CHEM 3.4 (External)

Standard 91390 Demonstrate understanding of thermochemical principles and the properties of particles and substances

This standard can be divided to three parts

1. **Atomic chemistry**
    a. s, p, d electron configuration
    b. Periodic table trends
        i. Ionisation energy
        ii. Atomic and ionic radius
        iii. Electronegativity
2. **Molecular chemistry**
    a. Lewis diagrams and molecular shapes
    b. Attractions force between particles
3. **Thermodynamics**
    a. Definitions of enthalpy
    b. Energy calculations
        i. Hess's Law
        ii. Specific heat energy
    c. Enthalpy, entropy and Gibbs free energy

Please read **this document**
This standard requires **both writing** and **calculations**.

Knowledge of **CHEM 2.4** is assumed for this standard.
In my opinion, I consider CHEM 3.4 as the hardest out of all the standards in NCEA level 3 Chemistry.

Useful formulas and definitions

$q = m\,c\,\Delta T$ $c(H_2O) = 4.18\ J\,g^{-1}\,{}^oC^{-1}$ *(value will be given)*

$n = \frac{m}{M}$ $c = \frac{n}{V}$ $E = \Delta_r H^\circ \times n$

***Δ$_r$H°*, standard enthalpy of reaction** when reactants and products are in their **standard state** (usually the state at 25°C).
For example: $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$ ***Δ$_r$H°* (H_2O, *ℓ*) =** –570 kJ mol^{-1}
The term **mol^{-1}** means **per mole of reaction**, which is determined by the chemical equation;
ie 2 mol of H_2 reacting with 1 mol of O_2 to give 2 mol of H_2O.
***Δ$_f$H°*, standard enthalpy of formation**, per mole of product.
For example, the **standard enthalpy of formation** of liquid water:
$H_2(g) + 1/2O_2(g) \rightarrow H2O(\ell)$ ***Δ$_f$H°* (H_2, *ℓ*) =** –285 kJ mol^{-1}
***Δ$_c$H°*, standard enthalpy of combustion**, per mole of substance burnt in excess oxygen.
For example, the **standard enthalpy of combustion** of hydrogen gas to give liquid water:
$H_2(g) + ½\ O_2(g) \rightarrow H_2O(\ell)$ ***Δ$_c$H°* (H_2, *g*) =** –285 kJ mol^{-1}

Δ$_{fus}$H, enthalpy of **fusion** (melting) - at the melting point temperature
Δ$_{vap}$H, enthalpy of **vaporisation** (boiling) - at the boiling point temperature
Δ$_{sub}$H, enthalpy of **sublimation** - at the sublimation point temperature

Atomic chemistry

There are two themes for this part of the standard

1. s, p, d electron configuration
2. Periodic table trends
    a. Ionisation energy
    b. Atomic and ionic radius
    c. Electronegativity

s, p, d electron configurations

- In junior science, it was taught that electrons are arranged in different level where the
    - 1st level can hold 2 electrons
    - 2nd and 3rd levels can hold 8 electrons etc
- In CHEM 3.4 is going to expand this to another level (pun intended).
    - **Each energy level** is divided into (sub level) **different orbital types**.
    - **Each orbital types** contain **different number of orbitals**.
    - **Each orbital** can **contain two electrons**.
        - There are **three orbital types** and in CHEM 3.4
            - In the order of increasing in energy.
                - **s** type has **one orbital** containing total of **2 electrons.**
                - **p** type has **three orbitals** containing total of **6 electrons.**
                - **d** type has **five orbitals** containing total of **10 electrons.**
            - You do not need to learn the shape of the orbitals below in CHEM 3.4.

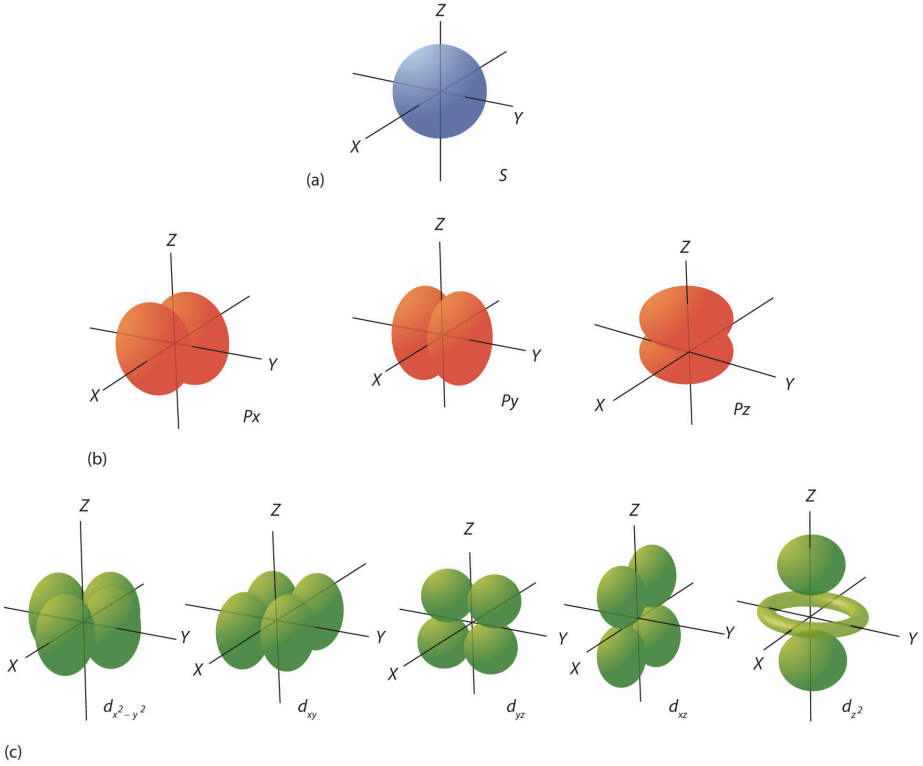
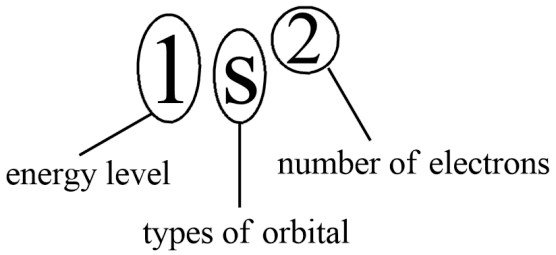


Figure 1.1- Orbital shapes[1]

- The **1st level** contains **s** orbital with a total of **2 electrons**
- The **2nd level** contains **s** and **p** orbitals with a total of **8 electrons**
- The **3rd level** contains **s**, **p** and **d** orbitals with a total of **18 electrons**

[1] https://www.pinterest.nz/pin/316026098827053558/ accessed on 25/11/2017

- The orbital types is written in this way



- The orbitals are arranged in this order with increasing energy
  - 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p
- **For atom**
  - Similar to the old electron configuration, the level with lower energy has to be filled before filling the next one.
  - **Example**
    - Oxygen ($8e^-$)- **$1s^2$, $2s^2$, $2p^4$**
    - Scandium ($21e^-$)- **$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^1$**
  - **With exceptions of Cr and Cu**
    - Cr ($24e^-$)- **$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, $3d^5$**
    - Cu ($29e^-$)- **$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, $3d^{10}$**
      - This is because there is a extra stability for the shell to be half filled
- **For cation**
  - Electrons always **loses** from the **highest energy level** (the big number in front) with the **highest energy orbital**, from the **atomic electron configuration**.
  - YOU LOSE 4s BEFORE 3d
  - **Example**
    - Iron atom- **$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^6$**
    - Iron (III) ion- **$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, ~~$4s^2$~~, $3d^{6-5}$ → $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^5$**
- **For anion**
  - Electrons always **gain** to the **highest energy level** (the big number in front) with the **highest energy orbital**, from the **atomic electron configuration**.
  - **Example**
    - Chlorine atom- **$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^5$**
    - Chloride ion- **$1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$**
- The periodic table can be divided into different blocks (see the diagram below)

