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* 1. **Introduction**

Thermochemistry is concerned with energy and heat accompanying a chemical reaction, physical transformations or both processes. During such changes, energy is either absorbed or given out. For example, the chemical reaction between hydrogen and oxygen gases during the formation of water is exothermic. However, the heat of vapourization of water is endothermic. Thermochemistry study these energy changes, particularly on the system‘s energy exchange with its surroundings. The heat that flows across the boundaries of a system ( to the surrounding) undergoing a change is a fundamental property that characterizes the process. Thermochemistry offers a quantitative method of measuring the heat and enthalpy changes in a system during reaction or phase transition.

Thermochemistry has some basic advantages. First it can be used, along with other thermodynamic parameters to predict the spontaneity or feasibility of a given reaction. Based on the exchange \*of heat between the system and the surrounding, chemical reactions can be classified into two, namely, exothermic and endothermic reactions. Endothermic reactions absorb heat from the surrounding while exothermic reactions release heat to the surrounding.

Thermochemistry offers a method of identifying exothermic or endothermic reaction through the bond energy of the reactant and that of the products. We shall see in this section that the heat of formation of an ionic compound can be estimated through the knowledge of reaction enthalpies of the various steps, into which the main reaction can be subdivided.

* 1. **Thermochemical equations**

In thermochemistry, some features of ordinary chemical reactions are modified. The following examples and highlights differentiate between ordinary chemical equation and thermochemical equations:

1. In thermochemical reactions, the physical state of the reactant and the products must be indicated. For example

**Ordinary chemical equation**: 2 H2 + O2→ 2 H2O 1

**Thermochemical reaction**: 2 H2(g) + O2(g)→ 2 H2O(l) 2

1. The heat change accompanying the reaction must be indicated. For example,

**Ordinary Chemical equation**: 2 H2 + O2→ 2 H2O 3

**Thermochemical equation**: 2 H2(g) + O2(g)→ 2 H2O(l) Δ*H* = –572 kJ 4

In the above thermochemical equation, the enthalpy change during the reaction is -572 kJ/mol. The negative sign of the enthalpy change indicates that the reaction is exothermic. If the sign of

the enthalpy change is positive (as in the equation below). It means that the reaction is endothermic:

H2O(l)  H2O(g) Δ*H* = 40.7 kJ 5

In the first example, 572 kJ of heat is given off to the surrounding but in the second example,

40.7 kJ of heat is absorbed from the surrounding. The quantity 40.7 is known as the *enthalpy of vaporization* (often referred to as ―heat of vaporization‖) of liquid water.

1. If we multiply or divide the reactant by a factor, the product and the enthalpy change must also be multiplied by the same factor. For example, if we divide equation 4 by a factor of 2, we will have,

H2(g) + ½O2(g)→ H2O(l) Δ*H* = – 286 kJ 6

1. The standard states as well as properties involved in the reaction must be represented. For example,

H2O(l, 373 K, 1 atm) → H2O(g, 373 K, 1 atm) Δ*H0* = 40.7 kJ mol–1 7

The above equation shows that the standard state of water at 1 atm is the solid below 273 K, the liquid between 273 and 373 K and the gas above 373 K. A thermochemical quantity such as Δ*H* that refers to reactants and products in their standard states is denoted by *ΔH0.* The standard state of a substance is the most stable state of that substance. For example, hydrogen gas, oxygen gas and graphite are the most stable states of hydrogen, oxygen and carbon and these are their respective standard states. If the reaction is taking place in solution, the concentration of the dissolved species must be specified. For example, the neutralization of water

H+(*aq*, 1M, 298 K, 1 atm) + OH–(*aq*, 1M, 298 K, 1 atm) →H2O(*l*, 373 K, 1 atm) Δ*H* = —56.9

kJ mol–1

Generally, since most thermochemical equations take place at standard conditions. specification of temperature, pressure is not necessary, provided. Thus for the above reaction, we can represent is as,

H+(*aq*) + OH–(*aq*) →H2O(*l*) Δ*H0* = —56.9 kJ mol–1 8

# Standard enthalpies of reactions

As stated earlier, the enthalpy change for a chemical reaction is the difference between the enthalpy of the product and that of the reactant, thus,

