# **Unit 5: Energetics**

## 1. Introduction to Thermochemistry:

## **Thermochemistry**

Study of energy changes that accompanies physical, chemical and nuclear transformations of matter (energy + energy transfer)

## **Chemical Systems**

Set of reactants and products being studied and are often represented by chemical equations

## **Surroundings**

Matter around the system that is capable of absorbing/releasing energy (everything that is not a part of the chemical system)

#### **Types of Systems**

The goal is to achieve an isolated system where all of the matter/energy is kept inside

- Open (Matter + Energy can leave the system)
- Closed (only Energy)
- Isolated (No Matter + Energy can leave the system)

## **Physical Changes**

Change of state that require energy or releases energy. The energy required is used to break intermolecular bonds and the energy released comes from when bonds are formed.

## **Chemical Changes**

Breaking old chemical bonds and building new ones. The atoms within the molecules is also being rearranged.

## **Nuclear Changes**

Rearrangement of the nuclei of an atom and mass is converted into energy ( $E = mc^2$ ) and often produces lots of energy.

## **Strength of Reactions**

## Physics ≤ Chemical < Nuclear

Nuclear reactions will always produce more energy than both physical and chemical changes. However, physical and chemical reactions are on the same order of magnitude and some physical reactions have greater energy released than chemical reactions.

## **Types of Reactions:**

- Endothermic
  - Heat is required from the environment
  - Goes from lower physical states to higher (solid liquid, liquid gas, solid gas)
- Exothermic
  - Heat is released from the reaction
  - o Goes from higher physical states to lower (gas liquid, liquid solid, gas solid)
  - **a.** NaOH (s) =  $Na^+$  (aq) + OH<sup>-</sup> (aq) Exothermic (generally require more information)
  - **b.**  $H_2O$  (s) =  $H_2O$  (l) Endothermic (solid --> liquid)
  - c.  $2H_2O(l) = 2H_2(g) + O_2(g)$  Endothermic (liquid --> gas)
  - **d. NaOH (aq) + HCl (aq) = NaCl (aq) + H\_2O -** Exothermic (Neutralization is always exothermic)

#### 2. Heat & Heat Transfer

#### **Heat Transfer**

The transfer of heat between the system and its surroundings. The quantity of energy is dependent on the mass, change in temperature and the specific heat capacity. The specific heat capacity is defined as the amount of energy required or released to raise the temperature of a substance of a given quantity by one degree Celsius or kelvin.

Higher specific heat capacity means more energy is required to raise its temperature and more energy must be removed to lower its temperature.

It is given by the following:

$$q=mc_{
m sp}\Delta T$$

- q = Quantity of energy (Joules)
- m = Mass (Grams, Kilograms)
- ullet  $c_{
  m sp}=$  Specific heat capacity (Joules/gram  $^{
  m o}$ C, Kilojoules/kilogram  $^{
  m o}$ C)
- $\Delta T =$  Change in temperature ( $T_{\rm Final} T_{\rm Initial}$ )

#### **Latent Heat**

Latent heat is the amount of energy required to change the state of a specific mass of a substance but not change its temperature (Ex. melt 10g of ice into water).

It is given by the following equation:

$$q = mL$$

- q = Quantity of Energy (Joules)
- m = Mass (Grams, kilograms)
- ullet L= Latent Heat that is constant for every material (Joules/gram, Kilojoules/Kilogram)
  - 1. A sample of ethylene glycol, used in car radiators, has a mass of 34.8g. The sample liberates 783J of heat. If the initial temperature of the sample was 22.1°C, what is its final temp? The specific heat capacity of ethylene glycol is 2.42 J/g°C

• 
$$q = -783J$$

• 
$$m = 34.8g$$

• 
$$c = 2.42J/g^{o}C$$

• 
$$\Delta T = T_{\text{Final}} - T_{\text{Initial}}$$

• 
$$T_{
m Initial}=22.1^{o}C$$

$$egin{aligned} q &= mc\Delta T \ &= mc(T_{ ext{Final}} - T_{ ext{Initial}}) \ &T_{ ext{Final}} = rac{q}{mc} + T_{ ext{Initial}} \ &= rac{-783J}{34.8g imes 2.42J/g^{\circ}C} + 22.1^{\circ}C \ &= 12.8^{\circ}C \end{aligned}$$

2. A piece of metal with mass 149 g is heated to 98.0°C. When the metal is placed in 75.0g of water at 20.0°C, the temperature of the water rises by 28.5°C. What is the specific heat capacity of the metal?