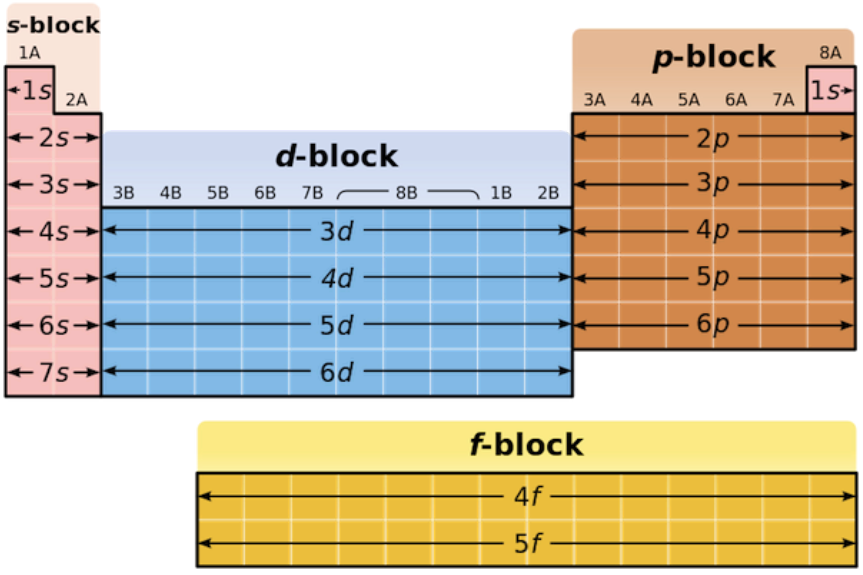


Figure 1.2- Blocks in the periodic table[2]

- **Orbital diagram**
  - Each orbital contains two electrons ↿ and ⇂.
  - The electron filled all unpaired to paired.

Electron Configurations of Several Lighter Elements

Element	Total Electrons	Obital Diagram					Electron Configuration
		1s	2s	2p		3s	
Li	3	↿⇂	↿				$1s^2 2s^1$
Be	4	↿⇂	↿⇂				$1s^2 2s^2$
B	5	↿⇂	↿⇂	↿			$1s^2 2s^2 2p^1$
C	6	↿⇂	↿⇂	↿	↿		$1s^2 2s^2 2p^2$
N	7	↿⇂	↿⇂	↿	↿	↿	$1s^2 2s^2 2p^3$

Figure 1.3- Orbital diagram[3]

Exercise for s, p, d electron configurations

1. Write the electron configuration and orbital diagram (as figure 1.3) of the followings
   a. Nitrogen atom (N)

   b. Sulfide (S^{2-})

   c. Vanadium (III) ion (V^{3+})

   d. Potassium atom (K)

   e. Sodium ion (Na^{+})

   f. Chromium ion (Cr^{3+})

   g. Magnesium atom (Mg)

[2] http://study.com/academy/lesson/s-block-elements-on-the-periodic-table-properties-lesson-quiz.html accessed on 25/11/2017

[3] http://ellesmere-chemistry.wikia.com/wiki/File:Spin_pairing.GIF accessed on 25/11/2017

Periodic table trend

- There are three periodic table trends to study in CHEM 3.4
    - **The First Ionisation energy**
    - **Atomic and ionic radius**
    - **Electronegativity**

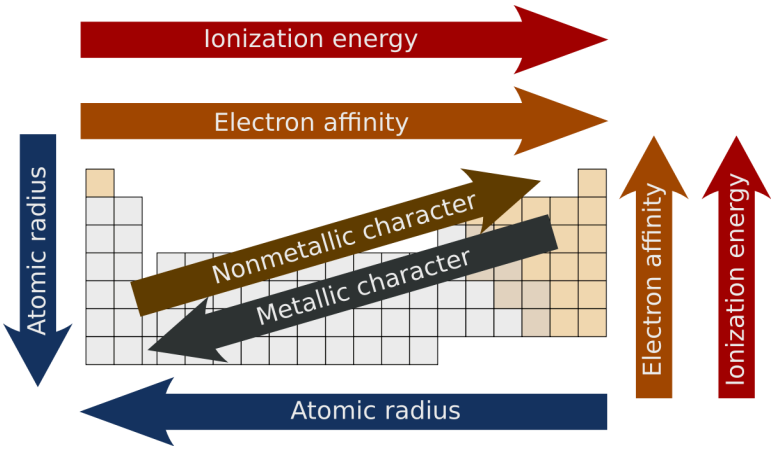


Figure 1.4- Periodic trend summary.[4]

The First Ionisation energy

- **The first ionization energy (1st *IE*) is quantitatively defined as the amount of energy required to remove the most loosely bound electron, the valence electron, of an isolated gaseous atom to form a 1+ gaseous cation.**
- **For example the first ionisation of Chlorine would be**
  $Cl_{(g)} \rightarrow Cl^{+}_{(g)} + e^{-}$
    - The **second ionization energy** (**2nd *IE***) is qualitatively defined as the **amount of energy required** to **remove the most loosely bound electron**, the valence electron, of an **isolated gaseous 1+ cation** to form a **2+ cation** and so on for **3rdIE** and **4th*IE***.
- **The general trends for first ionisation energy increase across (from left to right) and decrease down the periodic table.**
- As the **attraction** between the **valence electrons** and the **nucleus increases more energy** is needed **to remove** the valence electrons, thus **ionisation energy increase**.
- There are two factors affecting the ionisation energy
    - **Across the period**- the **number of protons** in the nucleus **increase**, **nucleus** become **more positive** (**increase in nuclei charge**) thus **increases the attraction** and the valence orbital have the same energy level therefore they have similar shielding.as a result **more energy** is needed **to overcome** the attractions. This leads to an increase in **ionisation energy across the Period**.
    - **Down the group**- as **go down the group**, the **energy level increases**. As the energy level increases, the distance between the Valence electrons and the nucleus increases, thus attraction decreases. Furthermore there are **more electrons between the nucleus and the valence electrons**. Although the number of protons in the nucleus increases, since core electrons and valence **electron repel each other** (this is called **shielding effect**) therefore the **attraction** between **the nucleus and the valence electron decreases**. As a result, the **energy required t**o remove the valence electron **decreases**. This leads to an decrease in **1st ionisation energy down the group**.

