# **CHEM 2.4**

Standard 91164 Demonstrate understanding of Bonding, Structure, Properties and Energy Changes

This standard should be taught after CHEM 2.1 as concepts of chemical calculations are involved. Click **here** for the NCEA page for this standard.

### Please read this document

This standard can be divided into 3 parts.

### 1. Structures of Solids and their properties

- a. Concept of solid lattice and physical properties
- b. Types of solids
  - i. Ionic solids
  - ii. Metallic solids
- c. Covalent network solids
  - i. Diamond and silicon dioxide
  - ii. Graphite
- d. Molecular solids

### 2. Molecular Substances

- a. Lewis diagrams and shapes of molecules
  - i. Lewis diagrams
  - ii. Shapes of molecules
- b. Polarity of bonds and molecules
  - i. Electronegativity, polarity of bonds
  - ii. Overall dipoles and polarity of molecules
  - iii. Water as a solvent

### 3. Thermodynamics

- a. Concept of exothermic and endothermic reactions
  - i. Concept of enthalpy
  - ii. Energy diagrams
- b. Enthalpy calculations
  - i. Stoichiometry
  - ii. Bond enthalpy

### Formulas involve\*

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

\* Formulas will not be given in any assessment

## Structure of Solids and their properties

There are two major themes in this part of standard:

- 1. Concept of Solid Lattice and Physical Properties
- 2. Types of Solids
  - a. Ionic solids
    - b. Metallic solids
    - c. Covalent Network solids
      - i. Diamond and Silicon Dioxide
      - ii. Graphite
    - d. Molecular solids

Note: This part of the standard require lots of writing.

## Concept of Solid Lattice and Physical Properties

- Solid is a physical state of a substance where the particles are arranged in a fixed regular position vibrating. This results in a 3D lattice.
- Physical properties of a substance are determined by the **types of particles** and the **attraction forces** holding the particles together.
  - Melting point
    - The **temperature** which provides enough energy to break the attraction force between the particles of the solid.
    - The stronger the attraction force between the particles, the more energy needed to break the attractions resulting a higher melting point.
  - Solubility
    - Ability for the **solute** to dissolves in a **solvent**
    - Substances are able to dissolves with each other when their attraction force is similar type
      - More will be explained in the **polarity section**.
  - Electroconductivity
    - The ability of a substance to conduct electrical current
    - In order for a substance to conduct electrical current, it requires movable charge particles within the substance (delocalised (free) electrons or ions)
  - Malleability and Ductility
    - Ability to change its shape by physical mean
    - In order for a substance to be malleable or ductile, the force between the particle has to be nondirectional.
  - Hardness
    - The ability to withstand forces
    - It requires strong directional force between the particles.

## Types of Solids

There are 4 common types of solids

- Ionic solids for ionic substance (compound made out of metals and nonmetals)
  - $\circ$  MgO, NaCl, CaCl<sub>2</sub> etc
- Metallic solids for metallic substance (elemental metals)
  - Mg, Zn, Fe etc
- Covalent network solids (network lattice formed by bonding of nonmetal atoms)
  o For CHEM 2.4 diamond, graphite and silicon dioxide
- Molecular solids for molecular substance (discrete molecules of nonmetal atoms)
  - $H_2O$ ,  $CO_2$ ,  $N_2$ ,  $O_2$  etc

## Ionic Solids

- **Ionic solids** are made out of **positive cations** and **negative anions** held **strongly** together by **electrostatic force** called **ionic bonds**.
- For Melting Point
  - Since the **force** between the particles (cation and anion) are **strong** therefore it requires **lots of energy to break**, as a result, ionic substance usually has a **high melting point**.
- For Electroconductivity
  - In an ionic solid, the electrons are "trapped" inside the ion and unable to be freely move within the solid, and since the ions are fixed position in the solid, therefore in solid, ionic substance does not conduct electricity.
  - However when the ionic substances are dissolved or molten, the ions will be free to move.
    Since by definition ions are charged particles, therefore when dissolved or molten, ionic substance are able to conduct electricity.