• 
$$m_1 = 149g$$

• 
$$T_{\text{Initial}_1} = 98.0^{\circ}C$$

• 
$$m_2 = 75.0g$$

• 
$$T_{\text{Initial}_2} = 20.0^{\circ}C$$

$$ullet$$
  $\Delta T_2=28.5^oC$ 

$$egin{aligned} \Delta T_1 &= T_1 - (T_{ ext{Initial}_2} + \Delta T_2) \ &= 98.0^o C - (20.0^o C + 28.5^o C) \ &= 49.5^o C \ q &= mc \Delta T \ \\ m_1 c_1 \Delta T_1 &= m_2 c_2 \Delta T_2 \ &= 75.0 g \times 4.18 j/g^o C \times 28.5^o C \ &= 8934.75 j \ \\ 8934.75 j &= 149 g \times 49.5^o C \times c_1 \ c_1 &= 1.21 j/g^o C \end{aligned}$$

- 3. How much energy is needed to change 12 g of ice at 0.00 °C to 12 grams of water at  $0^{\circ}$ C (3.3 x  $10^{5}$  J/kg= heat of fusion of water)
  - m = 12g = 0.012kg
  - $L = 3.3 \times 10^5 j/g$

$$q = mL$$
 $= 0.012g \times 3.3 \times 10^{5} j/g$ 
 $= 3960$ 
 $= 3.96 \times 10^{3} j$ 

- 4. How much energy must be lost to change of 110.0 g of water at 0.00°C to 110.0 grams of ice at 0.00°C?
  - m = 110.0g = 0.110kg
  - $L = 3.3 \times 10^5 j/kg$

$$q = mL$$
 =  $0.110kg \times -3.3 \times 10^{5} j/kg$  =  $-11000$  =  $-1.1 \times 10^{4} j$ 

## 3. Calorimetry

## **Enthalpy**

Unlike heat, which contains only kinetic energy, enthalpy is the sum of both the kinetic and potential energy of a chemical reaction. It is denoted by the  $\Delta H$  sign.

- If the surrounding temperature increases : the potential energy has been converted into kinetic energy, hence the  $\Delta H$  is negative .
- If the surrounding temperature decreases : the kinetic energy has been converted into potential energy, hence the  $\Delta H$  is positive .

The magnitude of  $\Delta H$  scales with the coefficient of the reactants as more reactants will produce a greater change in enthalpy. The sign of the enthalpy identifies whether a reaction is endothermic or exothermic from the perspective of the chemical system.

## Calculate the $\Delta H$ to produce 1 mole of oxygen gas given:

$$egin{aligned} \mathrm{H_2O}\left(\mathrm{l}
ight) &\longrightarrow \mathrm{H_2}\left(\mathrm{g}
ight) + rac{1}{2}\,\mathrm{O_2}\left(\mathrm{g}
ight)\,\Delta\mathrm{H} = 285.8\,\mathrm{kJ} \ & \ 1\,\mathrm{Mole}\ \mathrm{of}\ \mathrm{O_2}\left(\mathrm{g}
ight) = 2\, imes rac{1}{2}\,\mathrm{O_2}\left(\mathrm{g}
ight) \ & \ = 285.8\,\mathrm{kJ}\, imes 2 \ & \ = 571.6\,\mathrm{kJ} \end{aligned}$$

Enthalpy can also be included as a term in a balanced chemical equation. However, you cannot have a negative enthalpy value in a chemical equation, instead, it should be moved to the other side of the equation.

- Endothermic: Reactants + Energy = Product
- Exothermic: Reactants = Product + Energy

Possible subscripts to  $\Delta H$  for different types of reactions include:

- $\Delta H_{combustion}$
- $\bullet \ \Delta H_{freezing}$
- $\Delta H_{rxn}$  or  $\Delta H_{reaction}$
- $\Delta H_{lattice}$
- $\bullet \ \Delta H_{vaporization}$
- $\Delta H_{neutralization}$

## **Standard Molar Enthalpy**

The enthalpy required to carry out one mole of reaction under SATP conditions (not STP).

#### **SATP vs STP Conditions:**

The standard ambient temperature and pressure (SATP) indicates that a reaction occurs at 25°C or 298K and 100kPa (not 101.3 kPa). However, standard temperature and pressure (STP) conditions are 0°C or 273K and 100kPa.