[4] https://en.wikipedia.org/wiki/Periodic_trends accessed on 25/11/2017

- **With the exceptions as you go across the period**
    - **Small decrease** between **group 2** and **group 3**
    - **Small decrease** between **group 5** and **group 6**

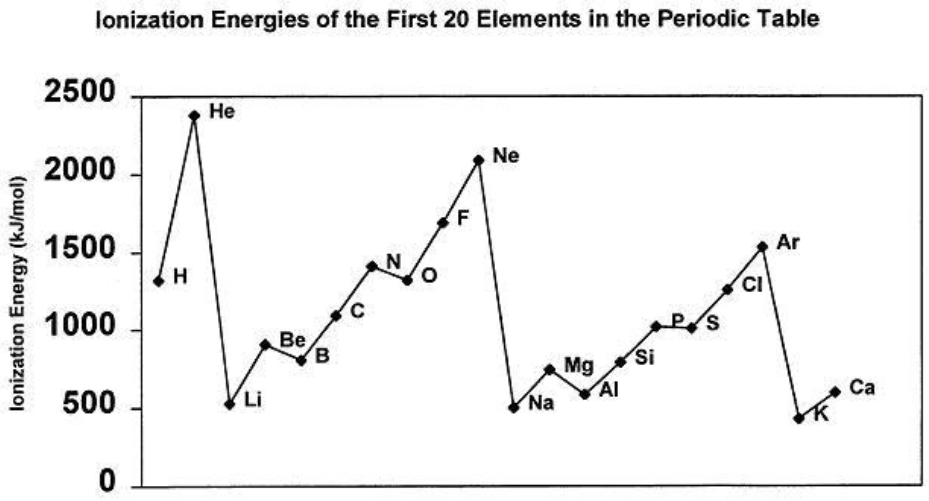


Figure 1.5- First ionisation energy for the first 20 elements[5]

- The small decrease between **group 2** and **group 3** is because there are **small increase** in energy level (between **s** and **p orbital**) therefore it increases the **shielding effect**, **decreases** in **attraction between** the **nucleus, therefore decrease** in **ionisation energy**.
- The small decrease between **group 5** and **group 6** is because there the **p orbital** is **half filled at group 5** while there is a **paired electrons in the p orbital in group 6**. This **increases** in **electron** in a **confined space**, results in an **increase in repulsion**, less energy is needed to be removed, therefore **ionisation energy decreases**.

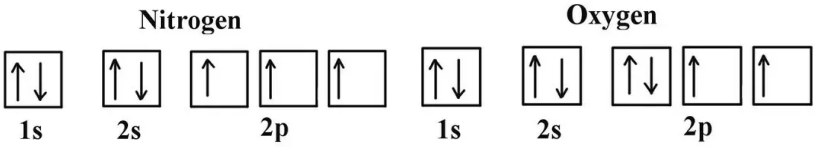


Figure 1.6- orbital diagram between group 5 and group 6. [6]

- For atom of the same element, *IE* (1st, 2nd and 3rd) increases dramatically when it changed into a lower energy level.

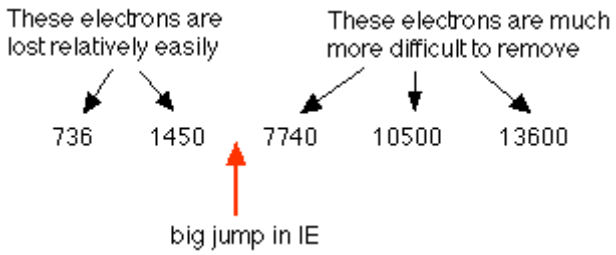


Figure 1.7- Successive ionisation energies of magnesium.[7]

[5] https://socratic.org/questions/why-is-the-ionization-energy-of-neon-higher-than-sodium-in-regards-of-periodicit accessed on 25/11/2017

[6] https://www.quora.com/What-causes-oxygen-and-sulfur-to-be-lower-in-ionization-energy-compared-to-the-elements-before-them accessed on 25/11/2017

[7] https://www.chemguide.co.uk/atoms/properties/moreies.html accessed on 25/11/2017

Atomic and ionic radii

- **Atomic and ionic radii is the distance between the nucleus and the valence electrons**
- Similar to ionisation energy, there are two factors that contributed to atomic and ionic radius.
    - Nuclei charge
    - Energy level
        - As the attraction increases, the radius decreases.
- **Atomic radii**
    - **Across the periodic**, the number of **protons increases** in the nucleus. The **attractions** between the valence electrons and the nucleus **increases**, the drag force between the nucleus and valence electron increases, thus the **radii decreases**.
    - **Down the group**, the **energy level increases**, this **decreases the attractions** resulting in an **increase of atomic radii.**
- **Ionic radiii**
    - **For cations**
        - The **energy level decreases** to form cations, the ionic radius of a **cation** is **smaller** than its **atom**.
    - **For anions**
        - The **number of electrons increases** in the **same energy level**, this **increases** the **electron - electron repulsion**. As a result radius of an **anion** is **bigger** than **atom**.
- **Isoelectric**
    - If the **electron configuration is the same**, the **higher** the number of **protons**, the **smaller** the **particle**
        - **For example care the radius of Na^+, Ne and F^-.**
        - Na^+, Ne, F^- has the **same electron configuration $1s^2$, $2s^2$, $2p^6$**
        - Na^+ has **$11p^+$**, Ne has **$10p^+$** and F^- has **$9p^+$**
        - Therefore **$Na^+ < Ne < F^-$**

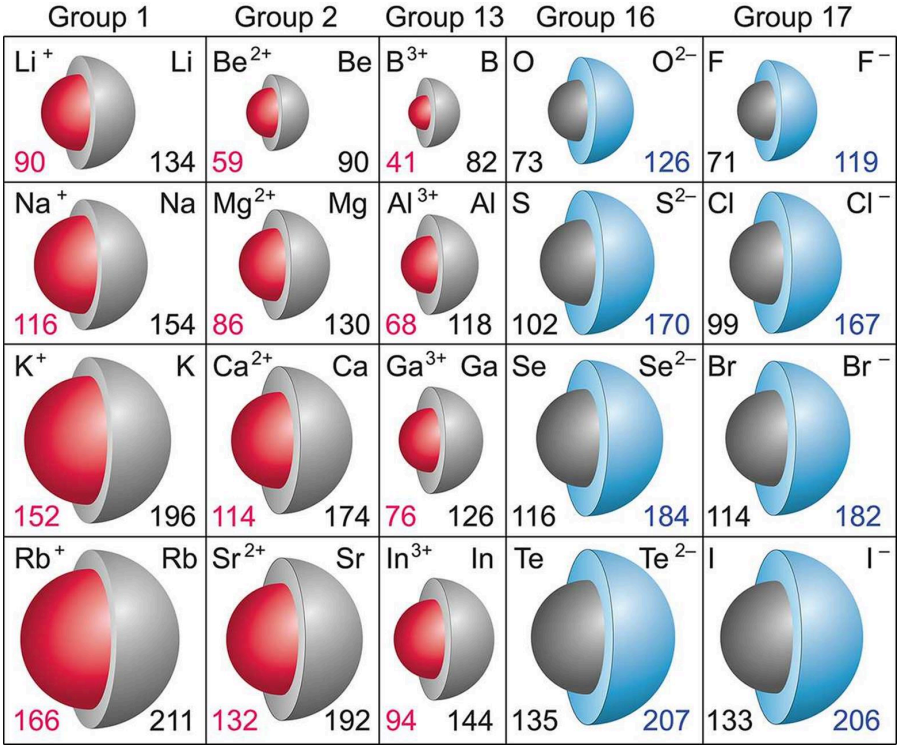


Figure 1.8- Grey is atom, red is cation, blue is anion.[8]

[8] http://schoolbag.info/chemistry/mcat_2/12.html accessed on 25/11/2017

Electronegativity

- **Electronegativity is the ability of an atom to attracts electrons in a chemical bond.**
- Once again, as the **attractions** between the **nucleus** and the **valence electron increases**, the ability to **attracts electron** in a chemical bond **increases**, **electronegativity increases**.
- **Electronegativity increases across the periodic table and decreases down**.
    - **Fluorine atom is the most electronegative element.**