Δ*H* = *Hproducts – Hreactants* 9

If the reaction under consideration is for the formation of one mole of the compound from its elements in their standard states, the enthalpies of the elements can be set at zero and the heat of formation will become, *Hf ° =* Σ*Hf °products –* Σ*Hf °reactants*= Δ*H*– 0 . For example, in the following reaction, 2 H2(g) + O2(g)→ 2 H2O(l) *Hf ° =* Σ*Hf °products –* Σ*Hf °reactants*= -582– 0 = -586 kJ, which defines the *standard enthalpy of formation* of water at 298K.The value *Hf* ° = –586 kJ tells us that when hydrogen and oxygen, at a pressure of 1 atm (respectively) and at 298 K react to form 1 mol of liquid water at 25°C and 1 atm pressure, 586 kJ will be given out to the surrounding. The negative sign indicates that the reaction is exothermic and that the enthalpy of the product is smaller than that of the reactants. Therefore, the standard enthalpy of formation of a compound is defined as the heat associated with the formation of one mole of the compound from its elements in their standard states. In general, the *standard enthalpy change for a reaction* is given by ΔΣ*Hf °products –* Σ*Hf °reactants* . where ΔΣ*Hf °products* and Σ*Hf °reactants* are the sum of the standard enthalpies of formations of all products and reactants reapectively. This definition allows us to predict the enthalpy change of any reaction once the standard enthalpies of formation of the products and reactants are known.

# Standard enthalpy of formation

Standard enthalpy of formation is the enthalpy change associated with the formation of one mole of the substance at standard temperature and pressure. In estimating the enthalpy of formation, the following information must be taken into consideration.

1. The thermochemical equation defining standard enthalpy of formation must be written in terms of one mole of the substance in question. For example,

N2(g) + 3H2(g)→ 2NH3(g) Δ*H*° = –92.2 kJ 10

The above equation shows that 1 mol of N2 gas react with 2 mol of H2 gas to form 2 mol of ammonia in an exothermic reaction, liberating 92.2 kJ of heat. This enthalpy change does not represent the standard enthalpy change since it is not the enthalpy change associated with the formation of 1 mol of ammonia. In order to write the thermochemical equation that shows the standard enthalpy change for the formation of ammonia, we divide the entire equation by a factor of 2, thus

½ N2(g) + 3/2 H2(g)→ NH3(g) Δ*H*° = –46.1 kJ (per mole of NH3) 11

1. The standard heat of formation of a compound should be considered based on the most stable form of the compound at 237 K and at 1 atmospheric pressure. This means for elements that exhibit allotropy, the most stable allotrope should be considered when defining standard enthalpy of formation of a compound involving such elements. For example, carbon can exist as diamond or graphite and the formation of CO2 from each of these allotropes leads to the release of -393.5 and 395.8 kJ/mol of heat respectively (as shown in the equations below). However, since graphite is the most stable allotrope, the standard heat of formation of CO2 will refer to the reaction involving graphite and not diamond

C(graphite) + O2(g) → CO2(g) Δ*H°* ≡ *Hf °* = –393.5 kJ mol–1 12

C(diamond) + O2(g) → CO2(g) Δ*H°* = –395.8 kJ mol–1 13

1. If the product is not the stable one at 273 K, the physical state of the product must be indicated in the thermochemical equation representing standard enthalpy change. For example, water exists in gaseous and liquid states and the enthalpy changes for the two states are as shown in the equations below. However, the one associated with water in the aqueous phase is normally taken for standard enthalpy change.

H2(g) + ½ O2(g) → H2O(aq) Δ*H°* ≡ *Hf °* = –285.8 kJ mol–1 14

H2(g) + ½ O2(g) → H2O(g) Δ*H°* = –241.8 kJ mol–1 15

It is significant to note that the differences in enthalpy value between the two states is -44 kJ/mol and this represents the heat of vaporization of water.

