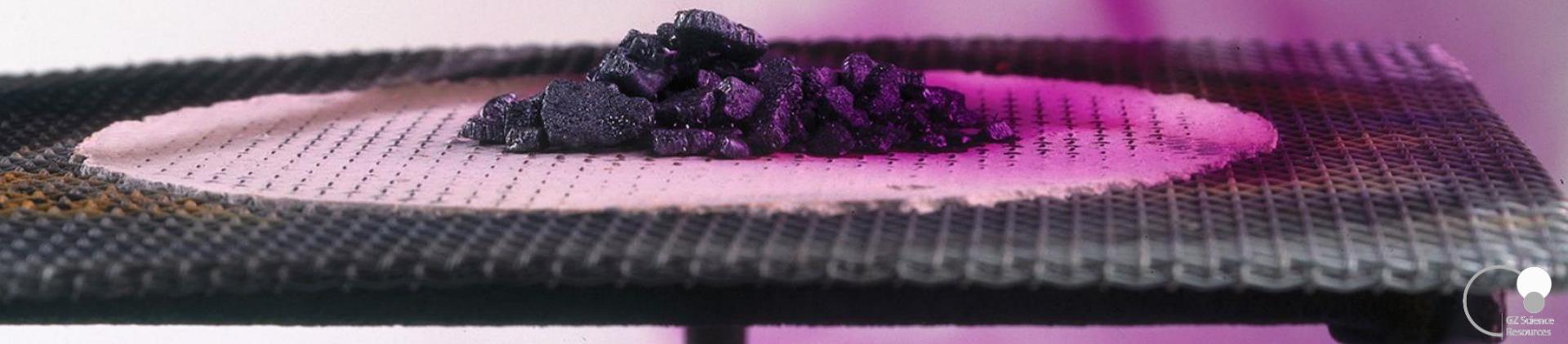


Question 3b (i): Write an equation for the sublimation of iodine below.



Question 3b (ii) : Define the enthalpy of sublimation for iodine.

This is the **heat energy** required to change one mole of a substance from solid state to gaseous state (at a given combination of temperature and pressure).



Entropy

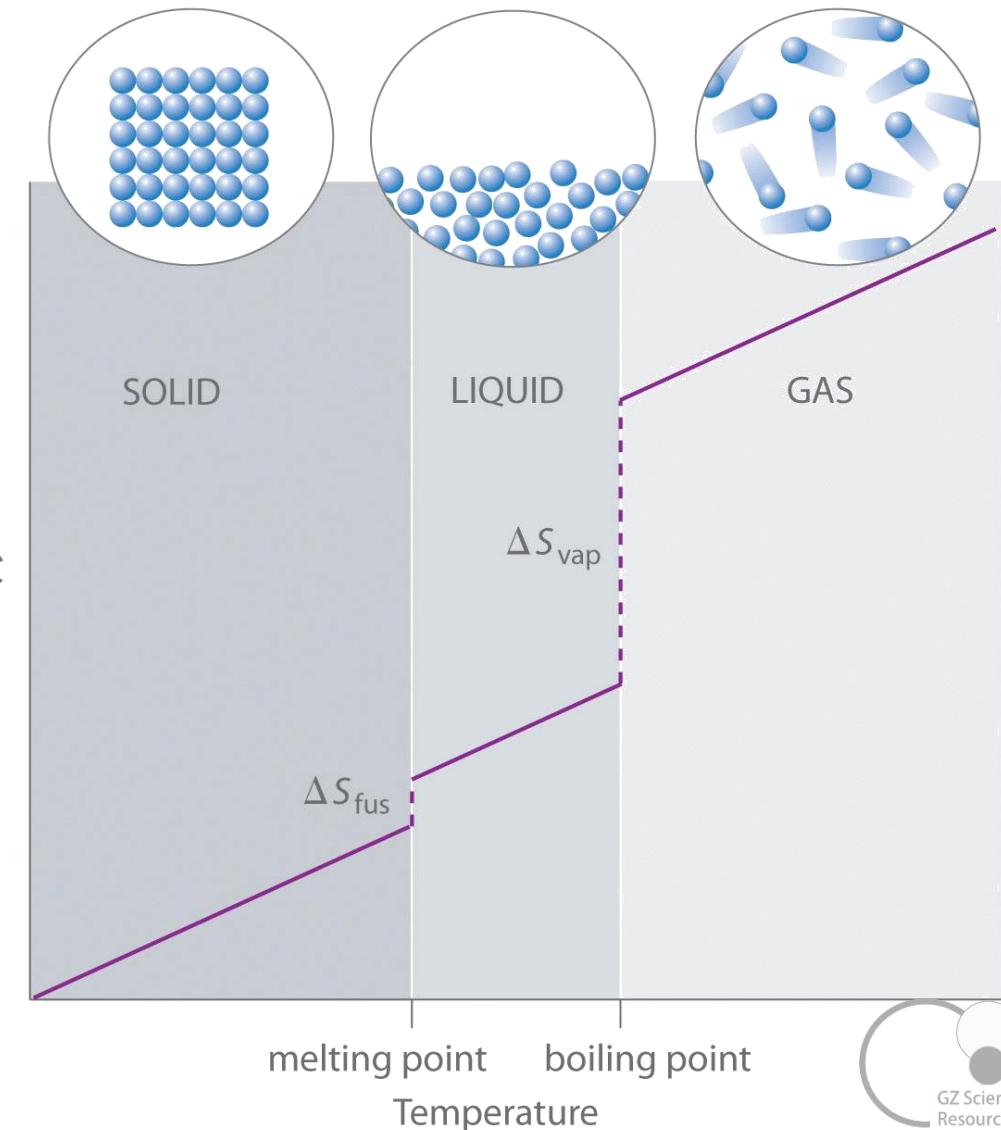
Entropy is the measure of the disorder of a system, usually denoted by the letter S. A highly ordered system has low entropy. Entropy is the measure of the disorder of a thermodynamic system. Disorder increases then as a result the entropy of a system increases.

Molecules in the gaseous state have greater entropy than liquid state because there is less "order" in gaseous molecules. Gas molecules move in random chaos without any restrictions. Therefore, going from liquid to gas you have increased the entropy of the system.

Molecules in the liquid state have a greater entropy than those in the solid state.

Molecules in the solid state are almost fixed in one spot. They are highly ordered and so liquid molecules have more disorder.

So melting increases entropy of a system.

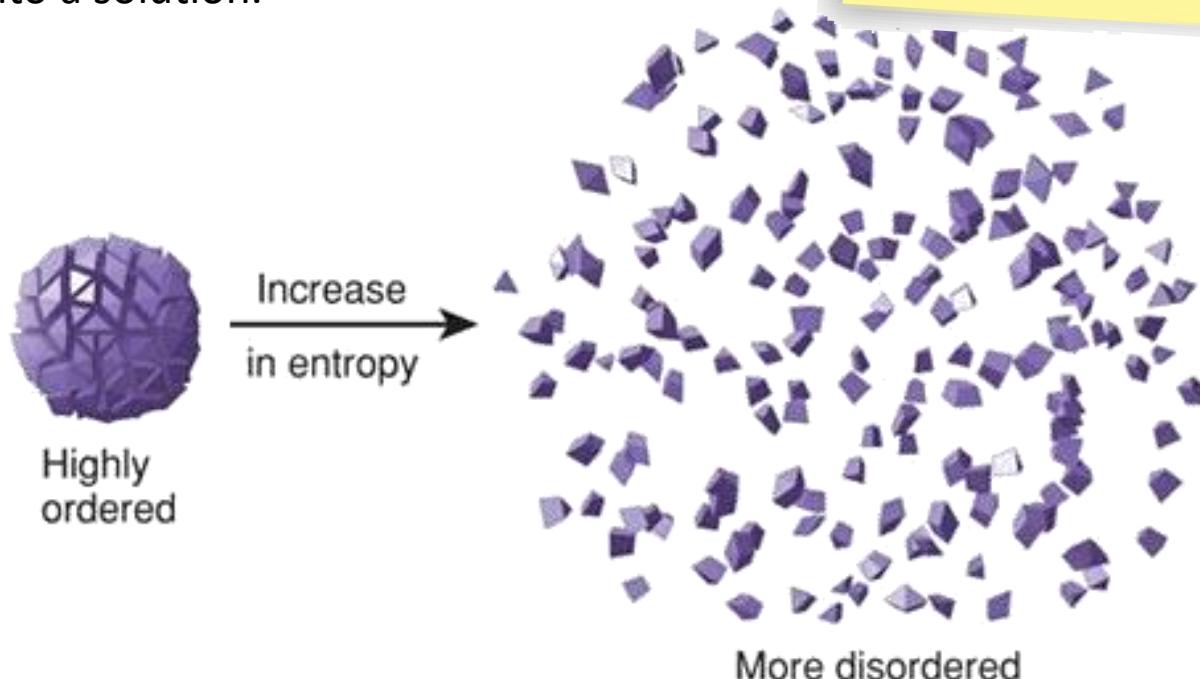


entropy - measure of disorder

The majority of spontaneous reactions are exothermic due to a natural tendency towards “minimum enthalpy”. Some endothermic reactions do occur spontaneously because of a different tendency towards “maximum entropy”. Entropy increases the “disorderliness” of a system. For example there is more “disorder” when a solid melts or a liquid boils or a solid dissolves into a solution.

$$\Delta S = S_{\text{final}} - S_{\text{initial}}$$

A positive $+\Delta S$ means Entropy has increased



Entropy

A reaction **will be spontaneous** if it results in the **enthalpy decreasing** and the **entropy increasing**. A reaction will not occur spontaneously if the enthalpy increases and the entropy decreases.