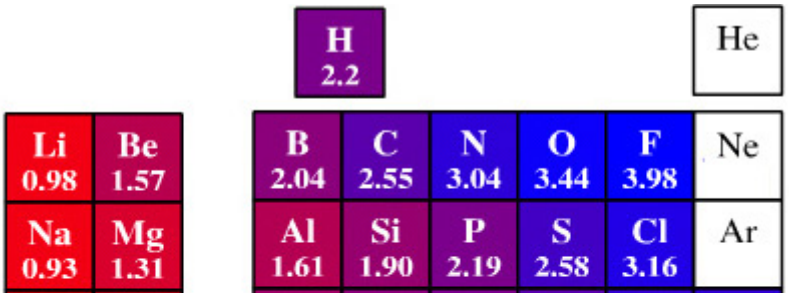


Figure 1.9- Electronegativity for the first 18 elements.[9]

Exercise for periodic table trend

1. Write the equation for the first ionisation of chlorine.

2. Explain why ionisation energy of an element is an endothermic reaction.

3. Rank S, F and O with the increase of 1st ionisation energy. Justify your answer.
   Include electron configuration (s, p and d) in your answer

4. Discuss the general trend of atomic and ionic radius across period 2. Justify your answers.

5. Explain why on ***figure 1.8***, the electronegativity of Group XVIII (the inert gas) is not given.

6. Predict the magnitude differences between the 1st, 2nd and 3rd ionisation energy of magnesium atom.

[9] http://www.meta-synthesis.com/webbook/30_timeline/timeline.html accessed on 25/11/2017

Molecular chemistry

There are two major themes in this part of the standard.

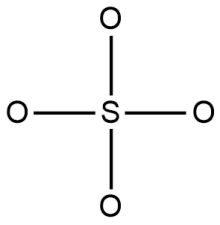
1. Lewis diagrams and molecular shapes
    a. Lewis diagrams
    b. Molecular shapes
2. Attractions force of particles

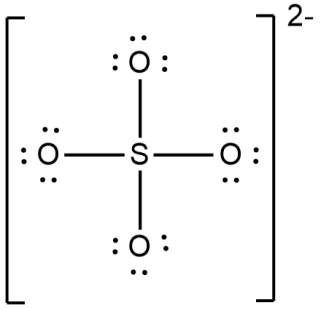
Lewis diagrams and molecular shapes

Lewis diagrams

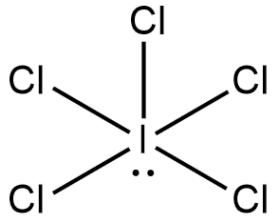
- The steps for the lewis diagram are the same as CHEM 2.4 with a minor adjustment (shown in bold).
    1. Calculate the total number of valence electrons, add the extra electrons from the charge (**Add the negative, subtract the positive**).
    2. Calculate the number of electrons needed to fill the shells of the outer atoms (2 for Hydrogen 8 for the rest)
    3. Step 1 - Step 2 = nonbonding electrons in the central atom.
    4. Draw the molecule with a single bond for each outer atom and the nonbonding electrons in pairs at the central atom.
    5. If the central atom has less than eight electrons (Boron 6), create a double bond until it is full. **If it is over eight, do nothing**.
    6. Filled the outer atom.
    7. **Draw a square bracket and state the overall charge if appropriate.**

- **For example lewis diagram for SO_4^{2-}**

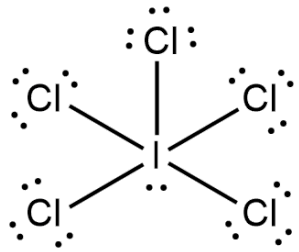
    1. S + O × 4 + -'ve charge × 2 = 6 + 6 × 4 + 2 = 32
    2. 4 × outer atom = 4 × 8 = 32
    3. 32 - 32 = 0 nonbonding electron in the central atom
    4. 
    5. Already 8 electrons in the central atom, move to step **6.** and **7.**.
    6. And 7.



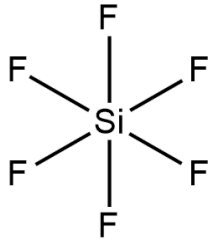
- **For example lewis diagram for ICl_5**

1. I + Cl × 5 = 7 + 7 × 5 = 42
2. 5 × outer atom = 5 × 8 = 40
3. 42 - 40 = 2 nonbonding electrons in the central atom
4. 

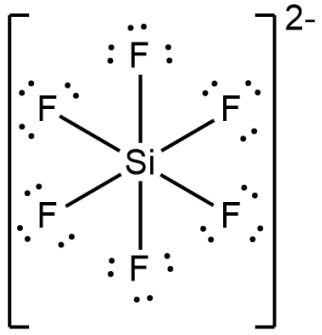
5. Already more than 8 electrons in the central atom, move to step **6.** and **7.**.
6. And 7.



- **For example lewis diagram for SiF_6^{2-}**

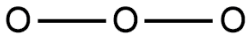
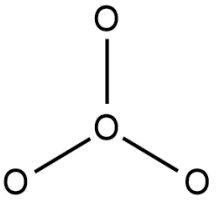
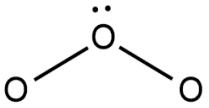
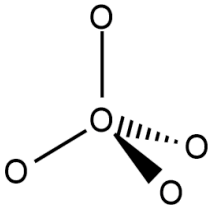
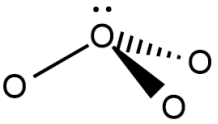
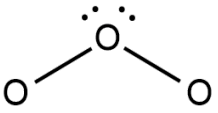
1. Si + F × 6 + (negative charge) = 4 + 7 × 6 + 2 = 48
2. 6 × outer atom = 6 × 8 = 48
3. 48 - 48 = 0 nonbonding electron in the central atom
4. 

5. Already more than 8 electrons in the central atom, move to step **6.** and **7.**.
6. And 7.

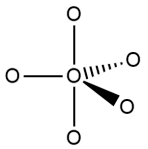
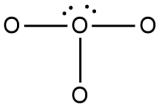
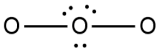
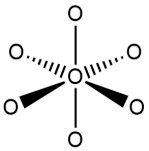
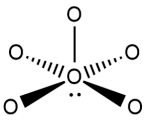
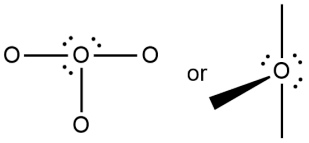
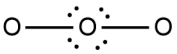


Molecular shapes

- Electron clouds (region of negativity) repel each other to achieve maximum stability.

Number of electron clouds	Number of outer atoms	Number of nonbonding pair	Name of the shape	Bond angle	Diagram for the shape
2	2	0	Linear*	180º	
3	3	0	Trigonal planar*	120º	
3	2	1	Bent (120)	120º (117.5)	
4	4	0	Tetrahedral*	109.5º	
4	3	1	Trigonal pyramidal	107º	
4	2	2	Bent (109)	105.5º	

- The additional shapes for CHEM 3.4 are on the next page
    - **Pay particular attention** to the base shape of **trigonal bipyramid**.
    - It is a combination of a **trigonal planar** and **linear**
    - The **linear part** of the shape is called **axial** and it is **perpendicular (90º)** from the trigonal planar part of the shape.
    - The **trigonal planar part** with a **bond angle of 120º** and is called the **equatorial**.
    - Since the nonbonding pair has greater repulsion, so for maximum stability, lone pair is located on the equatorial positions.