## **Standard Enthalpy of Reaction**

The standard enthalpy of reaction is the enthalpy of a reaction that takes into account the following:

- Energy required to change the reaction from SATP to initiate the reaction
- Energy released during the reaction
- Energy released following the reaction as the products are cooled to SATP conditions

### **Energy/Reaction Profile**

The visual representation of the changes in the chemical and potential energy between reactants and products. The graph should have reaction progress (or time if done experimentally) as the x-axis and the change in Enthalpy (kJ/J) as its y-axis. Ensure that each reaction also has a hump that is required to initiate the reaction and enthalpy is measured from the starting value, not the top of the hump. Arrows are used to indicate the direction of the reaction.

#### **Calorimetry**

Inorder to study energy changes, an isolated system is ideally needed. Calorimeter is an instrument used for studying energy changes. It should be insulated, keeps the matter in and reduces heat lost/gained from the surroundings. The variable measured in a calorimeter is usually water (with 4.184  $J/g^{\circ}C$ ) and the temperature change between the start and end of the reaction is determined so that the enthalpy can be measured.

$$q_{\rm H2O} = -\Delta H_{\rm rxn}$$

An calorimetry experiment can be conducted with the following steps:

- 1. Find the heat transfer of the water  $(q_{H_2O})$
- 2. Set  $\Delta \mathrm{H}_{\mathrm{rxn}} = -\mathrm{q}_{\mathrm{H}_2\mathrm{O}}$
- 3. Convert to molar enthalpy or leave as is

Inorder to experimentally determine the enthalpy change through the use of calorimetry, certain assumptions must be made:

- All the energy released/absorbed by the system is transferred to/from the surroundings within the calorimeter (however, the percentage is dependent on the different calorimeters)
- No energy is transferred between the calorimeter and the environment (sufficient insulation)
- Calorimeter does not absorb/release energy
- Dilute aqueous solution is assumed to have a density and specific heat capacity equal to that of water at  $4.184 \text{ J/g}^{\circ}\text{C}$ .

## **Coffee Cup Calorimeter**

Basic calorimeter that is sufficient for measuring enthalpy change in dissolving, neutralization, heating, cooling among other basic chemical reactions. However, it cannot measure the heat transfer in a combustion reaction. A coffee cup calorimeter has the following components:

- Insulated container with lid (generally a coffee cup)
- Water
- Thermometer
- Stirrer
- Reactant

#### **Bomb Calorimeter**

Designed to measure the enthalpy change in a combustion reaction. Has an isolated "bomb chamber" made out a metal with very low specific heat capacity (ex. copper) that allows the heat from the reaction to easily transfer to the water surroundings. A bomb calorimeter h as the following components:

- Insulated container with lid
- Bomb chamber
- Water
- Thermometer
- Stirrer

## **Data Processing of Experimental Calorimetry**

Experimentally, the data collected from a calorimeter will have inaccuracies. The data collected from the experiment can be graphed in a reaction profile with the x-axis being the reaction progress and y-axis being the temperature.

- Reaction start: when the temperature start increasing/decreasing
- Reaction end: highest/lowest point (furthest away from starting)

Inorder to correct for the energy lost/gained, it is assumed that it is constant. Therefore, a straight line can be drawn through the energy lost/gain and extrapolate back to the start of the reaction to get the final temperature if the container had perfect insulation (note: if the reaction did not start at the axis, do not extrapolate back to the axis, only to where the reaction started)

1. In a calorimetry experiment, 7.46g of potassium chloride is dissolved in 100.0ml of water at an initial temperature of 24.1°C. The final temperature of the solution is 20.0°C. What is the molar enthalpy of solution of potassium chloride?

```
• m_{water} = 100.0 \, g
```

• 
$$T_{water-initial} = 24.1^{\circ}C$$

• 
$$T_{water-final} = 20.0^{\circ}C$$

• 
$$c_{water} = 4.18 \, J/g^{o}C$$

• 
$$m_{KCl} = 7.46 g$$

$$q_{
m water} = {
m mc}\Delta T$$

$$= 100.0\,{
m g}\, imes 4.18\,{
m J/g}^o{
m C}\, imes (20.0\,{
m ^oC} - 24.1\,{
m ^oC})$$

$$= -1713.8\,{
m J}$$

$$\Delta H_{\rm rxn} = -q_{\rm water}$$

$$= 1713.8\,{
m J}$$

$$= 1713.8\,{
m J}$$

$${
m Molar Mass KCl} = 39.10\,{
m g/mol} + 35.45\,{
m g/mol}$$

$$= 74.55\,{
m g/mol}$$

$$= 7.46\,{
m g}$$

$$= 0.100\,{
m moles}$$

$$74.55 \,\mathrm{g/mol}$$
 = 0.100 moles.  $\frac{1713.8 \,\mathrm{J}}{0.100 \,\mathrm{moles}} = 17138 \,\mathrm{J}$  = 17.1 kJ