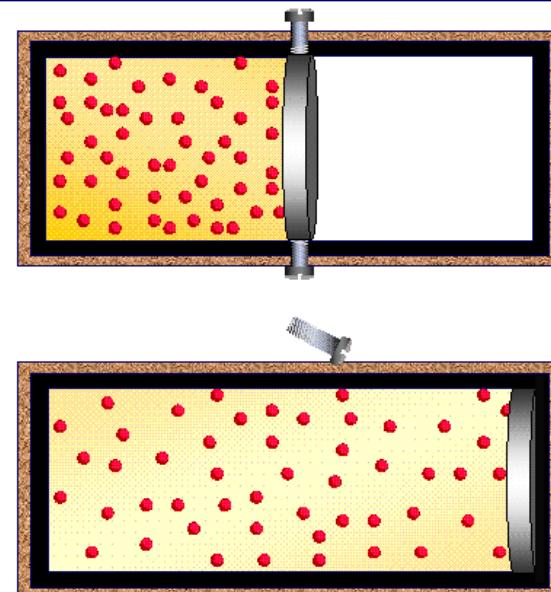
When the entropy and enthalpy oppose each other (they are both positive or both negative) then an equilibrium situation occurs. The overall result depends on the relative magnitude of the two tendencies.

Energy is constant, Entropy is maximized

Note: An adiabatic process is a process occurring without exchange of heat of a system with its environment

The gas occupies left volume,
right volume:
vacuum

Gas expands
adiabatically
and irreversibly



Entropy in solid, liquid and gas

Kinetic energy increases with increasing temperature so the **entropy factor becomes more important at higher temperatures**. This is why equilibrium constants, K_c , (which measure the equilibrium position), change with temperature.

For example in the case of melting ice, the tendency to minimum enthalpy favours the ice phase (less kinetic energy) whereas the tendency to maximum entropy favours the liquid phase (more randomness). Above the melting point of ice, the **entropy factor dominates** (as it increases with temperature) so spontaneous melting occurs. Below the melting point, the **enthalpy factor dominates** so spontaneous freezing occurs.



Entropy

Entropy increases as temperature increases because more kinetic energy means molecules are more disorderly.

Entropy increases in a reaction if the reaction produces more product molecules than it contains reactant molecules

Especially if you are going from a solid to a liquid or to a gas.

Entropy increases when solutions are formed from pure liquids or pure solids. Because there is greater disorder in aqueous solutions than liquids that are pure or solids that are pure.

The entropy of the universe which equals the entropy of system + entropy of surrounding

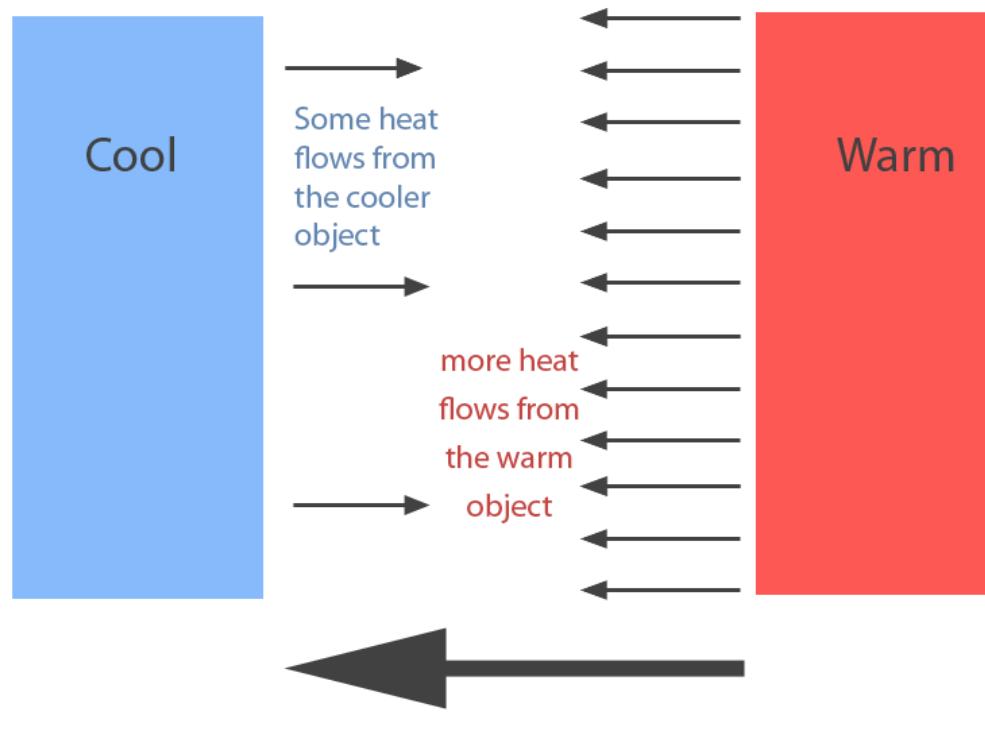
ΔS universe always increases.



Temperature effect can be explained by recognising that entropy increases with temperature and the system temperature changes significantly whereas the temperature of the “universe” is essentially invariant

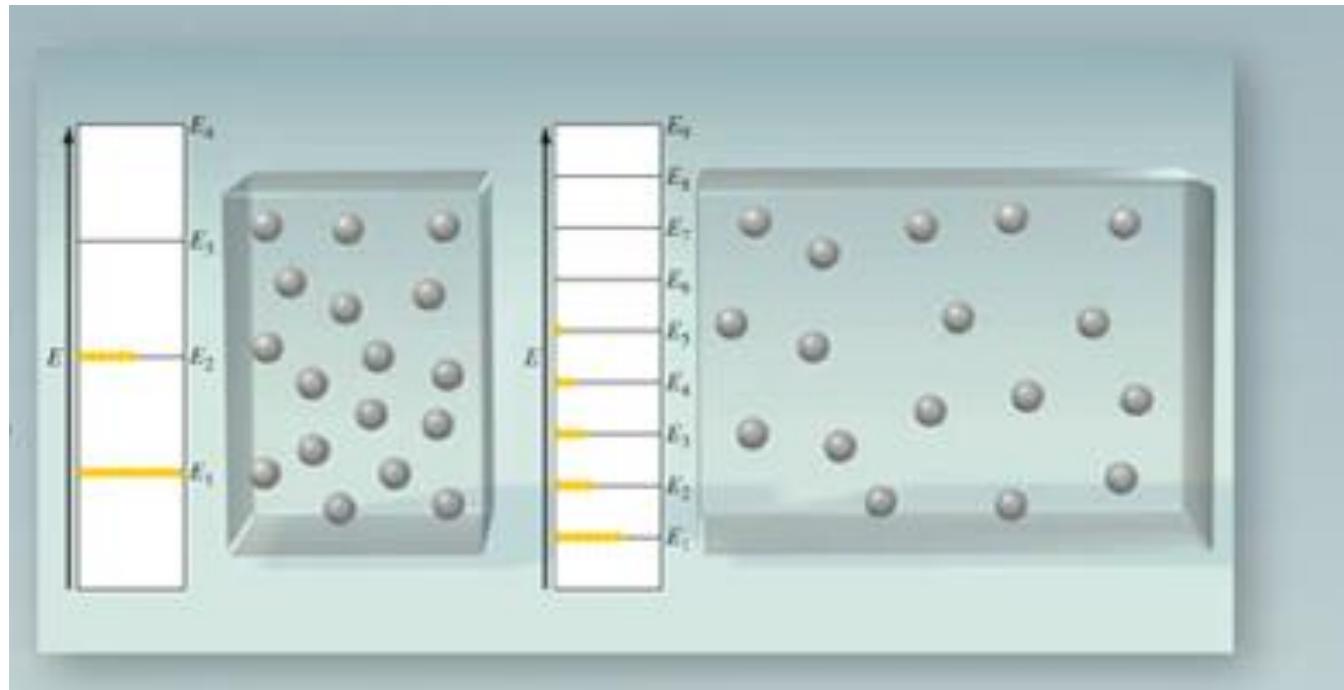
Entropy

The **second law of thermodynamics** states that in a reversible process, (such as change of state) the entropy of the universe is constant, whereas in an irreversible process, such as the transfer of heat from a hot object to a cold object, the entropy of the universe increases.



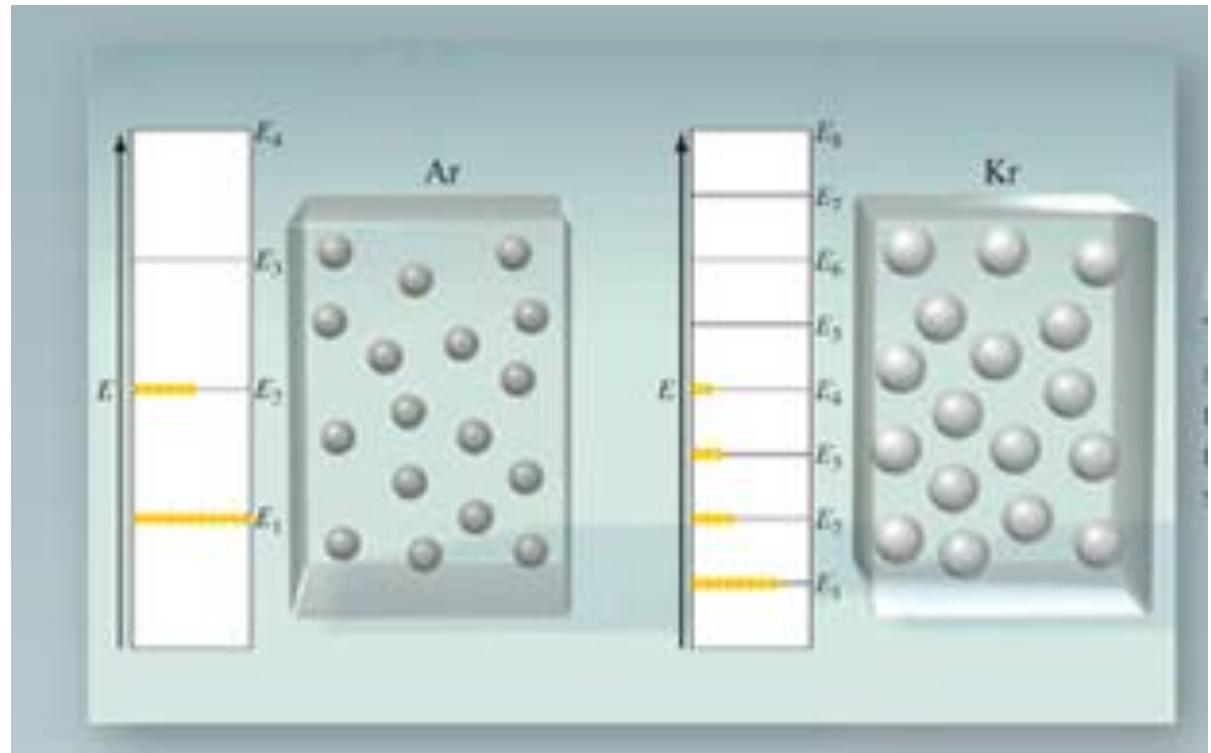
Factors that influence the Entropy of a system – Volume Change