Number of electron clouds	Number of outer atoms	Number of nonbonding pair	Name of the shape	Bond angle	Diagram for the shape
5	5	0	Trigonal bipyramid*	90° & 120°	
5	4	1	Seesaw	90° & 120°	
5	3	2	T-shape	90°	
5	2	3	Linear*	180°	
6	6	0	Octahedral*	90°	
6	5	1	Square pyramidal	90°	
6	4	2	Square planar*	90°	
6	3	3	T-shape	90°	
6	2	4	Linear	180°	

- The **symmetrical shapes*** where all the **dipole cancelled out** are:
    - **Linear, trigonal planar, tetrahedral, trigonal bipyramid, octahedra**l and **square planar** if **all the outer atoms are the same**.
    - **Trigonal bipyramid** when the **axial contain one type of atoms** and **equatorial another type of atoms**.
    - **Square planar** when the **opposite side atoms are the same**.

Exercise of lewis diagram and molecular shape

1. For the following molecules or ions
    a. Draw the lewis diagram
    b. If appropriate, shape of molecule draw the possible isomers.
    c. For the molecules identify the polarity of the molecules (not ions)
        i. ICl_5
        ii. SF_4
        iii. XeF_2Cl_2
        iv. SO_3^{2-}
        v. PCl_4^{+}
        vi. SF_3^{+}
        vii. PO_4^{3-}

Attraction forces between particles

- All the substances attractions force from **CHEM 2.4** are assumed:
    - Metallic substance- **metallic bond (strong)**
    - Ionic substance- **ionic bond (strong)**
    - Covalent network- **covalent bond (Extremely strong)**
    - Molecular substance- **intermolecular force** also known as van der Waals forces **(weak)**
- There are three types of intermolecular forces with increase in strength
    - **Temporary dipole-dipole (instantaneous dipole) (aka van der waal force)**
        - As the size (number of contact points (length) of the molecule increases (increase in number of electrons), temporary dipole-dipole increases.
    - **Permanent dipole-dipole**
        - Attractions between slightly positive and slightly negative side of the molecules and slight positive side of the molecules.
    - **Hydrogen bonding**
        - Strong interaction between the nonbonding pair (in O, N or F) and hydrogen giving it extra stability.

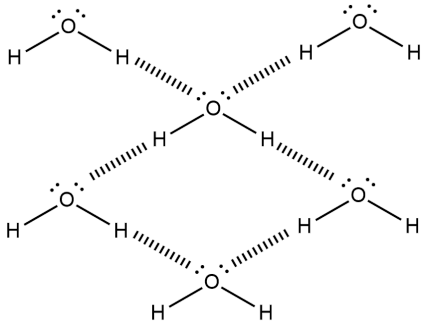


Figure 2.1- Hydrogen bonding of water.

- The strength of hydrogen bond is 10% of a covalent bond.

        - This attraction is directional with a particular bond angle
            - These are the attractions used to hold the DNA strands in a double helix.

	Temporary dipole-dipole	Permanent dipole-dipole	Hydrogen bonding
Nonpolar molecules	✓		
Polar molecules	✓	✓	
Molecules containing H-N, H-O or H-F	✓	✓	✓

- As the attraction force between the particle increases, the energy required to separate the particles increases.
- This results
    - A higher melting point, boiling point and sublimation point.
    - More energy is needed to change in phrases (states)
        - $\Delta_{fus}H$, enthalpy of **fusion** (melting) - at the melting point temperature.
        - $\Delta_{vap}H$, enthalpy of **vaporization** (boiling) - at the boiling point temperature.
        - $\Delta_{sub}H$, enthalpy of **sublimation** - at the sublimation point temperature.
- During phase change, the temperature does not increase as the energy used to increase the temperature is used to break the attraction force between the particles.

- $\Delta_{vap}H > \Delta_{fus}H$ because more energy is needed to separate the particle to from liquid to gas (vaporization) than from solid to liquid (fusion)

Exercise of attraction forces between particles

1. **Complete** and **discuss** the table below are of the second period of the periodic table.

	Li	**Be**	**B**	**C**	**N**	**O**	**F**	**Ne**
Structure			Giant covalent lattice					Discrete atom
$\Delta_{vap}H$ or $\Delta_{sub}H$*	136	309	540	715*	2.79	3.41	3.16	1.80
Electrical conductivity			no	Depending on structure				

Thermodynamics

There are three themes in this part of the standard

1. Definitions of enthalpy
2. Energy calculations
    a. Hess's law
    b. Specific heat energy
4. Enthalpy, entropy and Gibbs free energy

This part of the standard require calculations, see **p.1** for equations and definitions that are useful.

Definitions of enthalpy

***$\Delta_r H°$*, standard enthalpy of reaction, the enthalpy** when reactants and products are in their **standard state** (usually the state at 25°C).
For example: $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$ $\quad$ ***$\Delta_r H°$* (H_2O, ℓ) = –570 kJ mol^{-1}**
The term **mol^{-1}** means **per mole of reaction**, which is determined by the chemical equation;
ie 2 mol of H_2 reacting with 1 mol of O_2 to give 2 mol of H_2O.

***$\Delta_f H°$*, standard enthalpy of formation**, per mole of product.
Enthalpy change to **form (produce)** one mole of substance from its elements in standard state.

For example, the **standard enthalpy of formation** of liquid water:
$H_2(g) + ½\ O_2(g) \rightarrow H_2O(\ell)$ $\quad$ ***$\Delta_f H°$* (H_2O, ℓ) = –285 kJ mol^{-1}**

- **Note- By definitions the $\Delta_f H^o$ of any elements are zero**
- Here is another example

The standard enthalpy of formation of liquid ethanol C_2H_5OH
$2C(s) + 3H_2(g) + ½\ O_2(g) \rightarrow C_2H_5OH\ (l)$

***$\Delta_c H°$*, standard enthalpy of combustion**
Enthalpy change when one mole of substance is completely burnt in excess oxygen forming its oxides.
For example, the **standard enthalpy of combustion** of hydrogen gas to give liquid water:
$H_2(g) + ½\ O_2(g) \rightarrow H_2O(\ell)$ $\quad$ ***$\Delta_c H°$* (H_2, g) = –285 kJ mol^{-1}**
Another example of Standard enthalpy of combustion of glucose
$C_6H_{12}O_6(s) + 6O_2 \rightarrow 6CO_2(g) + 6H_2O(l)$
O_2 by definition has a ***$\Delta_c H°$* equal to zero**

***$\Delta_{fus} H$*, enthalpy of fusion** (melting)
Enthalpy change to turn one mole of solid to liquid at the melting point temperature
***$\Delta_{vap} H$*, enthalpy of vaporization** (boiling)
Enthalpy change to turn one mole of liquid to gas at the boiling point temperature
***$\Delta_{sub} H$*, enthalpy of sublimation**
Enthalpy change to turn one mole of solid to gas at the sublimation point temperature

Exercise for definitions of enthalpy

1. Write the equation for the standard enthalpy of formation of the followings
    a. Ethanoic acid $CH_3COOH(l)$

    b. Sodium chloride NaCl(s)

    c. Copper Nitrate $Cu(NO_3)_2(s)$

2. Write the equation for the standard enthalpy of the followings
    a. Combustion of propane $C_3H_8(g)$

    b. Combustion of ammonia $NH_3(g)$

    c. Combustion of ethanol $CH_3CH_2OH(l)$

Energy calculations

- Presumed knowledge from the content from **CHEM 2.4**
  - Stoichiometry
  - Bond enthalpy
- These are additional content for CHEM 3.4
  - Hess's Law
  - Specific heat energy

Hess's Law

- **Hess's Law** states that the 'energy change' due to chemical reaction is independent of the route taken.
  - The energy change depends only upon the nature of reactants and products and is the same whatever "pathway" is taken
  - This was shown in the bond energy calculation in **CHEM 2.4**