- 2. In a chemistry experiment to investigate the properties of a fertilizer, 10.0g of urea, NH2CONH2(s) is dissolved in 150ml of water in a simple calorimeter. A temperature change from 20.4°C to 16.7°C is measured. Calculate the molar enthalpy of solution for the fertilizer urea.
  - $m_{water} = 150 g$
  - $T_{\text{water-initial}} = 20.4^{\circ}\text{C}$
  - $T_{\text{water-final}} = 16.7^{\circ}\text{C}$
  - $c_{water} = 4.18 \, J/g^{o}C$
  - $\bullet \ m_{urea} = 10.0\,g$

$$m q_{water} = mc\Delta T$$
 =  $150\,{
m g}\, imes4.18\,{
m J/g}^{
m o}{
m C}\, imes(16.7^{
m o}{
m C}-20.4^{
m o}{
m C})$  =  $-2319.9\,{
m J}$  
$$\Delta H_{rxn} = -{
m q}_{water}$$
 =  $2319.9\,{
m J}$  Molar Mass NH $_2$ CONH $_2 = 4\, imes1.01+2\, imes14.01+12.01+16.00 =  $60.07\,{
m g/mol}$$ 

$$\frac{2319.9 \,\mathrm{J}}{0.167 \,\mathrm{moles}} = 13935.64 \,\mathrm{J}$$
$$= 13.9 \,\mathrm{kJ}$$

 $\frac{10.0\,\mathrm{g}}{60.07\,\mathrm{g/mol}} = 0.167\,\mathrm{moles}$ 

#### 4. Hess Law

#### Hess's Law

The absolute enthalpy change is a state function and it is the same between reactants and products regardless of the steps taken to reach it. Therefore, it also indicates that the enthalpy change is additive seen in the following equation:

$$\Delta H_{reaction}^{\theta} = \sum \Delta H_{f\,of\,Products}^{\theta} - \sum \Delta H_{f\,of\,product}^{\theta}$$

It also states that the enthalpy change to go from products to reactants is the reverse enthalpy change of the reactants to products.

$$\Delta ext{H}^{ heta}_{ ext{products}} = -\Delta ext{H}^{ heta}_{ ext{reactants}}$$

$$\Delta ext{H}_{ ext{reactants}}^{ heta} = -\Delta ext{H}_{ ext{products}}^{ heta}$$

Usually within a Hess's Law question, they will give you

## **Enthalpy Cycles**

Enthalpy cycles are visual representations of Hess's Law. They have arrows that indicate the transformation of between the reactants, intermediate steps until the final product has been reached.

## **Standard Enthalpy of Formation**

The standard enthalpy of formation of quantity of energy associated with the formation of oenomel of a substance from its elements in their standard state. The units of standard enthalpy of formation is kj/mol. The formula for the standard enthalpy of formation is:

$$\Delta H_{rxn} = \sum \Delta H_{f ext{-product}}^{ heta} - \sum \Delta H_{f ext{-reactant}}^{ heta}$$

If the products of the reaction is identical to reactants then there is no net enthalpy change.

$$\mathrm{H_{2}\left( \mathrm{g}
ight) \longrightarrow H_{2}\left( \mathrm{g}
ight) }\Delta \mathrm{H_{f}^{ heta}}=0$$

$$\mathrm{Br}_{2}\left(\mathrm{l}
ight)\longrightarrow\mathrm{Br}_{2}\left(\mathrm{l}
ight)\Delta\mathrm{H}_{\mathrm{f}}^{ heta}=0$$

It is good to keep in mind the di-atomic molecules which can be memorized using HOFBrINCI (Hydrogen, Oxygen, Fluorine, Bromine, Iodine, Nitrogen, Chlorine) The product of a standard enthalpy of formation always has a coefficient of one. There should also never be a compound on the reactants side and every reactant should be in its standard state. Choose coefficient for the reactant to yield exactly one mole of products.