1. The standard enthalpy change for the formation of most compounds are negative (i.e exothermic) but there are cases where the enthalpy change is positive. By convention, such endothermic process is expected to represent instability but there are some endothermic compounds that are stable.
2. Thermochemical equations representing the enthalpy change of the formation of some compounds may not be feasible. For example, direct reaction of graphite (carbon) with hydrogen gas, does not give methane as simplified in the equation below:

C(graphite) + 2H2(g) → CH4(g) 16

1. The standard enthalpy change associated with the formation of gaseous atom from the element is called heat of atomization. Heats of atomization are always positive and they are very useful in the calculation of bond energies.
2. The standard enthalpy of formation of ions dissolved in water cannot be measured because this solution has several kinds of ions dissolved in it. Therefore, the general convention is to adopt a scale in which the enthalpy change of the H+(aq) is defined as zero. Therefore ionic enthalpies are expressed such that *Hf*° of the hydrogen ion at *unit activity* (1 M effective concentration) is defined as zero, as shown in the equation below,

½H2(g) → H+(aq) Δ*H°* ≡ *Hf °* = 0 kJ mol–1 17

Based on this, the enthalpy of formation of other ionic compounds can be calculated by combining it with the above equation. For example, in the formation of HCl, H2 gas combine with Cl2 gas as shown below:

½H2(g) + ½Cl2(g) → HCl(aq) Δ*H°* ≡ *Hf °* = –167 kJ mol 18

Since the enthalpy for the formation of H+(aq) is zero, the enthalpy for the formation of HCl is - 167 kJ/mol.

# Laws of thermochemistry

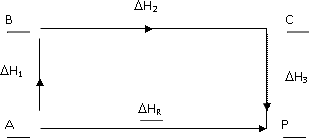
Thermochemistry is based on the framework of two major laws, namely: Hess law and Laplace law. These laws are essential because they aid in thermochemical calculations.

The first thermochemical law was formulated by Hess in 1840. Germain Henri Hess (1802-1850) was a Swiss-born professor of chemistry at St. Petersburg, Russia. This principle, known as *Hess’ law of independent heat summation* is a direct consequence of the enthalpy being a state

function. Hess‘ law is one of the most powerful tools of chemistry. It allows the change in the enthalpy (and in other thermodynamic functions) of huge numbers of chemical reactions to be predicted from experimental data. ***Hess law states that the overall enthalpy of a chemical reaction is the sum of the enthalpies of the various steps into which the reaction can be subdivided***.

Let us consider a chemical reaction leading to the formation of a product C and the enthalpy of reaction is HR. If the different steps that bring about the product are A to B, B to C and C to P, characterised with enthalpies, H1, H2 and H3 . Then according to Hess law, HR = H1 +

H2 +H3. This concept is demonstrated in the diagram shown below



# Bond enthalpy

Chemical bonds hold compounds together. This maybe electrovalent or covalent. Most often, the reactants have their individual bonds associated with it. Therefore, before they can react, bonds have to be broken and before products formation, new bonds must be formed Bonds are broken in the reactants while new bonds are formed in the products. Bond enthalpy is the energy needed to break bond in gaseous molecules under standard condition. Due to some complications that may arise in using actual values of bond enthalpy, average bond enthalpies are often used. For example, water consists of two OH bonds and it has been found that the energy needed to break the first O-H bond is significantly higher than the energy needed to break the second O-H bond. Also, the energy needed to break OH bond in molecule such as ethanol is quite different from the energy needed to break the O-H bond in water and other molecules. Hence the use of average bond enthalpy is justified.

Let us consider the bond enthalpy associated with the breaking of H and O bonds in water and hydroxyl.

𝐻2(g) → 𝐻(g) + 𝑂𝐻(g) ∆𝐻0 + 502 𝑘𝐽/𝑚𝑜𝑙

𝑂(g) → 𝐻(g) + 𝑂(g) ∆𝐻0 + 427 𝑘𝐽/𝑚𝑜𝑙

𝐻2(𝑔) → 𝐻(𝑔) + 𝐻(𝑔) + 𝑂(𝑔) ∆𝐻0 (502 + 427) 𝑘𝐽/𝑚𝑜𝑙 = 929 𝑘𝐽/𝑚𝑜𝑙

Therefore, the average bond enthalpy for O-H is 929/2 = 464.50 kJ/mol. The average bond enthalpies and the corresponding bond lengths for some bonds are presented in the Table 2. All bond energies are obtained in the gaseous state so that the enthalpy change associated with the breaking and formation of intermolecular force can be eliminated.

Bond breaking is an exothermic process while the formation of new bond is an endothermic process. The amount of energy absorbed during the formation of bond is the same as the amount of energy liberated during the breaking of bond. This is the consequence of the second law of thermochemistry (i.e Laplace law), which states that the enthalpy change needed for the formation of a compound is the same as the enthalpy change (but with reverse sign) needed for the decomposition of the compound.