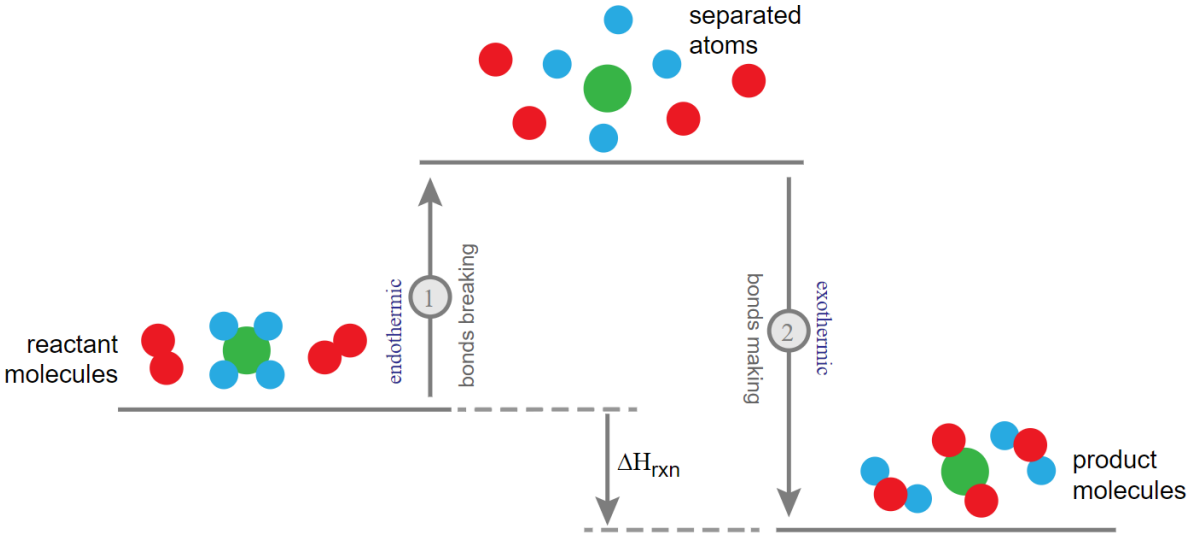
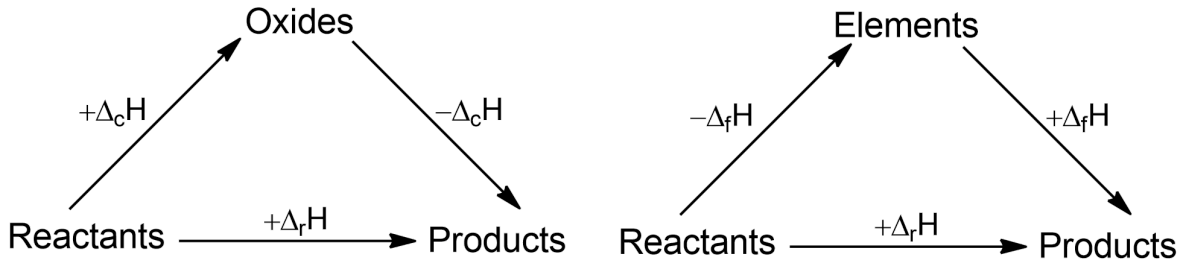


Figure 3.1 - Diagram for Bond Enthalpies[10]

  - In the diagram above, the pathway is reactants → atoms → products
  - Same concepts can be applied to $\Delta_f H°$ and $\Delta_c H°$.



- **In summary**
  - $\Delta_r H^o = \sum BE_{breaking} - \sum BE_{making}$ $\quad\quad$ $\Delta_r H^o = \sum BE_{reactants} - \sum BE_{products}$
  - $\Delta_r H^o = \sum \Delta_c H^o_{reactants} - \sum \Delta_c H^o_{products}$
  - $\Delta_r H^o = \sum \Delta_f H^o_{products} - \sum \Delta_f H^o_{reactants}$*
  - Same concepts can be applied to more complicated situations

[10] https://ch301.cm.utexas.edu/section2.php?target=thermo/thermochemistry/enthalpy-bonds.html accessed on 19/11/2017

- **Example of $\Delta_c H^o$ calculations**
  - With the $\Delta_c H^o$ given below, calculate the $\Delta_f H^o$ for $CH_3(CH_2)_3SH$.

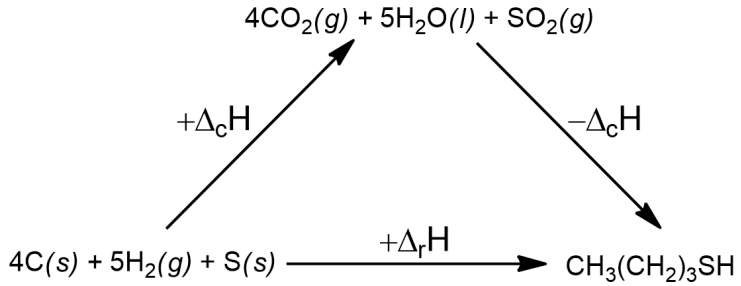
    $4C(s) + 5H_2(g) + S(s) \rightarrow CH_3(CH_2)_3SH$

    $\Delta_c H^o (C(s)) = -394$ kJ mol^{-1}

    $\Delta_c H^o (H_2(g)) = -286$ kJ mol^{-1}

    $\Delta_c H^o (S(s)) = -297$ kJ mol^{-1}

    $\Delta_c H^o (CH_3(CH_2)_3SH) = -3215$ kJ mol^{-1}
    - $\Delta_r H^o = \sum \Delta_c H^o_{reactants} - \sum \Delta_c H^o_{products}$



    - $(4 \times -394 + 5 \times -286 + -297)-(-3215) = -88.0$ kJ mol^{-1}

- **Example of $\Delta_f H^o$ calculations**
  - With the $\Delta_f H^o$ given below, calculate the $\Delta_c H^o$ for $NH_3(g)$

    $NH_3 + 1¼\ O_2 \rightarrow NO_2 + 1½\ H_2O$

    $\Delta_f H^o (NH_3(g)) = -46$ kJ mol^{-1}

    $\Delta_f H^o (NO_2(g)) = +33.18$ kJ mol^{-1}

    $\Delta_f H^o (H_2O(l)) = -286$ kJ mol^{-1}
    - $\Delta_r H^o = \sum \Delta_f H^o_{product} - \sum \Delta_f H^o_{reactant}$
    - $(+33.18 + 1½ \times -286) - (-46) =$

- **Example of more complicated Hess's Law example**
  - Using the following information, calculate the $\Delta_f H^o (CO(NH_2)_2(s))$

$2NH_3(g) + CO_2(g) \rightarrow CO(NH_2)_2(s) + H_2O(g)$ $\quad \Delta_r H^o = +5$ kJ mol^{-1}

$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g)$ $\quad \Delta_r H^o = -41$ kJ mol^{-1}

$½N_2(g) + 1½H_2(g) \rightarrow NH_3(g)$ $\quad \Delta_r H^o = -46$ kJ mol^{-1}

$C(s) + ½O_2(g) \rightarrow CO(g)$ $\quad \Delta_r H^o = -111$ kJ mol^{-1}

$C(s) + ½O_2(g) + N_2(g) + 2H_2(g) \rightarrow CO(NH_2)_2(s)$ $\quad \Delta_r H^o =$? kJ mol^{-1}

ANSWERS

$C(s) + ½O_2(g) \rightarrow$ ~~$CO(g)$~~ $\quad \Delta_r H^o = -111$ kJ mol^{-1}

$N_2(g) + 3H_2(g) \rightarrow$ ~~$2NH_3(g)$~~ $\quad \Delta_r H^o = 2 \times -46 = -92$ kJ mol^{-1}

~~$CO(g)$~~ + ~~$H_2O(g)$~~ $\rightarrow$ ~~$CO_2(g)$~~ + $H_2(g)$ $\quad \Delta_r H^o = -41$ kJ mol^{-1}

~~$2NH_3(g)$~~ + ~~$CO_2(g)$~~ $\rightarrow CO(NH_2)_2(s) +$ ~~$H_2O(g)$~~ $\quad \Delta_r H^o = +5$ kJ mol^{-1}

$C(s) + ½O_2(s) + N_2(g) + 2H_2(g) \rightarrow CO(NH_2)_2(s)$. $\quad \Delta_r H^o = -239$ kJ mol^{-1}

Specific heat energy

- The specific heat energy of water (c = 4.18 J g^{-1} $^oC^{-1}$) is the amount of energy (q in J) needed to 1 g of water by 1 ^oC.