### • For Malleability

- When **external force applied** to an ionic lattice, the **ions** will be forced to move closer to the **ions of the same charge**.
- This movement causes repulsion between the ions of the same charge resulting a breakdown of the ionic lattice.
- As a result, ionic substance is brittle



Figure 2.1- When external force applied to an ionic lattice<sup>1</sup>

### For Hardness

- Ionic bonds are **directional**.
- Since the bond is **strong**.
- $\circ$   $\;$  It requires lots of energy to force the ions to change its position.
- Therefore, ionic solids are hard.

<sup>&</sup>lt;sup>1</sup> <u>http://saintschemistry10.weebly.com/ionic-bonding.html</u> accessed on 20/11/2017

## **Metallic Solids**

• Metallic solids are made out of metal atoms, where their valence electrons of the metal atoms interact with each other throughout the solid, and since there is always a lack of valence electrons to complete the outer shell, therefore the electron is delocalised. Metallic solid is often described as lattice cation in sea of delocalised electrons (see figure 2.2) The metal atoms held together strongly by electrostatic force between the cation and the delocalised electrons. This attraction is called metallic bonds.



Figure 2.2- Structure of ionic lattice<sup>2</sup>

- For Melting Point
  - Since the electrostatic forces between each metal atoms (cation and delocalised electrons) is strong, therefore it will require lots of energy to break. As a result, metallic substance usually have a high melting point.

### • For Electroconductivity

- The **electrons** are **free to move** within the metallic lattice.
- Therefore metallic substances are good electroconductor.
- For Malleability
  - Metallic bonds are **nondirectional bonds**.
  - When external forces applied, the attractions between the metal cation and delocalised electrons remains. (see figure 2.3)
  - As a result, metallic substances are malleable.



Figure 2.3- When external force applied to metallic substances<sup>3</sup>

#### • For Hardness

- Since metallic bond is nondirectional.
- Therefore metal is soft and required impurity to increase its hardness (such as carbon as an impurity for iron in steel)

<sup>&</sup>lt;sup>2</sup> <u>http://chemistry.tutorvista.com/physical-chemistry/metallic-bonding.html</u> accessed on 20/11/2017

<sup>&</sup>lt;sup>3</sup> <u>http://chemistry.tutorvista.com/physical-chemistry/metallic-bonding.html</u> accessed on 20/11/2017

## **Covalent Network Solids**

• Covalent Network Substances are made out of nonmetal atoms held extremely strongly together by covalent bonds (sharing electrons).

Diamond and Silicon Dioxide

- **Diamond** is made out of **carbon atoms**. Each **carbon atoms** are bonded to **four other carbon** atoms in a **tetrahedral shape**.
- Silicon dioxide is made out of silicon atoms and oxygen atoms. Each silicon atoms are bonded to four oxygen atoms and each oxygen atoms are bonded to two silicon atoms.
- In both cases, the covalent bonds are extremely strong and are directional.
- The strong covalent bonds results in a **very high melting point**.
- Since there are **no free moving charged particle** therefore diamond and silicon dioxide are **not electrical conductor** (insulator)
- Since this strong attraction is directional, therefore covalent network is extremely hard.



Figure 2.4- Structure of diamond (left) and silicon dioxide (right)

## Graphite

- Graphite is made out of carbon atoms. Each carbon atoms are bonded to three other carbon atoms in a trigonal planar shape resulting in a hexagonal carbon layer. The layers are held together by a weak attraction force due to the excess delocalised electrons. (see figure 2.5)
- The strong covalent bonds results in a very high melting point.
- The electrons between the layers are delocalised, therefore graphite is a good electroconductor.
- Since the **force between the layers** are **weak** and **nondirectional**, therefore **graphite is soft** as the **layers** are able to **slide past each other**.



Figure 2.5- Structure of graphite<sup>4</sup>

https://www.quora.com/Covalent-bonds-have-low-melting-and-boiling-points-But-why-do-diamond-and-graphite-havevery-high-melting-and-boiling-points accessed on 20/11/2017

Molecular Solids

 Molecular solids are made out of discrete molecules held together weakly by intermolecular force. (see figure 2.6)



Figure 2.6- Example of molecular solid (Ammonia NH<sub>3</sub>)

- For Melting Point
  - Since the attraction forces between the molecules (intermolecular force) are weak, therefore little energy required to overcome the attractions.
  - As a result, molecular solids has a low melting point.
- For Electroconductivity
  - Molecules are not charged and the electrons are trapped inside the molecules.
  - Therefore there are no free moving charged particle in a molecular solid.
  - As a result, molecular solid does not conduct electricity.
- For Malleability
  - Since the intermolecular force is weak, therefore molecular solids are brittle.