In the course of breaking bonds in the reactants and the formation of new bonds in the products the difference between the bond energies of the reactants and that of the products represents the enthalpy change of the reaction. That is,

𝐻 = ∑(𝑏𝑜𝑛𝑑 𝑏𝑟𝑒𝑎𝑘i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠 )– ∑(𝑏𝑜𝑛𝑑 ƒ𝑜𝑟𝑚i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠)

Therefore, when ∑(𝑏𝑜𝑛𝑑 𝑏𝑟𝑒𝑎𝑘i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠 ) > ∑(𝑏𝑜𝑛𝑑 ƒ𝑜𝑟𝑚i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠), the reaction is endothermic and when ∑(𝑏𝑜𝑛𝑑 𝑏𝑟𝑒𝑎𝑘i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠 ) < ∑(𝑏𝑜𝑛𝑑 ƒ𝑟𝑚i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠) , the reaction is exothermic. Bond breaking involves separation of atoms that were bonded in a molecule indicating that energy is required (i.e endothermic reaction). However bond forming involves bringing the atoms that are bonded by electrostatic attraction, hence energy is released.

# Table 2: Average bond enthalpy and bond length for some bonds

|  |  |  |
| --- | --- | --- |
| **Bond** | **Average bond enthalpy (kJ/mol)** | **Bond length (10-9 m)** |
| H-H | 436 | 0.074 |
| C-C | 347 | 0.154 |
| C=C | 612 | 0.134 |
| C-H | 413 | 0.108 |
| O=O | 498 | 0.121 |
| O-H | 464 | 0.096 |
| C=O | 746 | 0.120 |
| Cl-Cl | 243 | 0.199 |

**Solved problem 1**

Calculate the enthalpy change for the combustion of propane, which occurs according to the following equation,

𝐶3𝐻8(g) + 5𝑂2(g) → 3𝐶𝑂2(g) + 4𝐻2𝑂(g)

Given, ∆𝐻0(𝐶3𝐻8(g)) = −104.63 𝑘𝐽/𝑚𝑜𝑙, ∆𝐻0(𝐶𝑂2(g)) = −393.67 𝑘𝐽/𝑚𝑜𝑙,

ƒ ƒ

∆𝐻0(4𝐻2𝑂(𝑙)) = −287.20 𝑘𝐽/𝑚𝑜𝑙

ƒ

# Solution

The standard enthalpy change of formation of an element in its most stable form is zero. There is no chemical change and so no enthalpy change when an element is formed from itself. Therefore ∆𝐻0(𝑂2(g)) is zero. Generally, the enthalpy change of the reaction is the difference between the enthalpy change of the product and that of the reactant. That is,

ƒ

∆𝐻0 = ∑ ∆𝐻0 − ∑ ∆𝐻0

𝑟𝑒𝑎𝑐𝑡i𝑜𝑛

𝑃𝑟𝑜𝑑𝑢𝑐𝑡

𝑅𝑒𝑎𝑐𝑡𝑎𝑛𝑡

=[ 3(-393.67) + 4(-287.20)] – [-104.63] kJ/mol = ( -1181.01- 1148.80) + 104.3

= -2225.51 kJ/mol

# Solved problem 2

Given the following bond energies (in KJ/mol) ,calculate the heat of combustion of propene. C=C = 613, C-C = 349, O=O = 496, O=C = 744, O-H = 464 and C-H = 452

# Solution

The equation for the combustion is

𝐶𝐻3𝐶𝐻 = 𝐶𝐻2 +

The change in enthalpy is given as,

9

2 𝑂2 → 3𝐶𝑂2 + 3𝐻2𝑂

∆𝐻 = ∑(𝑏𝑜𝑛𝑑 𝑏𝑟𝑒𝑎𝑘i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠 )– ∑(𝑏𝑜𝑛𝑑 ƒ𝑜𝑟𝑚i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠)

**Bond breaking energies are**, 6C-H bonds = 6 x 456

C=C bond =1 x 613

4.5O=O bond = 4.5 x 498

∑(𝑏𝑜𝑛𝑑 𝑏𝑟𝑒𝑎𝑘i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠 ) = 6(456) + 613 + 4.5(498) = 5590 𝑘𝐽/𝑚𝑜𝑙