$$C\left(s\right)+O_{2}\left(g\right)\longrightarrow CO_{2}\left(g\right)$$

$$H_{2}\left(g\right)+rac{1}{2}\,O_{2}\left(g
ight)\longrightarrow H_{2}O\left(l
ight)$$

$$C(s) + 2H_2(g) + \frac{1}{2}O(2)(g) \longrightarrow Ch_3OH(g)$$

All of the reactions of formation are assumed to occur at SATP conditions and the state of the elements can be memorized as follows. The only two elements that are in liquid form at SATP is Mercury and Bromine. The gases are: Hydrogen, Nitrogen, Oxygen, Fluorine, Chlorine and all of the Noble Gases.

## **Bond Enthalpies**

Another application of Hess's Law can be used to determine the enthalpy change of a reaction from the bond enthalpy of the reactants and products. The breaking of chemical bonds requires energy from the surroundings, making it an endothermic process. The reverse is true for the formation of chemical bonds, as it releases energy into the surroundings, making it a exothermic process.

$$\operatorname{Cl}_2\left(\mathrm{g}
ight)\longrightarrow 2\operatorname{Cl}\left(\mathrm{g}
ight)\Delta \mathrm{H}^{ heta} = +242\,\mathrm{kJ/mol}$$

$$\mathrm{H}\left(\mathrm{g}\right) + \mathrm{H}\left(\mathrm{g}\right) \longrightarrow \mathrm{H}_{2}\left(\mathrm{g}\right) \Delta \mathrm{H}^{\, heta} = -\,436\,\mathrm{kJ/mol}$$

The bond enthalpy of an element is the amount of energy required to break 1 mole of a given bond when the reactants and products are in a gaseous state. The bond enthalpy values found in the data booklet is always given as average values as the exact bond enthalpy depends on the molecular environment in which the bond exists in.

For example,  $\mathrm{CH_4}$  has different exact bond enthalpy than  $\mathrm{CHF_3}$  because Fluorine is more electronegative hence changes the  $\mathrm{C-H}$  bond enthalpy.

$$\Delta H = \sum Energy$$
 to break reactant bond  $-\sum Energy$  to brak product bond

## 1. Calculate the heat of reaction for:

$$PbCl_{2}(s) + Cl_{2}(g) \longrightarrow PbCl_{4}(l)$$

Given:

$$Pb(s) + Cl_2(g) \longrightarrow PbCl_2(s) \Delta H = -359.4 kJ$$
 (1)

$$Pb\left(s\right) + 2\operatorname{Cl}_{2}\left(g\right) \longrightarrow Pb\operatorname{Cl}_{4}\left(l\right)\Delta H = -329.3\,\mathrm{kJ} \tag{2}$$

**Solution:** 

$$\begin{split} PbCl_{2}\left(s\right) &\longrightarrow Pb\left(s\right) + Cl_{2}\left(g\right) \, \Delta H = 359.4 \, kJ \\ \\ PbCl_{2}\left(s\right) + Pb\left(s\right) + 2 \, Cl_{2}\left(g\right) &\longrightarrow Pb\left(s\right) + Cl_{2}\left(g\right) + PbCl_{4}\left(l\right) \, \Delta H = -688.7 \, kJ \\ \\ PbCl_{2}\left(s\right) + Cl_{2} &\longrightarrow PbCl_{4}\left(l\right) \, \Delta H = -688.7 \, kJ \end{split}$$

#### 2. Calculate $\Delta H$ for the following reaction:

$$4 \, \text{NH}_3 \, (\text{g}) + 5 \, \text{O}_2 \, (\text{g}) \longrightarrow 4 \, \text{NO} \, (\text{g}) + 6 \, \text{H}_2 \, \text{O} \, (\text{g})$$

Given:

$$egin{aligned} \mathrm{N_2\left(g
ight)} + \mathrm{O_2\left(g
ight)} &\longrightarrow 2\,\mathrm{NO\left(g
ight)}\,\Delta\mathrm{H} = -180.5\,\mathrm{kJ} \ \\ \mathrm{N_2\left(g
ight)} + 3\,\mathrm{H_2\left(g
ight)} &\longrightarrow 2\,\mathrm{NH_3\left(g
ight)}\,\Delta\mathrm{H} = -91.8\,\mathrm{kJ} \ \\ 2\,\mathrm{H_2\left(g
ight)} + \mathrm{O_2\left(g
ight)} &\longrightarrow 2\,\mathrm{H_2O\left(g
ight)}\,\Delta\mathrm{H} = -483.6\,\mathrm{kJ} \end{aligned}$$