#### Exercises for concept of solid lattice and physical properties and types of solids

- 1. Identify the type of solid in the following substances
  - a. Copper metal
  - b. Calcium carbonate
  - c. Carbon dioxide
  - d. Diamond
- 2. Compare and contrast the electroconductivity between magnesium (Mg) and magnesium chloride (MgCl<sub>2</sub>)

3. Explain why Graphite is often used as a solid lubricant

4. Explain why carbon dioxide (CO<sub>2</sub>) has a low melting point whereas silicon dioxide (SiO<sub>2</sub>) has a extremely high melting point.

## Molecular substances

There are two themes in this part of the standard.

- Lewis diagrams and shapes of molecules
  - Lewis diagrams
  - Shapes of molecules
- Polarity of bonds and molecules
  - Electronegativity, polarity of bonds
  - Overall dipoles and polarity of molecules
  - Water as a solvent

## Lewis diagram and Shape of Molecules

- Molecular substances are made out of discrete molecules.
- Unlike ionic substance where electrons are transferred from one atoms to another to achieve full shell stability, in molecular substance, the nonmetal atoms are held together by sharing electrons.
- This attraction between the atoms are called covalent bonds, and this results in molecules.

## Lewis Diagrams

- 1. There are many ways to draw lewis diagram, I personally find the follow steps a quick and accurate way to draw lewis diagram.
  - 1. Calculate the total number of valence electrons.
  - Calculate the number of electrons needed to complete the outer atoms (Hydrogen = 2, the rest = 8)
  - 3. Step 1 Step 2 = number of nonbonding electrons in the central atom.
  - 4. Draw the molecule out with the number of nonbonding electron in the central atom and single bond with other atoms.
  - Create double bond until the central atom is filled (Boron = 6, the rest =8)
  - Filled the out atoms (Hydrogen = 2, the rest = 8)
- 2. For example: The lewis diagram of carbon dioxide (CO<sub>2</sub>)
  - 1. Total number of valence electron (C = 4, O = 6,  $4 + 6 \times 2 = 16$ )
  - 2. Electrons needed to complete outer atoms (2 × oxygen = 2 × 8 = 16)
  - 3. Step 1 Step 2 = 16 16 = 0 (no nonbonding electrons in the central atom.
  - 4.



Shape of Molecules

- The shape of molecules is determined by the number of electron clouds (regions of negative) in the central atoms.
- Since electrons clouds are negatively charged, therefore they repel each other to achieve maximum stability.
- The more electron clouds, the smaller the bond angle.
- All of the below contribute one single electron clouds.
  - $\circ$  Nonbonding electron pairs  $\cdots$
  - $\circ$  Single bond  $^{\scriptscriptstyle -}$
  - Double bond =
  - Triple bond ≡
- The table below is the list of shapes and their bond angle

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	180	0=00
3	3	0	Trigonal planar	120	
3	2	1	Bent (120)	120	0 <sup>0</sup> 0
4	4	0	Tetrahedral	109	
4	3	1	Trigonal pyramidal	109	0
4	2	2	Bent (109)	109	0,0000

- Regular line = on the plane of the paper
- Solid triangle = coming out of the page
- Dash triangle = going into the page ·····

## Polarity of Bonds and Molecules

- The word **polar** means **opposite ends**.
- In the case of bonds or molecules, this means **slightly charged ends** due to an **uneven distribution of electrons**.

## Electronegativity and Polarity of Bonds

- Electronegativity is the ability of an atom of an element to attracts electrons in a chemical bond.
- Electronegativity increases across (left to right) and decreases down in the periodic table.
  - Of all the elements, fluorine has the highest electronegativity.
  - Hydrogen has a low electronegativity.
- When atoms of **different elements** bonded together, there will be **difference in electronegativity** resulting in a **polar bond**.
- A polar bond results in a dipole  $(\Box)$  which is a force to "drag" electron in a particular direction.