Bond forming energies are 6C=O = 6 x 744 = 4464 kJ/mol

6O-H = 6 x 464 = 2784 kJ/mol

∑(𝑏𝑜𝑛𝑑 ƒ𝑜𝑟𝑚i𝑛𝑔 𝑒𝑛𝑒𝑟𝑔i𝑒𝑠 ) = 4464 𝑘𝐽/𝑚𝑜𝑙 + 2784 𝑘𝐽/𝑚𝑜𝑙 = 7248 𝑘𝐽/𝑚𝑜𝑙

∆𝐻 = (5590 − 7248)𝐽/𝑚𝑜𝑙 = −1658 𝑘𝐽/𝑚𝑜𝑙

# Solved problem 3

Given the following thermochemical equations,

3

𝑆 + 𝑂

→ 𝑆𝑂

∆𝐻𝜃 = −396 𝑘𝐽/𝑚𝑜𝑙

(𝑠) 2 2(g)

3(g)

𝑆𝑂

1

+ 𝑂

→ 𝑆𝑂

∆𝐻𝜃 = −99 𝑘𝐽/𝑚𝑜𝑙

2(g) 2 2

3(g)

Calculate the standard enthalpy change for the reaction, (𝑠) + 𝑂2(g) → 𝑆𝑂2(g)

# Solution

The second equation can be reversed and be added to the first equation as follows;

𝑆𝑂

→ 𝑆𝑂

1

+ 𝑂

∆𝐻𝜃 = +99 𝑘𝐽/𝑚𝑜𝑙

3(g)

3

𝑆 + 𝑂

2(g)

2

→ 𝑆𝑂

2(g)

∆𝐻𝜃 = −396 𝑘𝐽/𝑚𝑜𝑙

(𝑠)

2 2(g)

3(g)

(𝑠) + 𝑂2(𝑔) → 𝑆𝑂2(𝑔) ∆𝐻𝜃 = (99 − 396)𝑘𝐽/𝑚𝑜𝑙 = −297 𝑘𝐽/𝑚𝑜𝑙

# Solved problem 4

Given the under listed thermochemical equations, calculate the standard enthalpy change for the reaction, 2𝐶(𝑠) + 2𝐻2(g) → 𝐶2𝐻4(g)

(𝑠) + 𝑂2(g) → 𝐶𝑂2(g) ∆𝐻𝜃 = −395 𝑘𝐽/𝑚𝑜𝑙 1

𝐻 + 1 𝑂

→ 𝐻 𝑂

∆𝐻𝜃 = −287 𝑘𝐽/𝑚𝑜𝑙 2

2(g)

2 2(g)

2 (g)

𝐶2𝐻4(g) + 3𝑂2(g) → 2𝐶𝑂2(g) + 2𝐻2𝑂(g) ∆𝐻𝜃 = −1416 𝑘𝐽/𝑚𝑜𝑙 3

# Solution

The first step requires, reversing equation 3 and then multiplying equations 1 and 2 by a factor of

2. The three equations are then added together as follows,

2(𝑠) +  ~~2𝑂~~~~2(g)~~ → ~~2𝐶𝑂~~~~2(g)~~ ∆𝐻𝜃 = −790 𝑘𝐽/𝑚𝑜𝑙 1

2𝐻2(g) +  ~~𝑂~~~~2(g)~~ → 2~~𝐻~~~~2~~𝑂~~(g)~~ ∆𝐻𝜃 = −574 𝑘𝐽/𝑚𝑜𝑙 2

~~2𝐶𝑂2(g)~~ + ~~2𝐻2~~𝑂~~(g)~~ → 𝐶2𝐻4(g) +  ~~3𝑂2(g)~~ ∆𝐻𝜃 = 1416 𝑘𝐽/𝑚𝑜𝑙 3

2(𝑠) + 2𝐻2(𝑔) → 𝑪2𝐻4(𝑔) ∆𝐻𝜃 = (−790 − 574 + 1416)𝑘𝐽/𝑚𝑜𝑙

= 52 𝑘𝐽/𝑚𝑜𝑙

# Solved problem 5

Calculate the entropy change associated with the follow/ing reaction. Given that the entropy data for C2H4, H2 and C2H6 are 219.56, 130.92 and 229.87 J/K/mol respectively. Based on the equation for the reaction, reconcile the expected direction of the entropy change with the calculated