Volume increase causes an increase in entropy. With an increase in volume there are more energy levels available therefore energy can be dispersed more.



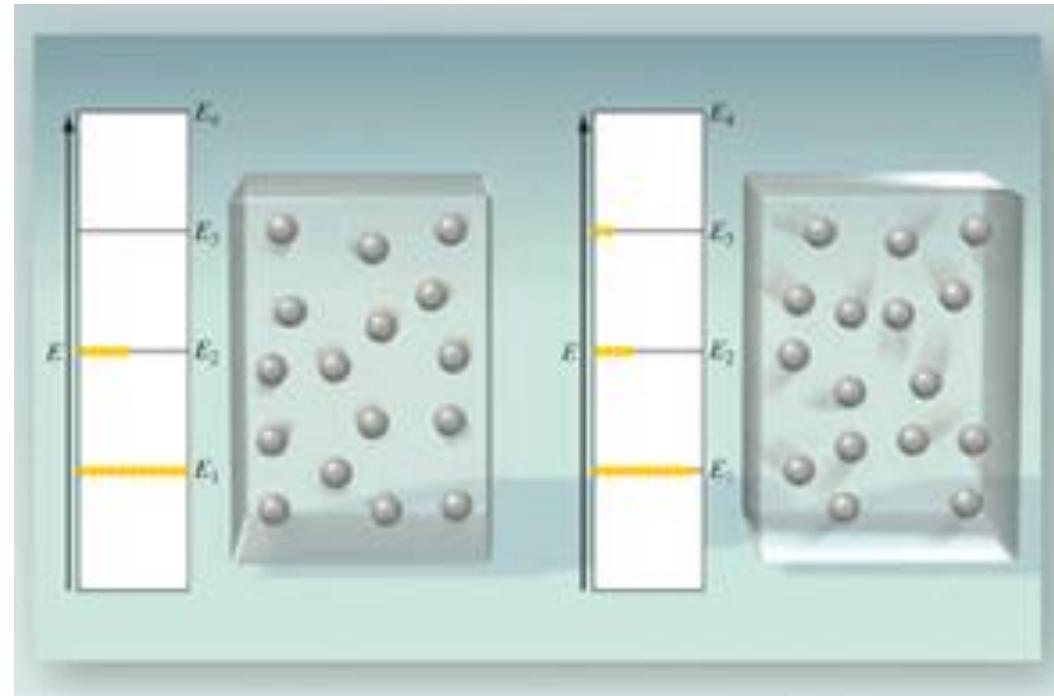
Factors that influence the Entropy of a system – Molar Mass

Molar Mass increase causes an increase in entropy. With an increase in mass there are more energy levels available therefore energy can be dispersed more.



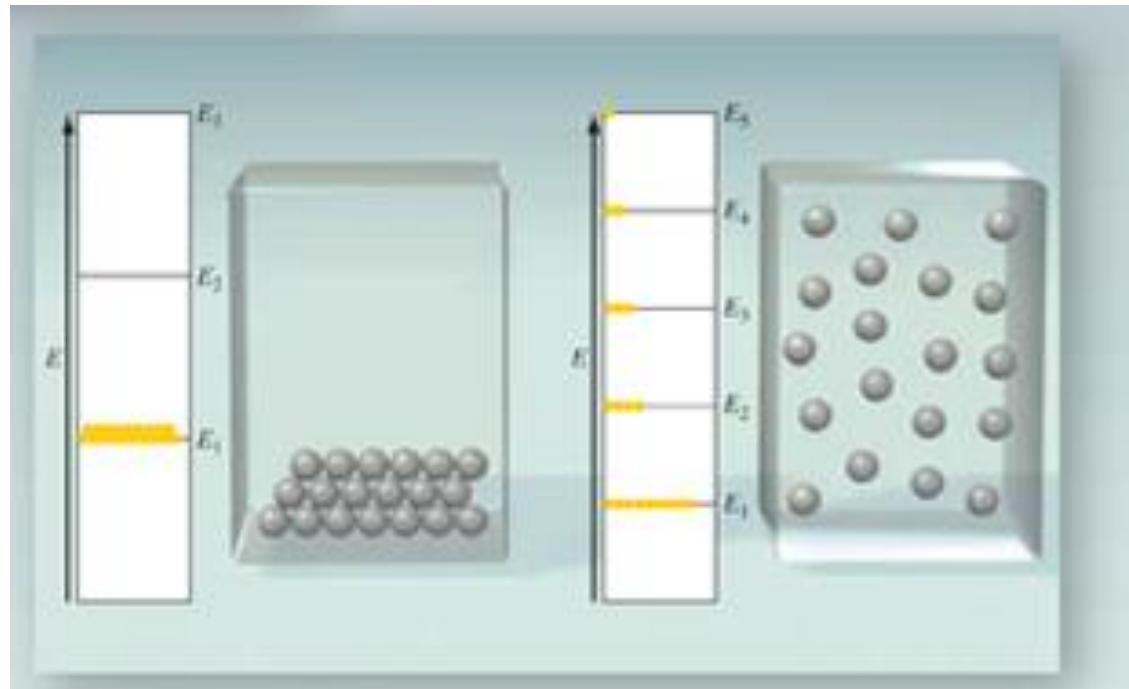
Factors that influence the Entropy of a system – Temperature Change

Temperature increase causes an increase in entropy. With an increase in temperature the molecules have greater kinetic energy making more energy levels available therefore energy can be dispersed more.



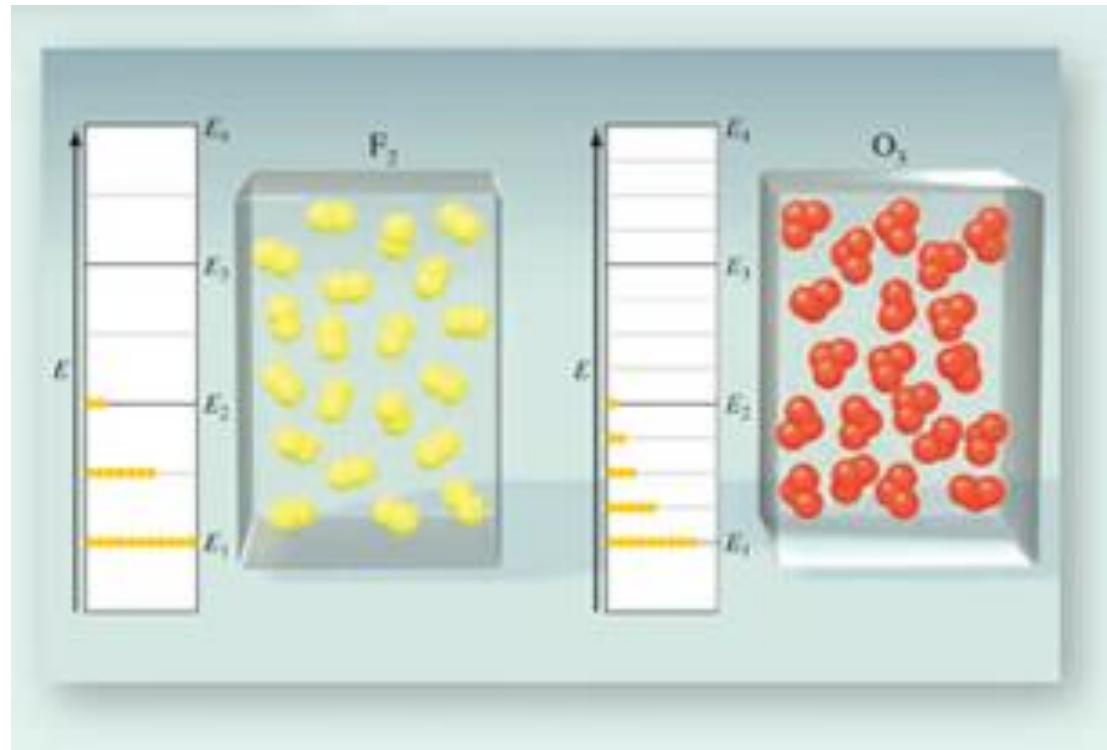
Factors that influence the Entropy of a system – Phase Change

Phase Change from solid to liquid to gas causes an increase in entropy. With an increase in mobility of particles from solid to liquid to gas there are many more possible arrangements of particles therefore increasing randomness.