## Overall Dipoles and Polarity of Molecules

- A polar molecules is a molecules that has a region of slightly positive (δ+) and slightly negative (δ-).
- This requires an overall dipole. This is caused by two factors:
  - The molecules contains **polar bonds**.
  - The **dipoles** from the polar bonds are **not cancelled out** because the shape of the molecules is **asymmetrical** (not symmetrical)
  - $\circ$   $\;$  In order for the molecules to be symmetrical it has to be:
    - One of these shapes
      - Linear, Trigonal planar or tetrahedral
    - And all outer atoms are identical.
- For example Methane (CH<sub>4</sub>) and Ammonia (NH<sub>3</sub>)



dipole cancelled out overall dipole

Figure 2.6- Polarity of methane and ammonia

Water as a solvent

- Because of its **polarity**, **water** is can **interact** with many **ionic compounds** making it a **very good solvent**.
- The **slightly negative** end of water (oxygen) is **attracted** to the **positive cation** (such as sodium) and the **slight positive** end of water (hydrogen) is **attracted** to the **negative anion** (such as chloride) (see figure 2.7)



Figure 2.7- Water dissolving sodium chloride<sup>5</sup>

- These attractions are strong enough to overcome the attraction between cation and anion in the ionic lattice, as a result, the ionic lattices is broken down into individual ions forming a solution.
- On the other hand, for **nonpolar substance**, it **requires nonpolar solvent** to dissolves because **nonpolar solute** do not **attract to polar solvent** and vice versa **polar (or ionic) solute** does not attract **nonpolar solvent**.
- Like dissolves like.
  - Polar dissolves in polar
  - Nonpolar dissolves in nonpolar

<sup>&</sup>lt;sup>5</sup> <u>http://ib.bioninja.com.au/standard-level/topic-2-molecular-biology/22-water/solvent-properties.html</u> acessed on 20/11/2017

### **Exercises for Molecular substances**

- 1) For the follow compounds
  - Draw the lewis diagram
  - Identify the shape of the molecule
    - Justify your answer
  - Identify the polarity of the compound
    - Justify your answer
- a) Hydrogen sulfide  $(H_2S)$

b) Sulfur dioxide (SO<sub>2</sub>)

c) Nitrogen (N<sub>2</sub>)

d) Methanal (CH<sub>2</sub>O)

## Thermodynamics

There are 2 major themes in this part of the standard:

- 1. Concept of Exothermic and Endothermic Reactions
  - a. Concept of Enthalpy
  - b. <u>Energy Diagrams</u>
- 2. Enthalpy Calculations
  - a. Stoichiometry
    - b. Bond Enthalpy

Note: This part of standard required calculations.

## Concept of Exothermic and Endothermic Reactions

## Concept of Enthalpy

- Each substances contains certain energy called **Chemical potential energy**.
  - When a reaction causes the **chemical potential energy to increase**, the reaction is called **Endothermic Reaction**.
  - Vice versa, a reaction causes the chemical potential energy to decrease, the reaction is called Exothermic Reaction.
- The amount of substances (mol) are important when it comes to chemistry, therefore, these changes of reaction are described as change in enthalpy ∆<sub>r</sub>H° with the unit kJ mol<sup>-1</sup> (change in energy (*E* in kJ) per amount (*n* in mol) of reaction)
  - The subscript r means reaction.
  - The superscript o means under standard conditions.
- The Enthalpy Values
  - In an **Endothermic Reaction**, chemical potential energy increases, therefore the change in enthalpy  $(\Delta_r H^\circ)$  would be **positive**.
  - On the other hand, in an **Exothermic Reaction**, since chemical potential energy decreases, therefore the change in enthalpy  $(\Delta_r H^\circ)$  would be **negative**.
- Because of the first law of thermodynamic (also known as the law of conservation of energy), When an Endothermic or Exothermic reactions occur, other form of energy is absorbed or released respectively.
- The concept of enthalpy can be applied to both physical change and chemical reaction.
  - For Physical Change
    - The changes in the kinetic energy of the particle is used to determine the enthalpy.
      - When the particles increase in kinetic energy and overcome the attraction force between the particles (for example melting), then the reaction is Endothermic △, H° = +'ve.
      - When the particles decreases in kinetic energy thus they form attraction force between the particles (for example freezing), then the reaction is exothermic △, H° = -'ve.
  - For Chemical Reaction

The changes in the surrounding energy such as heat is used to determine the enthalpy.