𝐶2𝐻4(g) + 𝐻2(g) → 𝐶2𝐻6(g)

# Solution

The entropy change for the reaction can be calculated using the following expression

∆𝑆0 = ∑ 𝑆0 − ∑ 𝑆0

𝑟𝑒𝑎𝑐𝑡i𝑜𝑛

𝑃𝑟𝑜𝑑𝑢𝑐𝑡

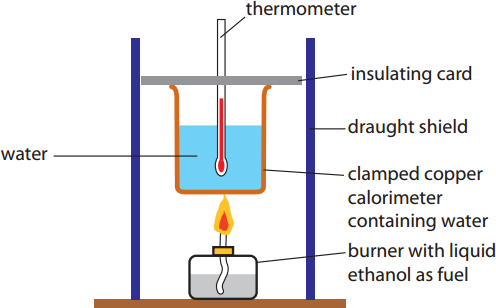
𝑅𝑒𝑎𝑐𝑡𝑎𝑛𝑡

= (229.87) – (219.56+130.92) = -120.61 J/K/mol

From the equation for the reaction, two moles of gases reacted to give one mole of a gas. Therefore, there is a decreasing order hence the change in entropy is expected to be negative as obtained from the calculation.

# Solved problem 6

1. Define the term, enthalpy change of combustion
2. The experimental set shown below was used to determine the heat of combustion of ethanol.



If the 0.46 g of ethanol was used to burn 200 g of water in the copper calorimeter and the resulting rise in temperature was 14 C, calculate the heat of combustion of ethanol. (Heat capacity of water = 4.18 )

# Solution

1. The heat produced when one mol of a substance is burn in excess oxygen is called the enthalpy change of combustion
2. The heat of combustion of ethanol will be equivalent to the heat used in raising the temperature of the water by 1 mole of ethanol.

𝑀𝑎𝑠𝑠 𝑜ƒ 𝑒𝑡ℎ𝑎𝑛𝑜𝑙 𝑢𝑠𝑒𝑑

𝑁𝑜 𝑜ƒ 𝑚𝑜𝑙𝑒𝑠 𝑜ƒ 𝑒𝑡ℎ𝑎𝑛𝑜𝑙 𝑢𝑠𝑒𝑑 i𝑛 𝑡ℎ𝑒 𝑐𝑜𝑚𝑏𝑢𝑠𝑡i𝑜𝑛 = 𝑀𝑜𝑙𝑎𝑟 𝑚𝑠𝑠 𝑜ƒ 𝑒𝑡ℎ𝑎𝑛𝑜𝑙

0.46

= 46 = 0.01 𝑚𝑜𝑙

𝐻𝑒𝑎𝑡 𝑟𝑒𝑐i𝑒𝑣𝑒𝑑 𝑏𝑦 𝑤𝑎𝑡𝑒𝑟 = 𝑀𝑎𝑠𝑠 𝑜ƒ 𝑤𝑎𝑡𝑒𝑟 𝑥 ℎ𝑒𝑎𝑡 𝑐𝑎𝑝𝑎𝑐i𝑡𝑦 𝑥 𝑐ℎ𝑎𝑛𝑔𝑒 i𝑛 𝑡𝑒𝑚𝑝𝑒𝑟𝑎𝑡𝑢𝑟𝑒

= −200 × 4.18 × 14 = −11704 𝐽/𝑚𝑜𝑙/𝐷𝑒𝑔

From the above, the combustion of 0.01 mol of ethanol produces -11704 J/mol/Deg of heat therefore, the combustion of 1 mol of ethanol will produce (-11704/0.01) x 1 J/mol of heat = 1170400 J/mol of heat = -1170.40 kJ/mol. This is the heat of combustion of ethanol.

# Born-Haber cycle

The Born-Haber cycle was developed by Max Born and Fritz Haber, who were German Chemists. The cycle analyse in detail enthalpies and lattice energy associated with the formation of ionic compounds from its constituent elements. Born-Haber cycle has found wider applications in calculating enthalpies and lattice energies of compounds that cannot be easily determined experimentally. Lattice energy is the enthalpy change involved in the formation of an ionic compounds from gaseous ions hence the process is exothermic. On the other hand, the endothermic process associated with the breaking of ionic compounds into gaseous ions is also equivalent to the lattice energy. Born-Haber cycle applies Hess law of thermochemistry to solve problems involving enthalpy change.