Factors that influence the Entropy of a system – Molecular complexity

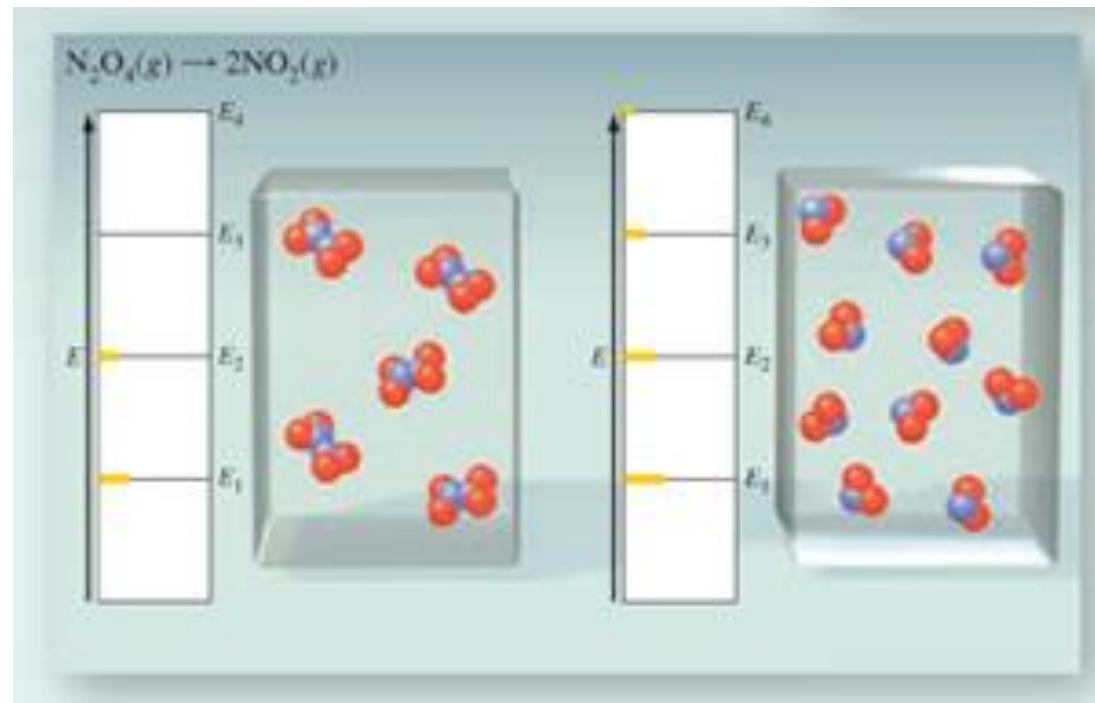
Greater complexity of molecules causes an increase in entropy.
With an increase in complexity of molecules there are an increased number of ways it can rotate and vibrate between each atom therefore increasing randomness.



Factors that influence the Entropy of a system – Number of Moles

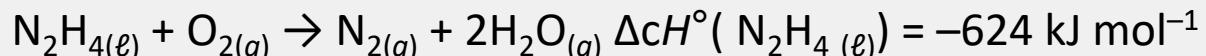
An increase in the number of mols in a reaction causes an increase in entropy.

With an increase in the number of mols in a chemical reaction the number of different arrangements of molecules increases therefore increasing randomness.



Question 3c:

Hydrazine is often used as a rocket fuel. When liquid hydrazine undergoes combustion, it forms nitrogen and water:



Explain why liquid hydrazine readily burns in oxygen.

Your answer should consider both enthalpy and entropy changes.



Answer 3c: Enthalpy change: The combustion of liquid hydrazine is an exothermic process since $\Delta_c H^\circ$ is negative. Exothermic reactions form products that have lower energy than the reactants / energy is released and this favours the spontaneous / forward reaction.

Entropy change: Exothermic reactions release heat to the surroundings, which makes the entropy change of the surroundings positive. As both the surroundings and the system gain entropy, this favours the spontaneous / forward reaction.

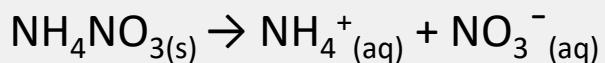
OR

The combustion reaction has more gas molecules in the products / goes from liquid to gas / increase in number of particles. Therefore the entropy of the system increases and this favours the spontaneous / forward reaction.

As both enthalpy and entropy are favoured, then hydrazine readily burns / the reaction is spontaneous.

Question 3b:

Ammonium nitrate is used in ‘cold packs’ to relieve symptoms of a sports injury. The dissolving of the solid crystals of ammonium nitrate (shown in the equation below) is spontaneous, despite being endothermic.



Explain why this is so, in terms of the entropy change for the reaction system.

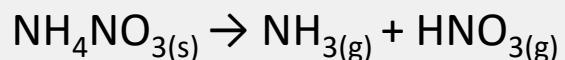
Answer 3b: Positive; or entropy increases. Ions in solution (generally) have higher entropy than solids as there is an increase in the dispersal of matter / degree of disorder..

Entropy Increases with...

- Melting (fusion) $S_{\text{liquid}} > S_{\text{solid}}$
- Vaporization $S_{\text{gas}} > S_{\text{liquid}}$
- Heating $S_{T_2} > S_{T_1}$ if $T_2 > T_1$
- Dissolving (usually) $S_{\text{solution}} > (S_{\text{solvent}} + S_{\text{solute}})$
- Molecular complexity entropy more bonds, more
- Atomic complexity neutrons more e^- , protons,

Question 3c:

Ammonium nitrate dissociates in an endothermic reaction, as shown in the equation below.



Below is a table outlining four statements about changes in entropy that may occur during any reaction.

Tick (✓) to the left of any statement that is correct for the above reaction.

Tick (✓)	Entropy statement
(✓)	The entropy of the system increases.
	The entropy of the surroundings increases.
	The entropy of the system decreases.
(✓)	The entropy of the surroundings decreases.

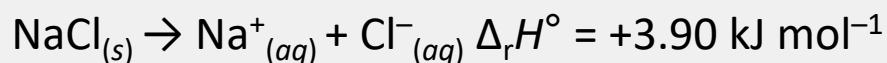
Answer 3c:

As a solid is converted into a gas, the **entropy of the system increases** due to the greater dispersal of matter, as the random motion of the gases is higher.

The **entropy of the surroundings decreases** because heat is transferred from the surroundings. This results in less random motion of the particles in the surroundings.

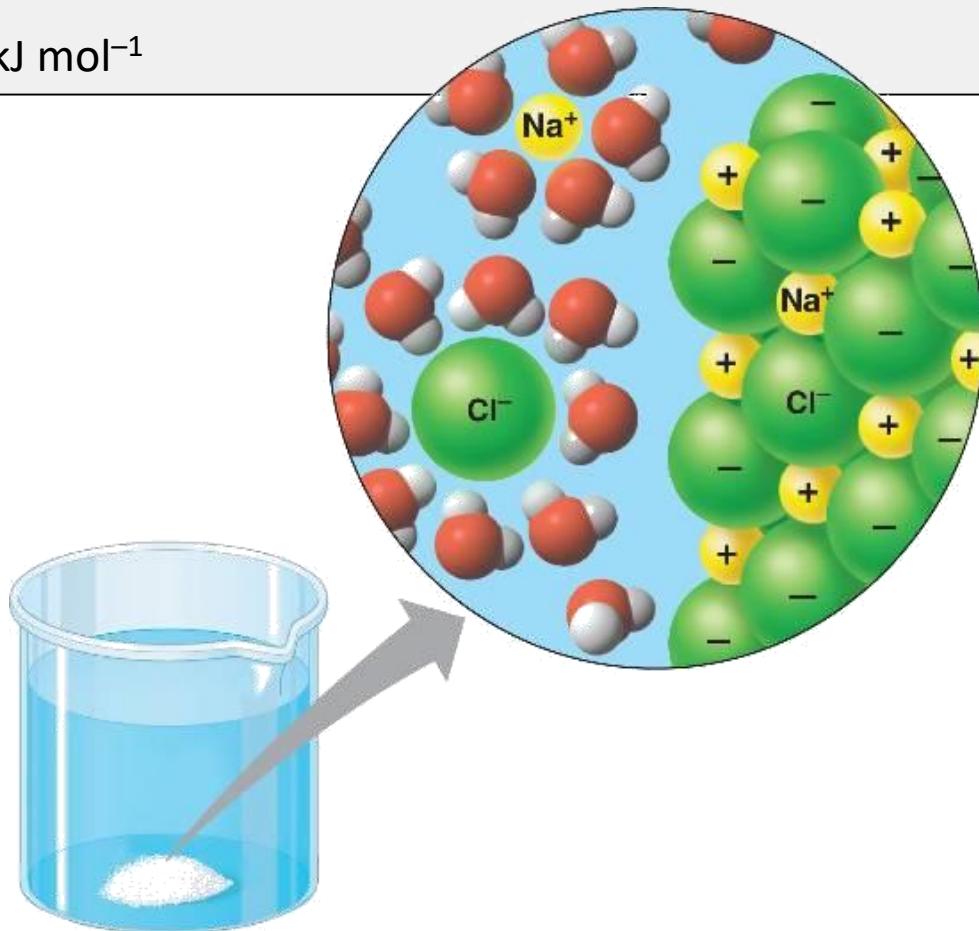
Question 2c (iii):

Why does NaCl readily dissolve in water, even though the process is slightly endothermic?



Answer 2c (iii):

When solid NaCl dissolves in water, there is an increase in the entropy of the system since the ions in solution have greater entropy than in the solid lattice, i.e. more random / disordered arrangement. Although the ions in solution have more energy / energetically less stable than in the solid lattice (since the process is endothermic), the increase in entropy makes the process spontaneous.