- When heat is being absorbed (decreases in temperature) that means increase in chemical potential energy, then the reaction is endothermic △,H° = -'ve.
- When heat is being released (increases in temperature) decreases in chemical energy (for example freezing), then the reaction is exothermic △, H° = +'ve.

## **Energy Diagrams**

- These change in energy can be expressed in a simple energy diagrams
  - A energy diagram should have the following features
    - x-axis Reaction Proceeds
    - y-axis Enthalpy (kJ mol<sup>-1</sup>)
    - Activation Energy
      - Energy needed to start the reaction
      - The change in y-axis from reactant to the top of the activation energy barrier
    - Labelled Reactants
    - Labelled Products
    - Enthalpy Change
      - The change in y-axis the reactant to product



Reaction proceeds

Reaction proceeds

Diagram 3.1 - Energy diagrams for Endothermic and Exothermic reactions

• Example

The energy diagram for the burning of methane gas (CH<sub>4</sub>)

 $\mathrm{CH_4} + \mathrm{2O_2} \rightarrow \mathrm{CO_2} + \mathrm{2H_2O}$ 



Reaction proceeds

#### Exercises for concept of Exothermic and Endothermic reactions

- (a) Instant cold packs are useful for treating sports injuries on the field. They contain salts such as ammonium nitrate,  $NH_4NO_3$ . When the packs are activated, the salt dissolves in water, causing the temperature to decrease.
  - (i) Is the reaction exothermic reaction or endothermic reaction?
  - (ii) Give a reason for your choice.
- (b) The equation for hydrating anhydrous copper sulfate is as follows:

$$CuSO_4(s) + 5H_2O(l) \rightarrow CuSO4.5H_2O(s)$$
  $\Delta_r H^\circ = -78.2 \text{ kJ mol}^{-1}$ 

- (i) Is the reaction exothermic reaction or endothermic reaction?
- (ii) Give a reason for your choice.

Enthalpy (kJmol<sup>-1</sup>)

(c) Draw, including labels, the energy diagram for the combustion (burning) of pentane,  $C_5H_{12}(l)$ . Pentane combustion:

 $C_5H_{12}(I)$  + 8 $O_2(g)$  → 5 $CO_2(g)$  + 6 $H_2O(I)$ Include in your diagram the reactants, products, and change in enthalpy.

Reaction proceeds

## **Enthalpy Calculations**

## Stoichiometry

- The change in enthalpy applies to the amount of reaction occurs
  - Change in enthalpy  $\Delta_r H^{\circ}$  is measured in kJmol<sup>-1</sup>
    - Change in energy (*E* in kJ) per amount (*n* in mole) of reaction
  - For example

 $Fe_2O_3(s) + 2AI(s) \rightarrow 2Fe(s) + AI_2O_3(s)$   $\Delta_r H^\circ = -852 \text{ kJ mol}^{-1}$ means the chemical potential energy decreased by 852 kJ when **one mole of Fe<sub>2</sub>O<sub>3</sub>** and

- two mole of AI is reacted forming two mole of Fe and one mole of AI<sub>2</sub>O<sub>3</sub>.
- $\circ$   $\;$  Here are the formulas needed

$$E = \Delta_r H^{\circ} \times n \ (kJ = kJ \ mol^{-1} \times mol$$
$$n = \frac{m}{M} \ (mol = \frac{g}{gmol^{-1}})$$
$$c = \frac{n}{V} \ (molL^{-1} = \frac{mol}{L})$$

- Note the final answer for CHEM 2.4 should be expressed in 3 significant figures (3s.f.).
- Example:

Using the reaction above, calculate the amount of energy release when 30.0 g of Aluminium powder (AI) is reacted with excess iron(III) oxide ( $Fe_2O_3$ ).