In order to analyse the Born-Haber cycle, let us consider the formation of NaCl(s). The steps involved are as follows,

1. Sodium atom in the solid state is changed into sodium atom in the gaseous state. The enthalpy change is called atomization energy, HAtom. i.e,

𝑁(𝑠) → 𝑁𝑎(g) ∆𝐻0 = +107 𝑘𝐽/𝑚𝑜𝑙

𝐴𝑡𝑜𝑚

1. Sodium ion in the gaseous state ionizes to lose one electron. The enthalpy change associated with the ionization is called ionization energy, HIE,

𝑁(g) → 𝑁𝑎+ + 𝑒− ∆𝐻0 = +496 𝑘𝐽/𝑚𝑜𝑙

(g) 𝐼𝐸

1. Chlorine molecule dissociates into chlorine atoms in the gaseous state. The enthalpy change associated with this process is called dissociation energy, ∆𝐻0,

𝐷

(g) 𝐷

1

2 𝐶𝑙2(g)

→ 𝐶𝑙− ∆𝐻0 = +243 𝑘𝐽/𝑚𝑜𝑙

1. The gaseous chlorine atom 𝐶(g)in one electron from that was lost by sodium and become ionizes into chloride ion. The enthalpy change associated with the ionization is called electron affinity, ∆𝐻0

𝐸𝐴

𝐶(g) + 𝑒− → 𝐶𝑙− ∆𝐻0 = −349 𝑘𝐽/𝑚𝑜𝑙

(g) 𝐸𝐴

1. Sodium ion (formed in step ii) and chloride ion (formed in step iv) combine together to form one mole of NaCl. The enthalpy change associated with this combination is called lattice energy,

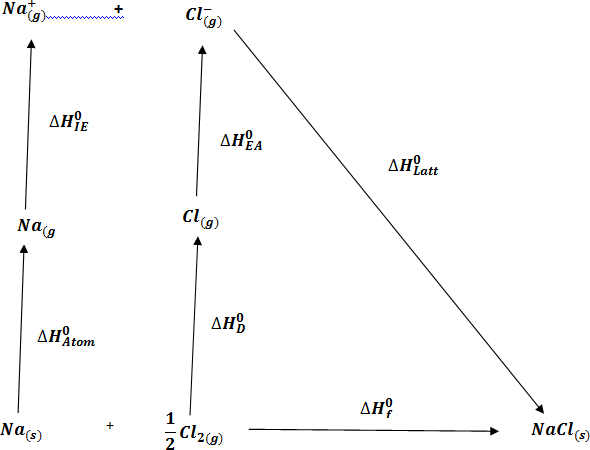
𝑁𝑎+ + 𝐶𝑙− → 𝑁𝑎𝐶(𝑠) ∆𝐻0 = ?

(g)

(g)

𝐿𝑎𝑡𝑡

The entire steps involved in the formation of NaCl from its constituent elements can be represented in a cycle called Born-Haber cycle as shown in the figure below



From the above diagram , it is evident that the underlisted equation represent conservation principle, according to Hess law

∆𝐻0 = ∆𝐻0 + ∆𝐻0 + ∆𝐻0 + ∆𝐻0 + ∆𝐻0

ƒ 𝐴𝑡𝑜𝑚

𝐼𝐸 𝐷

𝐸𝐴

𝐿𝑎𝑡𝑡

Therefore, if the value of ∆𝐻0 is known, the ∆𝐻0 can easily be computed using the following

equation,

ƒ 𝐿𝑎𝑡𝑡

∆𝐻0 = ∆𝐻0 + ∆𝐻0 + ∆𝐻0 + ∆𝐻0 − ∆𝐻0

𝐿𝑎𝑡𝑡

𝐴𝑡𝑜𝑚

𝐼𝐸 𝐷

𝐸𝐴 ƒ

Substituting for the respective values of the enthalpy, the lattice energy becomes,