NCEA 2016 Entropy

Excellence Question

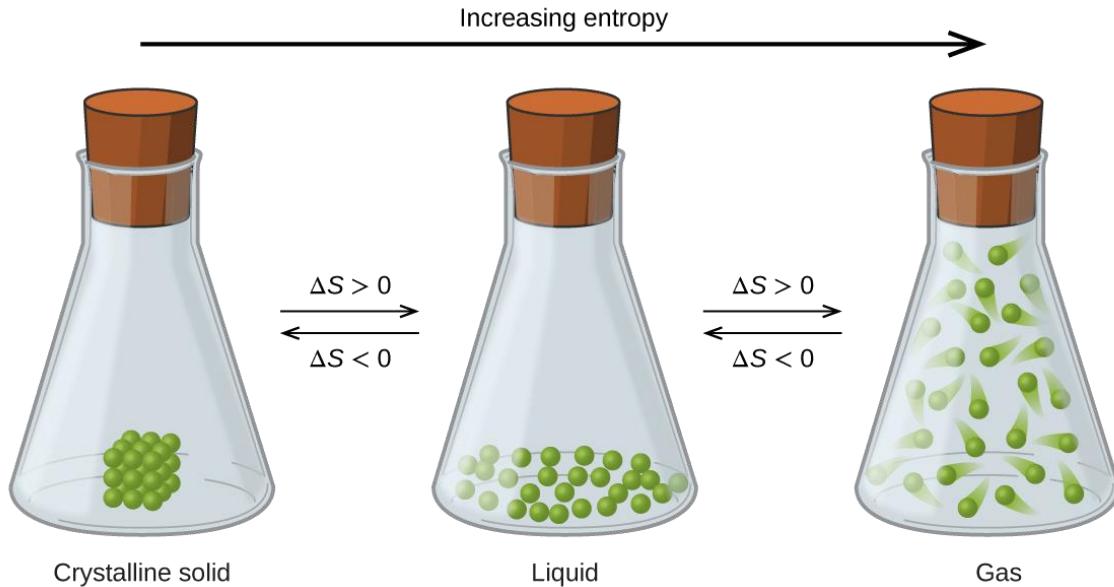
Question 3c (iii):

The equation for the evaporation of liquid methanol is:



Explain the entropy changes of the system and surroundings for the evaporation of methanol.

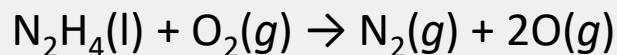
There is an increase in entropy since gaseous particles are formed; gaseous particles have a more random / disordered arrangement (greater dispersal of matter) than liquid particles.



The enthalpy of the surroundings decreases as the alcohol evaporates as energy is absorbed from the surroundings to break the intermolecular forces between methanol molecules; thus the entropy of the surroundings decreases.

Question 2d:

The reaction for the complete combustion of hydrazine is shown in the equation below.



This is an exothermic reaction.

Explain the entropy changes associated with this reaction.

System – as the number of gaseous molecules is greater on the product side than the reactant side, then there is an increase in disorder / the dispersal of matter / degree of randomness / dispersal of energy, thus the entropy of the system increases.

Surroundings – as the reaction is exothermic the entropy of the surroundings increases, as there is an increase in disorder / the dispersal of matter / degree of randomness / dispersal of energy.

Question 3b:

- (iii) Explain why the sublimation of iodine is spontaneous, even though the enthalpy of sublimation is a positive value.

Spontaneity is determined by the total entropy change (system + surroundings).

Entropy of the system increases as the solid becomes a gas because the gas particles are more disordered. The increase in entropy of the system outweighs the decreased entropy of the surroundings due to the positive enthalpy OR positive enthalpy due to the endothermic process of breaking bonds is offset by entropy changes in the system.



Enthalpy of Reaction using calorimetry

To measure enthalpy changes, the reaction it is carried out in an insulated container (such as a polystyrene cup) and the temperature change (in °C) is measured. Using this temperature change, ΔT , and the value of the specific heat capacity, c , the amount of heat energy (q) transferred to the mass m of substance (usually water) can be calculated using the expression

$$q = m c \Delta T$$

The specific heat capacity of the water is $4.18 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$.
Every 1mL of water can be taken as 1g due to its density

1. Calculate the mass of reactants – record in grams
(one ml liquid = one gram)
2. Measure the temperature of the reactants and the temperature of the products and calculate ΔT (°C)
3. Calculate q using formula above

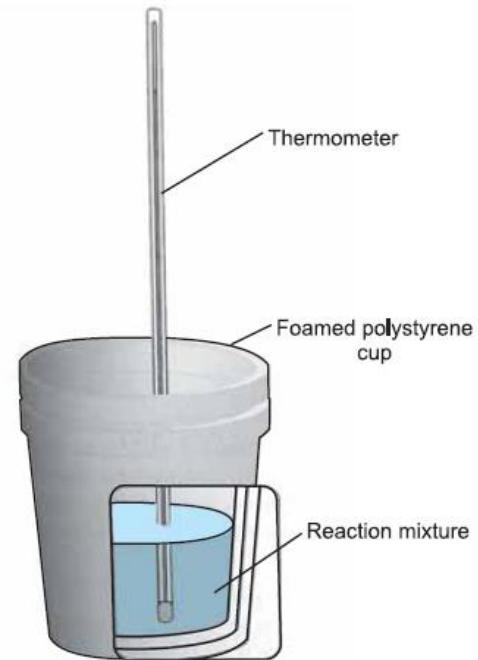


Fig. 6.8 Calorimeter for measuring heat changes at constant pressure (atmospheric pressure).

Calculating heat energy (q)

The energy change when a body of mass m experiences a temperature rise of ΔT is given by:

$$q = m c \Delta T$$

energy change = mass x specific heat capacity x change in temperature

Example: Calculate the energy change when a 9 kg mass of water increases its temperature by 20 °C.

$$q = m c \Delta T$$

$$q = 9000 \text{ g} \times 4.18 \text{ kJ } ^\circ\text{C}^{-1} \text{ kg}^{-1} \times 20 \text{ } ^\circ\text{C}$$

$$q = 752 \ 4000 \text{ J}$$

Note: m is grams and q will be calculated in J. This will need to be converted to kJ for the next step to calculate Δ_rH°

Using Q to calculate enthalpy of reaction ($\Delta_r H^\circ$)

Enthalpy of reaction $\Delta_r H^\circ$ can be calculated from heat energy (q) in the previous step if the number of moles of one of the reactants is known, or calculated.

$$\Delta_r H^\circ = -q / n$$

Note that the q is negative and will be in kJ

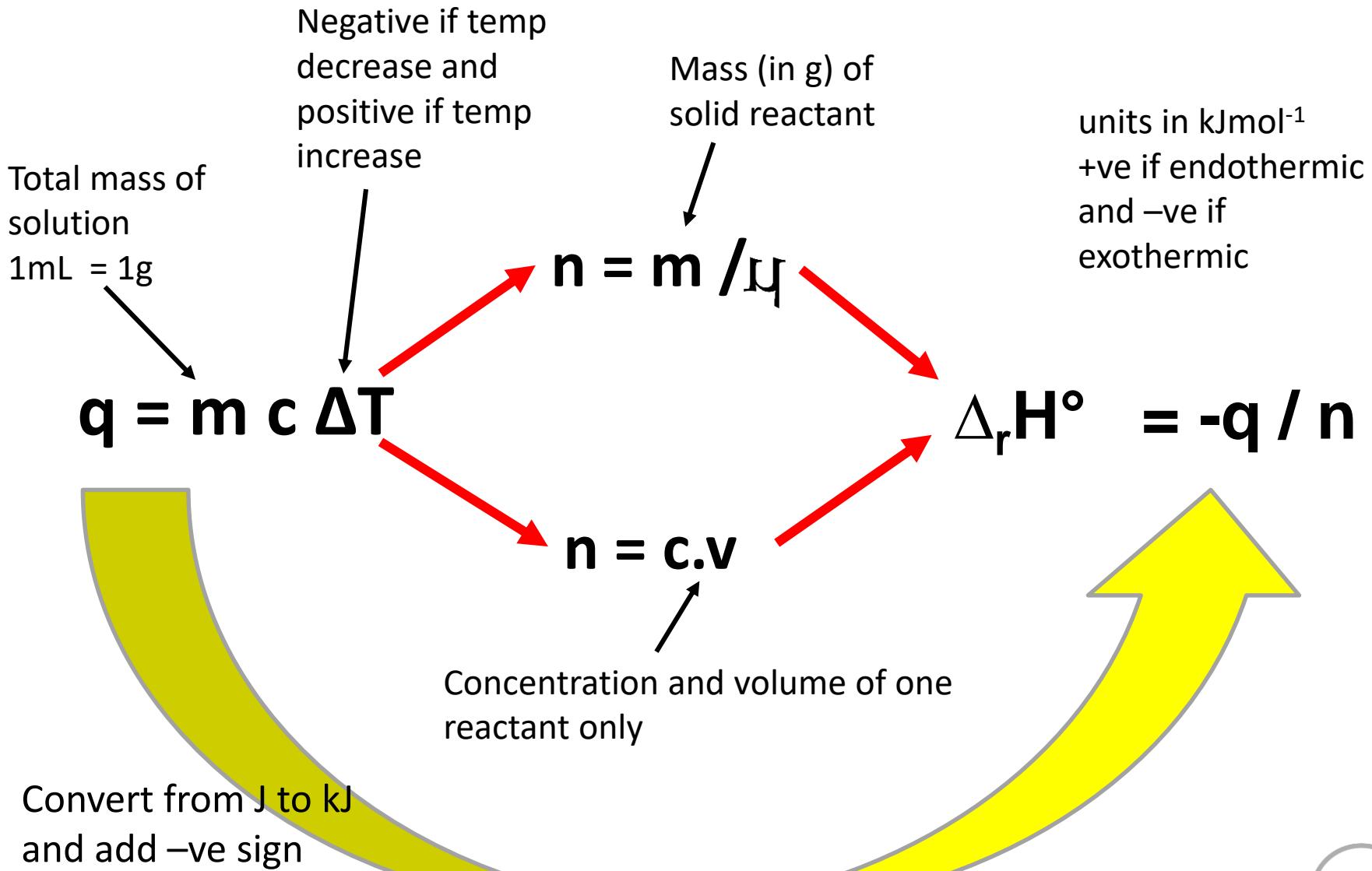
Moles (n) can be calculated from either mass of one of the reactants

$$n = m / M \quad M = \text{molar mass (gmol}^{-1}\text{)} \quad m = \text{mass (g)}$$

Or from the concentration and volume of one of the reactants

$$n = c \cdot v \quad c = \text{concentration (molL}^{-1}\text{)} \quad v = \text{volume (L)}$$

Using Q to calculate enthalpy of reaction (Δ_rH°) Summary



Question 2b(i): When 25.0 mL of a 1.00 mol L⁻¹ hydrochloric acid solution, HCl, is added to 25.0 mL of a 1.00 mol L⁻¹ ammonia solution, NH₃, a temperature rise of 6.50°C is recorded, as a neutralisation reaction occurs to produce aqueous ammonium chloride and water.