)

$$M(AI) = 27.0 \text{ g mol}^{-1}$$

The amount of Aluminium is

$$n = \frac{m}{M}$$
$$mol = \frac{30.0g}{27.0gmol^{-1}} = 1.11 mol$$

The ration between Aluminium and reaction is

- Therefore the amount of reaction would be 1.11 mol ÷2 = 0.556 mol
- Since the enthalpy of reaction Δ<sub>r</sub>H° = -852 kJ mol<sup>-1</sup>

$$E = \Delta_r H^\circ \times n$$
  
 
$$kJ = 852 \ kJ \ mol^{-1} \times 0.556 \ mol = -473 \ kJ \ (3s.f.)$$

 Therefore, there are 473 kJ of energy released, when 30.0 g of Aluminum powder is reacted with excess iron (III) oxide.

## Bond Enthalpy

- Since energy is needed to break attractions, therefore,
  - Bond Breaking is Endothermic,
  - Bond Making is Exothermic.
- Examples of bonds are:
  - Intermolecular forces between molecules,
  - Ionic bonds in an ionic lattice,
  - Metallic bonds in a metallic lattice,
  - Covalent bonds within a molecules.
- For molecular substances, each **covalent bond contains** a certain amount of **chemical potential energy** therefore the **enthalpy differences** between **total bonds breaking** and **total bonds making** would be the **change in enthalpy** as shown in the diagram below:



Figure 3.2 - Diagram for Bond Enthalpies<sup>6</sup>

- Bond enthalpy (BE) is the enthalpy change when one mole of bonds is broken.
  - Bond enthalpy is always positive as it is an Endothermic reaction.
  - Reactants break bonds to form atoms (1) and this process is Endothermic.
  - Atoms then make bonds to form products (2) and this process is Exothermic.
  - $\circ \quad \Delta_{\mathbf{r}} \mathbf{H}^{\mathbf{o}} = \sum \mathbf{B} \mathbf{E}_{\text{breaking}} \sum \mathbf{B} \mathbf{E}_{\text{making}}$
  - Example using the bond enthalpy values below, calculate the  $\Delta_{\mu}H$  for the reaction below.



hydrazine oxygen water nitrogen

*BE*<sub>(N-N)</sub> 158 kJmol<sup>-1</sup>, *BE*<sub>(N-H)</sub> 391 kJmol<sup>-1</sup>, *BE*<sub>(O=O)</sub> 498 kJmol<sup>-1</sup>, *BE*<sub>(O-H)</sub> 463 kJmol<sup>-1</sup>, *BE*<sub>(N=N)</sub> 945kJmol<sup>-1</sup>

 $\sum BE_{\text{breaking}} = 4 \times 391 \text{ kJ mol}^{-1} + 158 \text{ kJ mol}^{-1} + 498 \text{ kJ mol}^{-1} = 2220 \text{ kJ mol}^{-1}$   $\sum BE_{\text{making}} = 945 \text{ kJ mol}^{-1} + 4 \times 463 \text{ kJ mol}^{-1} = 2797 \text{ kJ mol}^{-1}$   $\Delta_{r}H^{\circ} = \sum BE_{\text{reactants}} - \sum BE_{\text{products}}$  $\Delta_{r}H^{\circ} = 2220 \text{ kJ mol}^{-1} - 2797 \text{ kJ mol}^{-1} = -577 \text{ kJ mol}^{-1}$ 

<sup>&</sup>lt;sup>6</sup> <u>https://ch301.cm.utexas.edu/section2.php?target=thermo/thermochemistry/enthalpy-bonds.html</u> accessed on 19/11/2017

#### **Exercises for Enthalpy calculation**

1. For the reaction

 $Fe_2O_3(s) + 2AI(s) \rightarrow 2Fe(s) + AI_2O_3(s)$   $\Delta_r H^\circ = -852 \text{ kJ mol}^{-1}$ Calculate the mass of iron(III) oxide needed to release 1000 kJ of energy with excess Aluminium.  $M(Fe_2O_3) = 160 \text{ g mol}^{-1}$ 

- Pentane, C<sub>5</sub>H<sub>12</sub>, is a liquid at room temperature. It evaporates at 36.1°C in an endothermic process.
  a. Explain why the evaporation of pentane is an endothermic process.
  - b. Using the bond energy values below, calculate the enthalpy change of the combustion (burning) of pentane.



Bond	Average bond enthalpy (kJmol <sup>-1</sup> )	Bond	Average bond enthalpy (kJmol <sup>-1</sup> )
C-C	346	C=O	799
C-H	413	0-н	463
0=0	495		