**Solution:** 

$$2\,\mathrm{N_2}(\mathrm{g}) + 2\,\mathrm{O_2}(\mathrm{g}) \longrightarrow 4\,\mathrm{NO}(\mathrm{g})\,\Delta\mathrm{H} = -361\,\mathrm{kJ}$$
  $4\,\mathrm{NH_3} \longrightarrow 2\,\mathrm{N_2}(\mathrm{g}) + 6\,\mathrm{H_2}(\mathrm{g})\,\Delta\mathrm{H} = 183.6\,\mathrm{kJ}$   $6\,\mathrm{H_2}(\mathrm{g}) + 3\,\mathrm{O_2}(\mathrm{g}) \longrightarrow 2\,\mathrm{H_2O}(\mathrm{l})\,\Delta\mathrm{H} = 571.6\,\mathrm{kJ}$   $4\,\mathrm{NH_3}(\mathrm{g}) + 5\,\mathrm{O_2}(\mathrm{g}) \longrightarrow 4\,\mathrm{NO}(\mathrm{g}) + 6\,\mathrm{H_2O}(\mathrm{g})\,\Delta\mathrm{H} = -1628.2\,\mathrm{kJ}$ 

## 3. Calculate $\Delta H$ for the following reaction:

$$2 H_2(g) + 2 C(s) + O_2(g) \longrightarrow C_2 H_5 OH(l)$$

Given:

$$\begin{split} \mathrm{C_2H_5OH}\left(l\right) + 2\,\mathrm{O_2}\left(g\right) &\longrightarrow 2\,\mathrm{CO_2}\left(g\right) + 2\,\mathrm{H_2O}\left(l\right)\,\Delta\mathrm{H} = -875\,\mathrm{kJ} \\ \\ \mathrm{C}\left(s\right) + \mathrm{O_2}\left(g\right) &\longrightarrow \mathrm{CO_2}\left(g\right)\,\Delta\mathrm{H} = -394.51\,\mathrm{kJ} \\ \\ \mathrm{H_2}\left(g\right) + \frac{1}{2}\,\mathrm{O_2}\left(g\right) &\longrightarrow \mathrm{H_2O}\left(l\right)\,\Delta\mathrm{H} = -285.8\,\mathrm{kJ} \end{split}$$

**Solution:** 

$$\begin{split} 2\,\mathrm{CO_2}(\mathrm{g}) + 2\,\mathrm{H_2O}(\mathrm{l}) &\longrightarrow \mathrm{C_2H_5OH}(\mathrm{l}) + 2\,\mathrm{O_2}(\mathrm{g})\,\Delta\mathrm{H} = 875\,\mathrm{kJ} \\ \\ 2\,\mathrm{C}(\mathrm{s}) + 2\,\mathrm{O_2}(\mathrm{g}) &\longrightarrow 2\,\mathrm{CO_2}(\mathrm{g})\,\Delta\mathrm{H} = -789.2\,\mathrm{kJ} \\ \\ 2\,\mathrm{H_2}(\mathrm{g}) + \mathrm{O_2}(\mathrm{g}) &\longrightarrow 2\,\mathrm{H_2O}(\mathrm{l})\,\Delta\mathrm{H} = -571.6\,\mathrm{kJ} \\ \\ 2\,\mathrm{H_2}(\mathrm{g}) + 2\,\mathrm{C}(\mathrm{s}) + \mathrm{O_2}(\mathrm{g}) &\longrightarrow \mathrm{C_2H_5OH}(\mathrm{l})\,\Delta\mathrm{H} = -486\,\mathrm{kJ} \end{split}$$

## 5. Born Haber Cycle

## **Born Haber Cycles:**

Diagrammatic representation of the formation of an iconic compound and is the sum of a series of processes which are to be done in the following order:

- 1. Convert the elements from their standard state (at SATP) to their gaseous state (  $\Delta H_{atom})$
- 2. Break the elements down to their individual atoms ( $\Delta H_{Bond\ Enthalpy}$ )
- 3. The less electronegative element will lose its electrons to form a cation ( Ionization Energy)
  - If the element loses more than one electrons, the total energy required would be the sum of the first and second ionization energy
  - The values of the first ionization energies can be found in Table 8 of the data booklet, second ionization energy must usually be provided in the question as it can not be found in the data booklet.
- 4. The other element will gain the electron to become an anion (Electron Affinity)
  - Same with ionization energy, the electron affinity of the second electron would be the sum of the first and second electron affinity values
  - The values of the first electron affinity energy is found in the same table (Table 8) and only the second electron affinity value for Sulfur and Oxygen are provided, others will also have to be provided within the question
- 5. Gaseous ions come together to form the final compound is known as the lattice enthalpy

In a question, you can be expected to be provided with the following information:

- $\Delta \mathbf{H}_f^{\theta}$ : S.E of formation
- $\Delta H_{atomization}^{ heta}$ : S.E of atomization
  - o For metals, this value must be given
  - o For non-metals, use bond enthalpy
- $\Delta H_{\mathrm{ionization}}^{ heta}$ : S.E of ionization
- $\Delta H_{affinity}^{ heta}$ : S.E of electron affinity

### **Standard Enthalpy of Atomization**

The enthalpy change required to change one mole of an element from its standard state at SATP to one mole of its gaseous state and is labelled as  $\Delta H_{\rm atomization}$ . The values are generally provided within the question.

$$Na(s) \longrightarrow Na(g)$$

$$Br_2(s) \longrightarrow Br(g)$$

## **Electron Affinity**

The enthalpy change when one mole of gaseous atoms gain electrons to form a mole of negatively charged gaseous anion. The enthalpy change when the first electron is gained is known as the first electron affinity and this value could be positive or negative. The second electron affinity is the enthalpy when the second electron is gained and is always a positive value. This is because since the atom is already negative, it requires energy to add another electron

$$A(g) + e^{-} \longrightarrow A^{-}(g)$$

$$A^-(g) + e^- \longrightarrow A^{2-}(g)$$

## **Ionization Energy**

The enthalpy change for one mole of gaseous atoms of an element to lose electrons to form one mole of positively charged cations. The enthalpy change when the first electron is lost is known as the first ionization energy and the second electron lost is the second ionization energy. All of the ionization energies will always be a positive value.

$$Q(g) \longrightarrow Q^+ + e^-$$

$$\mathrm{Q^+}(\mathrm{g}) \longrightarrow \mathrm{Q^{2+}} + 2\,\mathrm{e^-}$$

## **Lattice Enthalpy**

The formation of ionic compounds involves oppositely charged gaseous ions coming together to form an ionic lattice. This is always an exothermic process because there is strong attraction between the oppositely charged ions. Lattice enthalpy also provides a quantitative measurement to the stability of an ionic solid (greater the lattice enthalpy the greater the stability)

$$\mathrm{Na}^{+}(\mathrm{g}) + \mathrm{Cl}^{-}(\mathrm{g}) \longrightarrow \mathrm{NaCl}(\mathrm{s})$$

The lattice enthalpy value is affected by:

• Ionic Size:

Lattice enthalpy decreases as ionic radius increases because weaker attraction as distance between the nucleus and the valence electron increases. Increased charge separation decreases attraction between ion given the same difference in sizes.

• Ionic Charge:

Lattice enthalpy increases as the magnitude of charge difference increases which will be demonstrated by an equation below given the same approximate ionic radii

## **Actual vs Theoretical Lattice Enthalpy:**

The lattice enthalpy is given by the following equation where the numerator is the charge difference between the positive cation and the negative anion and the denominator is the radius of the two ions.

$$\Delta ext{H}_{ ext{lattice}}^{ heta} \ lpha rac{ ext{(charge} + ext{)(charge} - ext{)}}{ ext{(R^+)} + ext{(R-)}}$$

There is a difference between the theoretical lattice enthalpy value and the actual lattice enthalpy value because the theoretical value is calculated assuming 100% ionic character it is really rare for actual elements to have perfect ionic character. The biggest the covalent character, the bigger the difference between the theoretical and actual value.