Calculate Δ_rH° for this neutralisation reaction. The mass of the mixture is 50.0 g.
Assume specific heat capacity of the aqueous ammonium chloride = 4.18 J g⁻¹ °C⁻¹

Answer 2b(i):

$$q = mc\Delta T = 50 \times 4.18 \times 6.5 = 1358.5 \text{ J} = 1.3585 \text{ kJ}$$

$$n = c \times V = 1 \times 0.025 = 0.025 \text{ mol}$$

$$\begin{aligned}\Delta_rH^\circ &= \frac{-q}{n} = \frac{-1.3585 \text{ kJ}}{0.025 \text{ mol}} \\ &= -54.3 \text{ kJ mol}^{-1}\end{aligned}$$

Heat capacity value always given. Use it to help you remember units

Answer 2b(ii): Conditions were not standard.

Needed to carry out under standard conditions OR

Heat lost to atmosphere / beaker / surroundings.

Insulate equipment; ensure all / as much of the energy produced as possible is collected and measured.

Question 2b(ii):

When the Δ_rH° for the neutralisation above was found experimentally in a school laboratory, the value obtained was lower than the theoretical value.

Account for the difference in values, and suggest how this difference could be minimised.

NCEA 2016 Specific Heat Capacity

Question 3b (i): The enthalpy of combustion of liquid methanol, $\Delta_c H^\circ(\text{CH}_3\text{OH}_{(l)})$, can also be determined by burning a known mass of methanol and measuring the temperature change in a known mass of water above the burning methanol. If 2.56 g of methanol is burned, the temperature of 500 g water increases from 21.2°C to 34.5°C.

Using these results, calculate the experimental value of $\Delta_c H^\circ(\text{CH}_3\text{OH}_{(l)})$.
The specific heat capacity of water is $4.18 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1}$.

$$M(\text{CH}_3\text{OH}) = 32.0 \text{ g mol}^{-1}$$

Heat capacity value always given. Use it to help you remember units

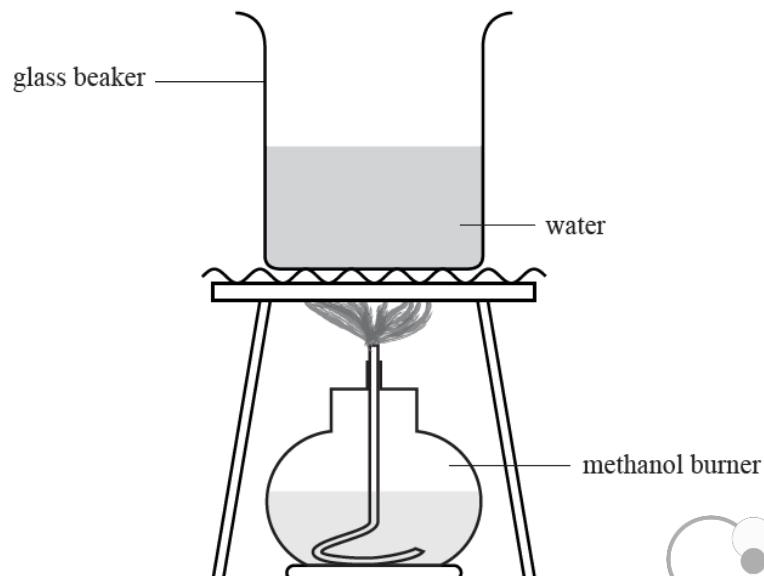
$$q = mc\Delta T$$

$$q = 500 \text{ g} \times 4.18 \text{ J } ^\circ\text{C}^{-1} \text{ g}^{-1} \times (34.5^\circ\text{C} - 21.2^\circ\text{C})$$

$$q = 27\ 797 \text{ J} = 27.797 \text{ kJ}$$

$$n(\text{CH}_3\text{OH}) = \frac{m}{M} = \frac{2.56}{32} = 0.08 \text{ mol}$$

$$\Delta_c H = \frac{-q}{n} = \frac{-27.797}{0.08} = -347 \text{ kJ mol}^{-1}$$

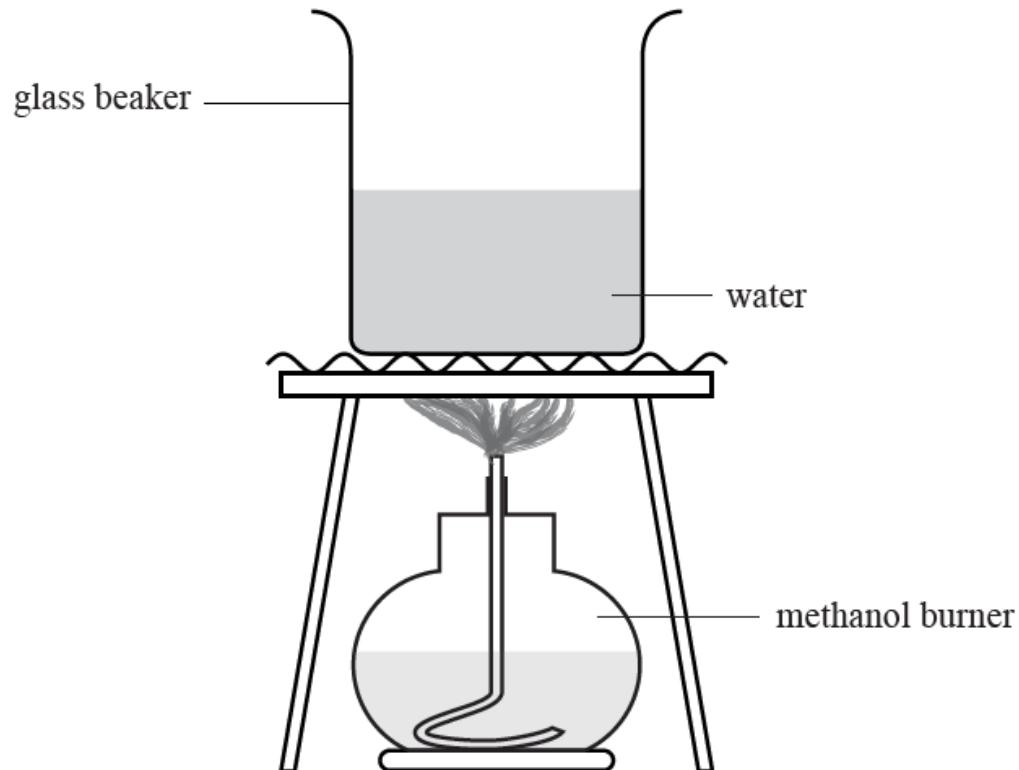


NCEA 2016 Specific Heat Capacity

Merit
Question

Question 3b (ii): Why is the experimental value obtained in the enthalpy of formation question less negative than the theoretical value determined in the specific heat capacity question?

Heat loss to surroundings / incomplete combustion which means the temperature of the water doesn't increase as much leading to a less negative enthalpy / the experiment wasn't insulated



Calculating Δ_rH° given the standard heats of formation of reactants and products.

The standard enthalpy of any reaction can be obtained by subtraction of the standard enthalpies of formation of reactants from those of the products.

$$\Delta_rH^\circ = \sum n \Delta_fH^\circ_{\text{products}} - \sum n \Delta_fH^\circ_{\text{reactants}}$$

where n is the stoichiometric coefficient of each substance in the reaction equation.

Example

Using the standard heats of formation of $\text{CO}_2(g)$, $\text{H}_2\text{O}(l)$, and $\text{C}_6\text{H}_{12}\text{O}_6(s)$, calculate the standard enthalpy of combustion of glucose.

$$\Delta_fH^\circ(\text{C}_6\text{H}_{12}\text{O}_6, s) = -1268 \text{ kJ mol}^{-1}$$

$$\Delta_fH^\circ(\text{CO}_2, g) = -394 \text{ kJ mol}^{-1}$$

$$\Delta_fH^\circ(\text{H}_2\text{O}, l) = -286 \text{ kJ mol}^{-1}$$

$$\Delta_fH^\circ(\text{O}_2, g) = 0 \text{ kJ mol}^{-1}$$

Note - Start by writing an equation for the combustion of 1 mole of glucose.



$$\Delta_rH^\circ = \sum n \Delta_fH^\circ_{\text{products}} - \sum n \Delta_fH^\circ_{\text{reactants}}$$

$$\Delta_rH^\circ = (6 \times -394 + 6 \times -286) - (1 \times -1268 + 6 \times 0) = -2812 \text{ kJ mol}^{-1}$$

NCEA 2013 Enthalpy of formation

Merit
Question

Question 3b:

Decane is a component of petrol. Carbon dioxide and water are formed when decane burns completely in oxygen.