∆𝐻0 = 107 + 1 (243) + 496 − 349 + 411 = 786.5 𝑘𝐽/𝑚𝑜𝑙

𝐿𝑎𝑡𝑡 2

Another method that can be used to calculate the lattice energy is the ionic model method. This method is based on the assumption that the crystal is formed from perfect spherical ions and that the only interaction is due to electrostatic force between the ions. For an ion pair, the energy needed to separate the ions depends on the sum of the ionic radii on the product of the ionic charges. Consequently, an increase in ionic charge will increase ionic attraction between them. In crystal, ions are surrounded by oppositely charge ions, hence the overall force of attraction between oppositely charged ion will overwhelm the force of repulsion between ions with same charge. The ionic model for calculating lattice energy can be expressed as follows,

∆𝐻0 = 𝐾𝑚𝑛

𝐿𝑎𝑡𝑡

(𝑅𝑀𝑛++ 𝑅K𝑚− )

where 𝐾𝑚𝑛 is a constant, which depends on the geometry of the lattice, 𝑅𝑀𝑛+𝑎𝑛𝑑 𝑅K𝑚− are ionic radius of the cation and anion respectively. In most cases, the ionic model has been found to yield theoretical values of lattice energy that are in good agreement with those calculated from Born-Haber cycle. Table 3 presents values of lattice energy calculated from Born-Haber cycle and ionic models for sodium and silver halides. The results generally show that the lattice energy

obtained from experiment (i.e Born-Haber cycle) are relatively higher than those calculated from ionic model. The difference can be attributed to polarization effects. For example, the small positively charged sodium ion can distort the electron cloud of the large and squashy iodide ion leading to the introduction of some covalent character in the compound. Since the ionic model does not take the effect of polarization into consideration, values of lattice energy obtained from this model is expected to be relatively lower than those obtained from Born-Haber cycle, which is an experimental method. The differences between the two set of results seems to increase from Cl- to I- due to increasing strength of polarization. Generally, electronegativity of halides

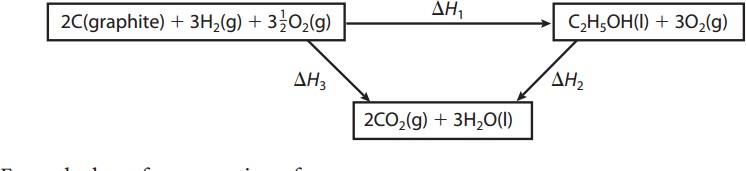
decreases from Cl- to I- which correspond to increase in covalent character, increase in ionic radii and expected increase in polarization.

# Table 3: Lattice energy for some sodium and silver halides calculated from Born-Haber cycle and ionic model methods

|  |  |  |  |
| --- | --- | --- | --- |
| **Compound** | **Born-Haber** | **Ionic model** | **% Difference** |
| NaCl | 790 | 769 | 2.7 |
| NaBr | 754 | 732 | 2.9 |
| NaI | 705 | 682 | 3.3 |
| AgCl | 918 | 864 | 5.9 |
| AgBr | 905 | 830 | 8.3 |
| AgI | 892 | 808 | 9.4 |

**Solved problem 7**

Consider the reaction pathways shown in the diagram below,



If H1 = -277 kJ/mol and H2 = -1367 kJ/mol , calculate H3

(b) State the standard conditions for reporting experimental data obtained for enthalpy change

**Solution**

1. From the law of conservation of energy, the enthalpy change in a complete cycle is zero, therefore,

H1 + H2 - H3 = 0 consequently, H3 = (H1 + H2) = (-277 -1367) = -1644 kJ/mol

1. The standard conditions for enthalpy changes are: i a temperature of 298 K or 25 °C
2. a pressure of 100 kPa
3. Concentration of 1 mol dm3 for all solutions iv, all substances in their standard states.

# 4.0 Summary

Thermochemistry studies the enthalpy change accompanying chemical reactions. It is based on two major laws. These laws can also be seen as extension of the first law of thermodynamics. The first law reveals that the total changes in enthalpies for a complete cycle is zero while the second law reveals that the heat of formation is the same as the heat of decomposition.

# 5.0 Conclusion

The study of thermochemistry is essential in identifying and solving some problems in thermodynamics. It has a wider application ranging from the calculation of enthalpy change to prediction of other parameters (such as heat of formation, etc).

# 6.0 Tutor mark assignment

1. What is thermochemistry? Hence differentiate between thermochemistry and thermodynamics
2. What is the advantages and disadvantages of using Born harber cycle to estimate the heat of formation of a compound?
3. State the basic thermochemical laws and list the features of thermochemical equations (Give suitable examples for each)