## Enthalpy of Solution ( $\Delta H_{sol}^{\theta}$ ):

Enthalpy change when one mole of a solute is dissolved in a solvent to infinite dilution (where there is a sufficiently large excess of water that adding more water does not cause any further heat to be absorbed or evolved) under standard conditions.

$$\mathrm{NH_4Cl}(\mathrm{s}) \longrightarrow \mathrm{NH_4}^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq})$$

## Enthalpy of Hydration ( $\Delta H_{hyd}^{\theta}$ ):

Enthalpy of hydration of an ion is the enthalpy change that occurs when one mole of gaseous ions is dissolved to form an infinitely dilute solution of one mole of aqueous ions under standard conditions.

$$Na^{+}(g) \longrightarrow Na^{+}(aq)$$

Hydration enthalpy is dependent on the ionic radius and ionic charge given as follows where increasing ionic radius results in a decrease in hydration enthalpy and the larger the charge the greater the enthalpy change.

$$\Delta ext{H}_{ ext{hyd}}^{ heta} lpha^- \, rac{ ext{An}}{ ext{R}_{ ext{ionic}}}$$

n = Ionic Charge

$$R_{ionic} = Ionic Radius$$

## Relationship between Hydration and Solution Enthalpy:

The enthalpy of solution is given by the sum of the hydration enthalpy of the two ions and the lattice enthalpy.

$$\Delta ext{H}_{ ext{sol}}^{ heta} = \Delta ext{H}_{ ext{lat}}^{ heta} + \Delta ext{H}_{ ext{hyd(Na}^+)}^{ heta} + \Delta ext{H}_{ ext{hyd(Cl}^-)}^{ heta}$$

1. Construct an enthalpy cycle for Calcium Chloride, showing the lattice enthalpy.

$$\Delta H_{atom} = 178 \, kJ/mol$$

$$\Delta \mathrm{H}_f \, \mathrm{CaCl}_2 = -796 \, \mathrm{kJ/mol}$$

$$\Delta H_{\rm 2nd~ionization}~Ca = 1150\,kJ/mol$$

$$\Delta 
m H_{Lattice} = 796\,kJ/mol + 178\,kJ/mopl + 590\,kJ/mol + 1150k\,J/mol - 2\, imes 349\,kJ/mol$$
  $= 2016\,kJ/mol$ 

## 6. Spontaneity

## **Spontaneity:**

Spontaneity predicts whether or not a reaction will occur under certain conditions

• Spontaneous: Will occur without adding energy beyond that required to overcome the activation energy barrier

• Non Spontaneous: Need energy to be invested to do work

## Entropy ( $\Delta S$ ):

The entropy value given by S increases in a spontaneous process and remains unchanged in an equilibrium process. The change in entropy of a reaction is given by the difference between the final and initial entropy of the elements:

$$\Delta S = S_{\rm final} - S_{\rm intitial}$$

$$\Delta S_{\mathrm{rxn}}^{\, heta} = \, \sum \mathrm{n}_p \, \mathrm{S}^{\, heta}(\mathrm{products}) - \, \sum \mathrm{n}_p \, \mathrm{S}^{\, heta}(\mathrm{reactants})$$

- ullet  $\Delta S>0$ : The system becomes more disordered
  - Mixing different types of particles (forming a solution)
  - $\circ$  Change in state where the distance between the particles increases (Ex. solid  $\longrightarrow$  Gas)
  - Increase in movement of particles (heating liquid or gas)
  - Increasing the number of particles
  - The greatest entropy change usually occurs when the number of particles in gaseous state increases
- ullet  $\Delta S < 0$ : The system becomes more ordered

#### **Absolute Entropy**

Unlike enthalpy, the absolute entropy value of a system can be determined. Tabulated entropy values at SATP conditions is represented as  $S^{\theta}$ . The absolute entropy values can be found in the data booklet.

## Gibbs Free Energy ( $\Delta G$ ):

Gibbs free energy is the energy associated with a chemical reaction or process that is available to do work and the change in Gibbs Free Energy  $\Delta G^{\theta}$  measures the free-energy change for a reaction under standard conditions when reactants are converted to products in their standard states.

- $\Delta G < 0$ : The reaction is spontaneous (exergonic)
- $\Delta G = 0$ : The reaction is in equilibrium
- $\Delta G > 0$ : The reaction is nonspontaneous (endergonic)

Gibbs Free Energy is given by the following equation:

$$\Delta G = \Delta H - T \Delta S$$

$$\Delta \mathrm{G}_{\mathrm{rxn}}^{\, heta} = \, \sum \mathrm{n}_p \, \Delta \mathrm{G}_f^{\, heta} \, (\mathrm{products}) - \, \sum \mathrm{n}_r \, \Delta \mathrm{G}_f^{\, heta} \, (\mathrm{reacants})$$