Calculate $\Delta_c H - (\text{C}_{10}\text{H}_{22(l)})$, given the following data:

$$\Delta_f H - (\text{C}_{10}\text{H}_{22(l)}) = -250 \text{ kJ mol}^{-1}$$

$$\Delta_f H - (\text{CO}_{2(g)}) = -393 \text{ kJ mol}^{-1}$$

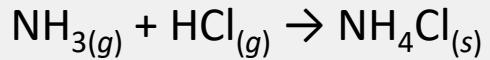
$$\Delta_f H - (\text{H}_2\text{O}_{(l)}) = -286 \text{ kJ mol}^{-1}$$

Answer 3d:

$$\begin{aligned}\Delta_r H^\circ &= \sum \Delta_f H^\circ \text{ products} - \sum \Delta_f H^\circ \text{ reactants} \\ &= [(10 \times -393) + (11 \times -286)] - (-250) \\ &= -6826 \text{ kJ mol}^{-1} \text{ or } (-6830 \text{ kJ mol}^{-1})\end{aligned}$$

Question 2c:

An equation for the reaction of ammonia gas with hydrogen chloride gas is:



Calculate the standard enthalpy change, $\Delta_r H^\circ$, for this reaction, using the following data.

$$\Delta_f H^\circ (\text{NH}_{3(g)}) = -46 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{HCl}_{(g)}) = -92 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{NH}_4\text{Cl}_{(s)}) = -314 \text{ kJ mol}^{-1}$$

Answer 3d:

$$\Delta_r H^\circ = \sum \Delta_f H^\circ \text{ products} - \sum \Delta_f H^\circ \text{ reactants}$$

$$= (-314) - (-46 + -92)$$

$$= -176 \text{ kJ mol}^{-1}$$

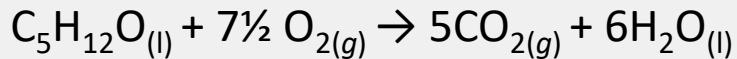
Use the mole coefficients from the equation.

we know it is a exothermic reaction with a Negative sign

NCEA 2015 Enthalpy of formation

Question 3d:

The equation for the combustion of pentan-1-ol is:



Calculate $\Delta_c H^\circ$ for pentan-1-ol, given the following data:

$$\Delta_f H^\circ (\text{C}_5\text{H}_{12}\text{O}_{(l)}) = -295 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{CO}_{2(g)}) = -394 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (\text{H}_2\text{O}_{(l)}) = -286 \text{ kJ mol}^{-1}$$

Answer 3d:

$$\Delta_c H^\circ = \sum \Delta_f H^\circ (\text{products}) - \sum \Delta_f H^\circ (\text{reactants})$$

$$= [(5 \times -394) + (6 \times -286)] - [-295]$$

$$= -3686 + 295$$

$$= -3391 \text{ kJ mol}^{-1}$$

Use the mole coefficients from the equation.

Because we know it is a combustion reaction check to make sure your answer is exothermic with a Negative sign

NCEA 2016 Enthalpy of formation

Question 3a:

The equation for the combustion of liquid methanol is:



Calculate the standard enthalpy of combustion of liquid methanol, $\Delta_c H^\circ(\text{CH}_3\text{OH}_{(l)})$, using the information in the table below.

Compound	kJ mol ⁻¹
$\Delta_c H^\circ(\text{C}(s))$	-394
$\Delta_c H^\circ(\text{H}_2(g))$	-286
$\Delta_f H^\circ(\text{CH}_3\text{OH}(l))$	-240

This question could be calculated using
 $\Delta_r H^\circ = \sum \Delta_f H^\circ \text{ products} - \sum \Delta_f H^\circ \text{ reactants}$
As the combustion reactions were the same as the formation reactions

Answer 3a:

$$\Delta_c H^\circ = -394 + (2 \times -286) - (-240)$$

$$\Delta_c H^\circ = -966 + 240$$

$$\Delta_c H^\circ = -726 \text{ kJ mol}^{-1}$$

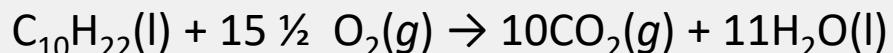
O₂ is left out as formation enthalpy of elements is 0

Hess's Law would also have worked to calculate the enthalpy of the reaction but it would have been a longer process

NCEA 2017 Enthalpy of formation

Question 2c:

Carbon dioxide and water are formed when decane burns completely in oxygen. The reaction is shown in the equation below.



Calculate the enthalpy of combustion for decane, given the following data:

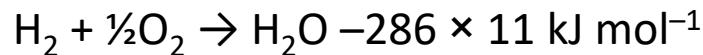
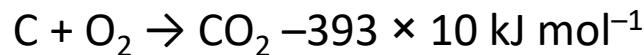
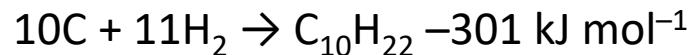
$$\Delta_f H^\circ (\text{C}_{10}\text{H}_{22}(l)) = -301 \text{ kJ mol}^{-1}$$

$$\Delta_c H^\circ (\text{C}) = -393 \text{ kJ mol}^{-1}$$

$$\Delta_c H^\circ (\text{H}_2) = -286 \text{ kJ mol}^{-1}$$

This question could be calculated using
 $\Delta_r H^\circ = \sum \Delta_f H^\circ \text{ products} - \sum \Delta_f H^\circ \text{ reactants}$
As the combustion reactions were the same as the formation reactions

Answer 2c:



$$\Delta H = +301 + (10 \times -393) + (11 \times -286)$$

$$= -6775 \text{ kJ mol}^{-1}$$

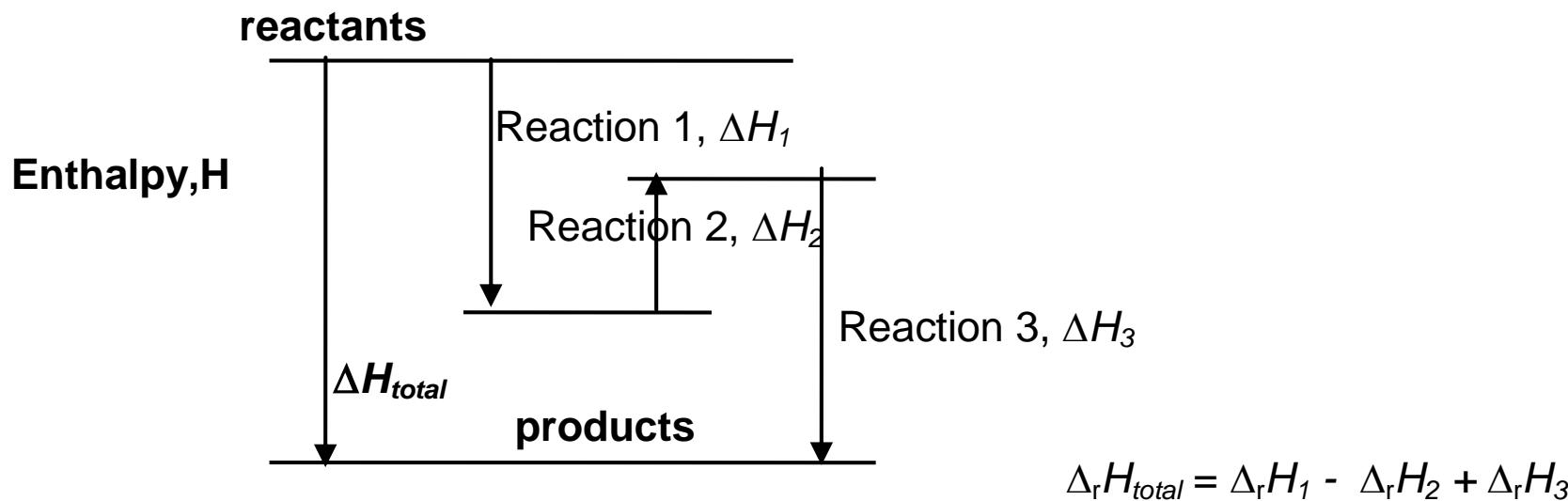
O_2 is left out as formation enthalpy of elements is 0

Hess's Law would also have worked to calculate the enthalpy of the reaction but it would have been a longer process

Hess's law

If an overall reaction can be broken down into a series of two or more steps, then the corresponding overall enthalpy of reaction is the sum of the enthalpies of the individual reaction steps. None of the steps need to be a reaction that can be carried out in the laboratory.

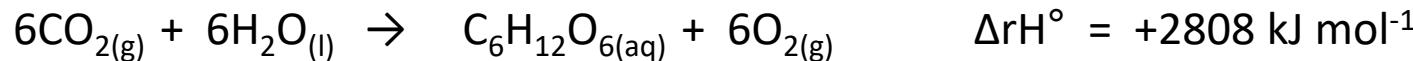
The energy difference depends only on the **difference in energy** between the reactants and products, not on the reaction path taken.