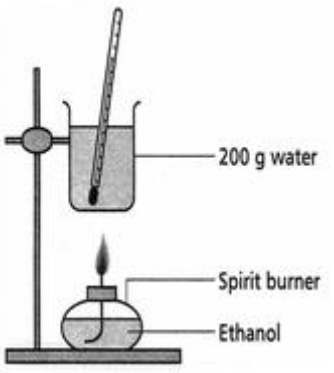
$$q = m\,c\,\Delta T$$

- **For example**
  - Calculate the amount of heat energy required to heat 200 g of pure water from 20 ^oC to its boiling point.
    - ΔT = 100 ^oC – 20 ^oC = 80 ^oC
    - m = 200 g
    - c = 4.18 J g^{-1} $^oC^{-1}$
    - $q = m\,c\,\Delta T$
    - q = 200 g × 4.18 J g^{-1} $^oC^{-1}$ × 80 ^oC = 66 880 J = 66.9 kJ (3 s.f.)

In calculation remember to change J to kJ by dividing it by 1000!!!

Exercise for energy calculation

1. An experiment was setup to determine the ***heat of combustion of ethanol***



A beaker containing 200 g of water at 22 ^oC was heated by the spirit burner with mass 184.5 g. The spirit burner was lit and used to heated. When the spirit burner was extinguished, the temperature of the water had reached 42 ^oC. The mass of the spirit burner was 184.3 g.

$M(CH_3CH_2OH)$ = 46.0 g mol^{-1}

200g x 20^oC x 4.18 $Jg^{-1}{}^oC^{-1}$ = 16720J = 16.72kJ that is absorbed by water
Meaning the reaction will release 16.72kJ
Mass of ethanol burnt is 184.5g - 184.3g = 0.2g
The amount of ethanol = 0.2g / 46.0 $gmol^{-1}$ = 4.35x10^{-3} mol
-16.72kJ / 4.35x10^{-3}mol = -3846 $kJmol^{-1}$ (4 s.f.)

2. Calculate the enthalpy of formation of propan-1-ol given the following information:
   $\Delta_c H^o$ ($C_3H_7OH(l)$) = -2021 kJ mol^{-1}
   $\Delta_f H^o$ ($H_2O(l)$) = -286 kJ mol^{-1} = $\Delta_c H^o(H_2)$
   $\Delta_f H^o$ ($CO_2(g)$) = -394 kJ mol^{-1} = $\Delta_c H^o(C)$

3. Use the following data to calculate $\Delta_c H^o$ ($C_2H_5OH(l)$).
   $\Delta_f H^o$ ($C_2H_5OH(l)$) = -1301 kJ mol^{-1}
   $\Delta_f H^o$ ($H_2O(l)$) = -286 kJ mol^{-1}
   $\Delta_f H^o$ ($CO_2(g)$) = -394 kJ mol^{-1}

Enthalpy & Entropy

- Entropy ΔS is the degree of randomness, the degree of disorder.
    - There are two types entropy to consider...
        - **Entropy of system, $\Delta S_{(system)}$ - The entropy of the change itself**
            - Examples one
                - $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$
                - **Reactants** has **four gas** particles and **product** has **two gas** particles.
                - **System decrease** in **randomness**, $\Delta S_{(system)}$ **= -'ve**
            - Example two
                - $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(l)$
                - **Reactants** has **one solid** and **six gas** particles and **product** as **six gas and six liquid** particles
                - **System increase** in **randomness**, $\Delta S_{(system)}$ **= +'ve**
        - **Entropy of surrounding, $\Delta S_{(surrounding)}$ - The entropy of the surroundings**
            - If reaction is **exothermic ΔH = -'ve** , the **temperature** of the **surrounding increases**.
                - The **particles** in the **surroundings** becomes **more random**.
                - Surrounding **increase** in **randomness**, $\Delta S_{(surrounding)}$ **= +'ve**
            - Vice-versa for endothermic reactions
    - The total entropies $\Delta S_{(Total)} = \Delta S_{(system)} + \Delta S_{(surrounding)}$
    - The second law of thermodynamic stated that in order for any changes to occur, the total disorder has to be increase.
    - When $\Delta S_{(Total)} > 0$**, reaction is spontaneous**
- As a result Gibbs free energy is defined as $\Delta G = \Delta H - T\Delta S_{(system)}$
- When ΔG **is negative**, a process will proceed **spontaneously**
- From the equation above
    - As the reaction becomes more exothermic (ΔH **= -'ve**) ($\Delta S_{(surrounding)}$ **increases)**, the reaction is **more spontaneous**.
    - As the **temperature increases**, the reaction is **more spontaneous**.
    - As the randomness increases (ΔS **= +'ve**), the reaction is **more spontaneous**.

Exercise for enthalpy, entropy and Gibbs free energy

The equation for the evaporation of liquid methanol is:

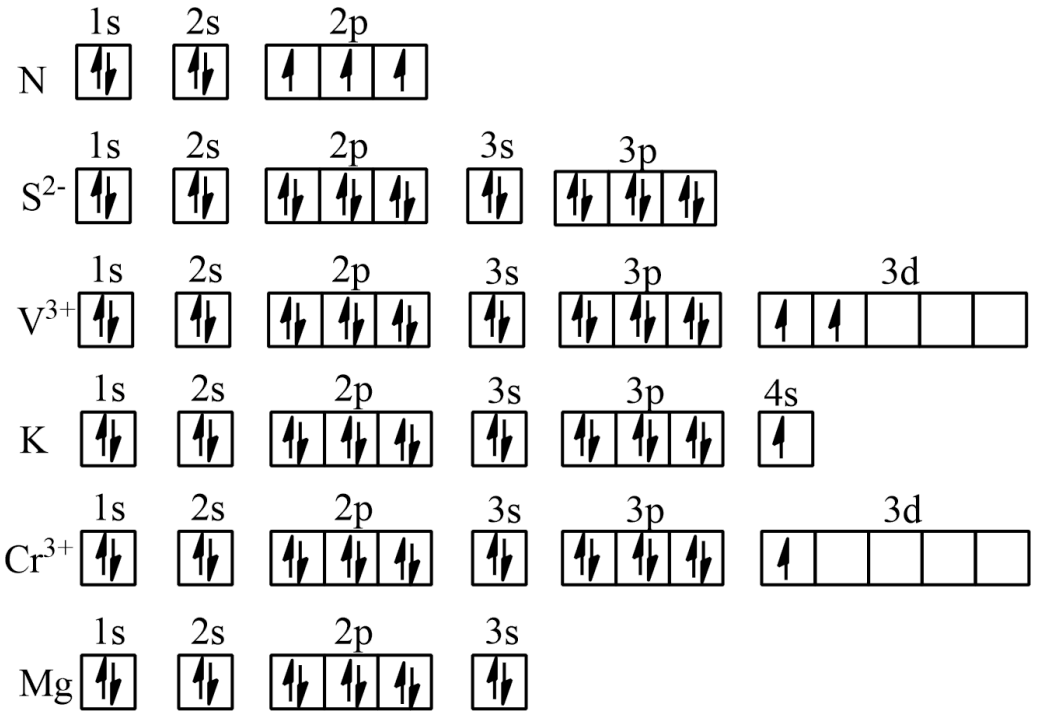
$$CH_3OH(l) \rightarrow CH_3OH(g)$$

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

Answers

Answers for s, p, d electron configurations

2. Write the electron configuration and orbital diagram (as figure 1.3) of the followings
    a. Nitrogen atom (N)
    $1s^2, 2s^2, 2p^3$
    b. Sulfide (S^{2-})
    $1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
    c. Vanadium (III) ion (V^{3+})
    $1s^2, 2s^2, 2p^6, 3s^2, 3d^2$
    d. Potassium atom (K)
    $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
    e. Sodium ion (Na^+)
    $1s^2, 2s^2, 2p^6$
    f. Chromium ion (Cr^{3+})
    $1s^2, 2s^2, 2p^6, 3s^2, 3d^3$
    g. Magnesium atom (Mg)
    $1s^2, 2s^2, 2p^6, 3s^2$



Answers for periodic table trend

1. Write the equation for the first ionisation of chlorine.

   $Cl(g) \rightarrow Cl^{+}(g) + e^{-}$

2. Explain why ionisation energy of an element is an endothermic reaction.

   Energy is needed to separate particles of the opposite charge. In this case, the negative outer electron and the positive nucleus.

3. Rank S, F and O with the increase of 1st ionisation energy. Justify your answer.
   Include electron configuration (s, p and d) in your answer.

   From highest to lowest, F > O > S
   1st ionisation energy is the energy required to remove an outer electron from one mole of gaseous atom. As the attraction between the outer electron increases, more energy is needed to remove the electron resulting a higher ionisation energy.
   The electron configuration of
   F is $1s^2$, $2s^2$, $2p^5$
   O is $1s^2$, $2s^2$, $2p^4$
   S is $1s^2$, $2s^2$, $2p^4$, $3s^2$, $3p^4$
   Comparing F and O, both atoms has the same outer energy level, 2p, meaning they have the same number of core electrons, meaning they have shielding. However there is one more proton in the F nucleus compared to O, therefore there is a strong attraction between the outer electron in F than O. Therefore F has a higher 1st ionisation energy is higher than O.
   Comparing O and S, the outer energy level for O is 2p and for S is 3p, although there are more proton in the S atom, there are also more shielding between the nucleus resulting O has a higher 1st ionisation energy than S.

4. Discuss the general trend of atomic and ionic radius across period 2. Justify your answers.

   Radius of an atom or ion is depending on the energy level of the particle as well as the nuclei charge of the particle. For atoms, across the period, the number of proton increases while the outer electron level remain the same, therefore atomic radius decreases across period 2. However for ionic radius, depending on the charge of the ion. For cation, since the energy level goes down a level, as a result, the ionic radius of a cation is smaller than the atom. On the other hand, for anion, since the number of electron increases, this increases the electron-electron repulsion in the smaller energy level. As a result, the anion radius is larger than its atom. As for general trend across the period, since the cation are isoelectric to each other, therefore as the proton number increases, the cations decreases in size across the across the period. Similarly for anion, since the anions are isoelectric, therefore it also decreases in size across the period.

5. Explain why on ***figure 1.8***, the electronegativity of Group XVIII (the inert gas) is not given.

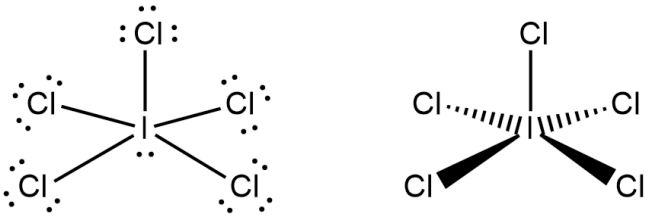
   Electronegativity is the ability of an atom to attracts electron in a chemical bond. Since Group XVIII (the inert gas) has a complete outer shell and it does not form chemical bonds normally, therefore, it has does not has electronegativity.

6. Predict the magnitude differences between the 1st, 2nd and 3rd ionisation energy of magnesium atom.

   The electron configuration of magnesium atom is $1s^2$, $2s^2$, $2p^6$, $3s^2$
   Between Mg^+ has an electron configuration of is $1s^2$, $2s^2$, $2p^6$, $3s^1$. Since the electron level is the same while the energy level is the same between Mg and $Mg^{+,}$, therefore only a small increase. However, Mg^{3+} has an electron configuration of $1s^2$, $2s^2$, $2p^5$. therefore the difference between the 1st and the 2nd ionisation energy is smaller than the 2nd and the 3rd ionisation energy.

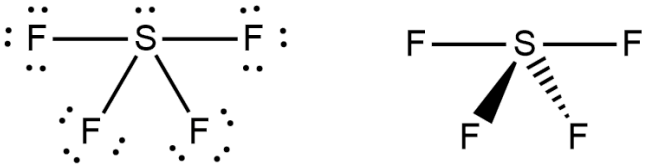
Answers of lewis diagram and molecular shape

2. For the following molecules or ions
   a. Draw the lewis diagram
   b. If appropriate, shape of molecule draw the possible isomers.
   c. For the molecules identify the polarity of the molecules (not ions)
      i. ICl_5



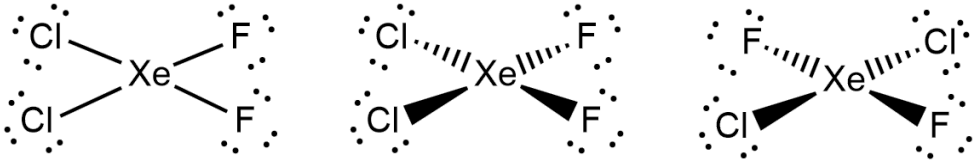
The shape is square pyramidal. The shape is asymmetrical, therefore it is polar.

      ii. SF_4



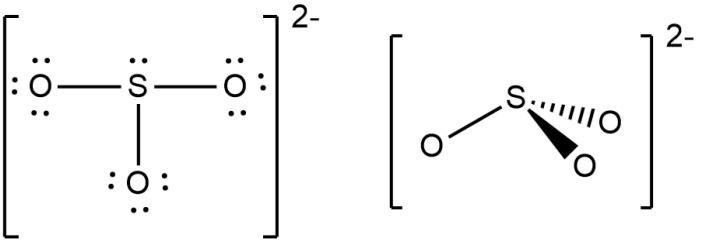
The shape is see-saw. The shape is asymmetrical, therefore it is polar.

      iii. XeF_2Cl_2



The shape is square planar, depending on the spatial arrangement of the molecules. If the Cl atoms are in the *cis* position then the molecule will be polar as the dipole does not cancelled out. On the other hand, if the Cl atoms are in the *trans* position, then the dipole cancelled out resulting in a non-polar molecule.

      iv. SO_3^{2-}



The shape is trigonal pyramidal. It is already charged as it is an ion.

Rest of the answer will come soon… sorry