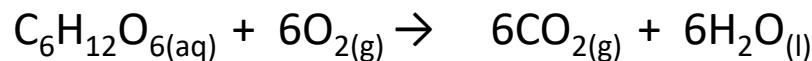
$$\Delta_r H_{total} = \Delta_r H_1 - \Delta_r H_2 + \Delta_r H_3$$

Application of Hess's law

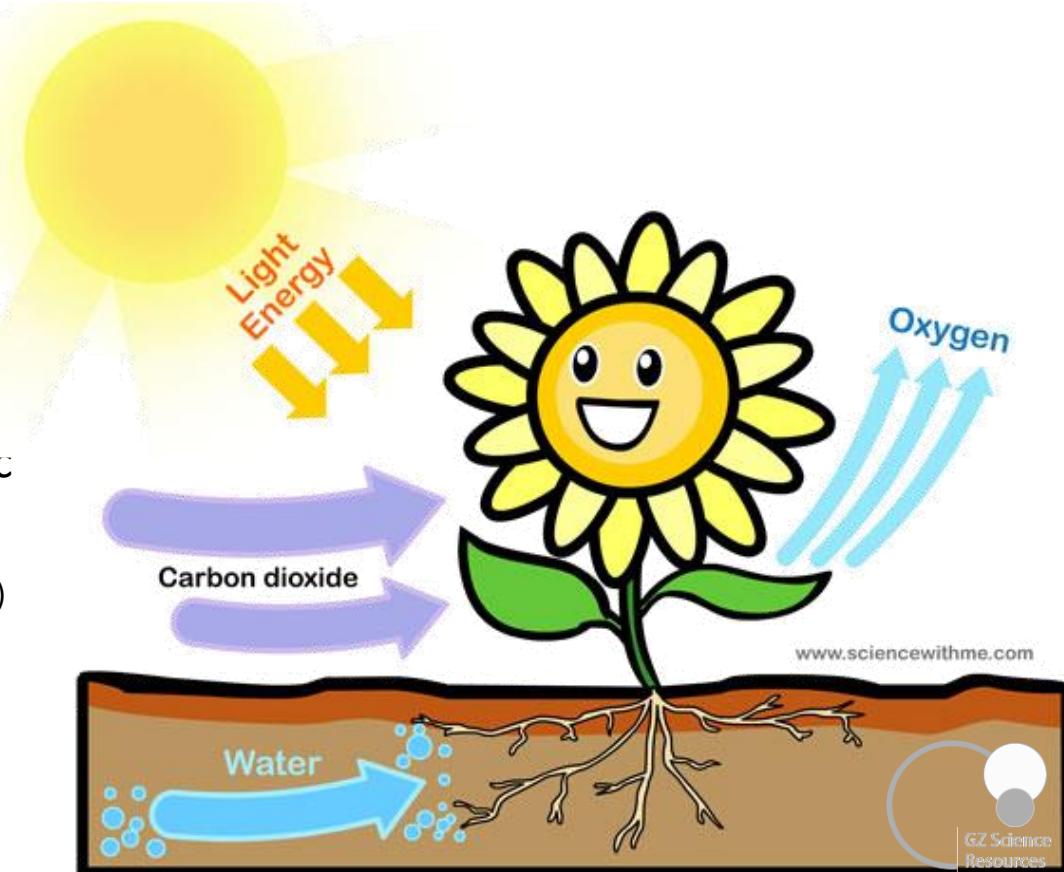
The process of photosynthesis is an endothermic process in which energy from the sun is trapped and stored in the bonds of glucose.



It is difficult reaction to measure enthalpy change so using the principle of Hess's law we can more easily measure the enthalpy change for the reverse reaction, the combustion of glucose (i.e. the process of respiration). The difference between reactants and products will be the same – we only need to reverse the sign from exothermic to endothermic



$$\Delta rH^\circ = -2808 \text{ kJ mol}^{-1}$$

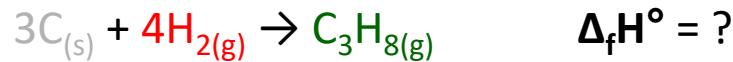


Steps to calculating enthalpy of reaction Hess's Law

Energy change due to a chemical reaction is independent of pathway taken

Example: calculate $\Delta_f H^\circ$ (C_3H_8)

Step 1. Write out equation for reaction to calculate



Step 2. Use given equations and rearrange until they match equation



Can multiply all by 3. multiply enthalpy as well



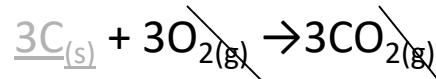
Can reverse so molecules on same side. Reverse enthalpy sign



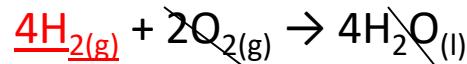
Hess's Law

Energy change due to a chemical reaction is independent of pathway taken

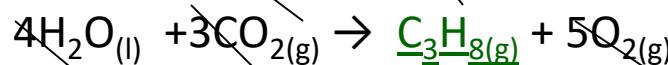
Step 3. cancel out any molecules on either side.



$$\Delta_c H^\circ = 3(-394\text{Kjmol}^{-1})$$

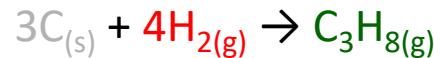


$$\Delta_c H^\circ = 4(-286\text{Kjmol}^{-1})$$



$$\Delta_c H^\circ = +2220\text{Kjmol}^{-1}$$

Step 4. ensure remaining molecules match reaction equation



Step 5. Add up enthalpies

$$\Delta_f H^\circ = 3(-394\text{Kjmol}^{-1}) + 4(-286\text{Kjmol}^{-1}) + +2220\text{Kjmol}^{-1}$$

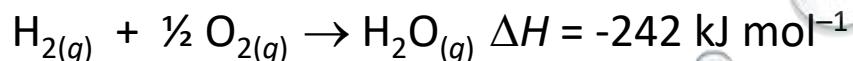
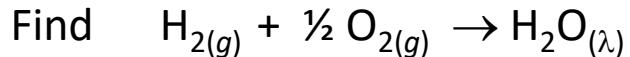
$$= -106\text{Kjmol}^{-1}$$

Question 3a (ii):

(ii) When gaseous hydrogen and oxygen are heated in a test tube, droplets of liquid water form on the sides of the test tube. Calculate $\Delta_f H - (H_2O_{(l)})$, given the following data:

$$\Delta_f H - (H_2O_{(g)}) = -242 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{vap}} H - (H_2O_{(l)}) = +44 \text{ kJ mol}^{-1}$$



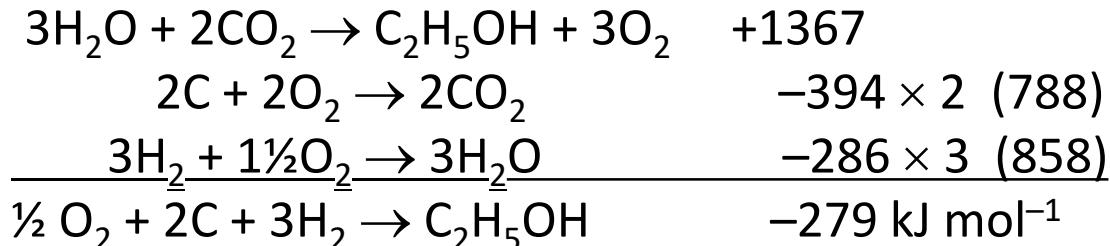
$$\Delta_f H^\circ(H_2O_{(\lambda)}) = -44 + (-242) = -286 \text{ kJ mol}^{-1}$$

If you reverse the equation then reverse the sign of the enthalpy

Question 3d (i):

Calculate the standard enthalpy of formation of liquid ethanol using the information given below.

Compound	kJ mol^{-1}
$\Delta_c H^\circ (\text{C}(s))$	-394
$\Delta_f H^\circ (\text{H}_2\text{O}(\ell))$	-286
$\Delta_c H^\circ (\text{C}_2\text{H}_5\text{OH}(\ell))$	-1367

Answer 3d:**Question 3d (ii):**

Discuss how the value of the enthalpy change would differ if the ethanol product formed was a gas rather than a liquid.

If you reverse the equation then reverse the sign of the enthalpy

The enthalpy change would be more positive.

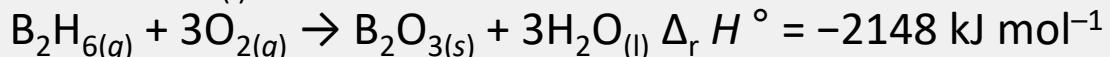
Heat energy is absorbed when converting a liquid to a gas. Therefore if the ethanol formed were in the gaseous state, less energy would be released in its formation / products would have a higher enthalpy.

Question 2c:

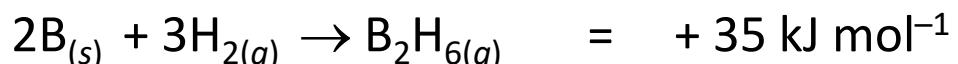
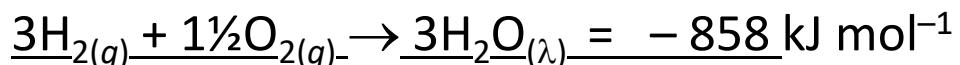
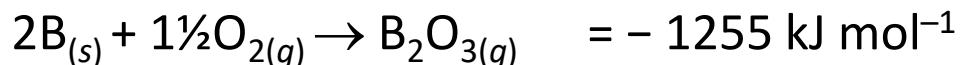
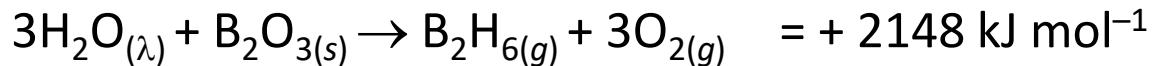
Calculate the $\Delta_f H^\circ$ for $B_2H_{6(g)}$, given the following data:

$$\Delta_f H^\circ (B_2O_{3(s)}) = -1255 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ (H_2O_{(l)}) = -286 \text{ kJ mol}^{-1}$$



The melting point of boron is 2300°C.

Answer 2c:

If you reverse the equation then reverse the sign of the enthalpy

Expand out all equations – Formation equations require the state elements at 25°
 Watch that the number of mols and state is the same for the final and starting equation