PART SEVEN
THERMOCHEMISTRY

Chapter 24

INTRODUCTION TO THERMOCHEMISTRY

Thermochemistry *is the branch of physical chemistry which deals with the study of measurement of heat change in various chemical reactions.* In the chemical reactions heat may be either evolved to the surroundings or absorbed from the surroundings. When heat is evolved to the surroundings the chemical reaction is said to be **exothermic** and when heat is absorbed from the surrounding the reaction is said to be **endothermic.**

IMPORTANT CONCEPTS AND DEFINITIONS

Before defining various terms concerning to thermochemistry, the reader should note the following points which are important for ensuring proper understanding of definitions:

- The terms relating to thermochemistry may **start with** the word 'standard' or **without** the word 'standard' e.g. **'standard** heat of reaction' or just, 'heat of reaction'
- **With** the word standard, the definition must end with *'under standard*
- *conditions (25°C and 1atm)."*
- **Without** the word standard, the definition must end with *'under given conditions of temperature and pressure.'*
- The *'standard conditions of temperature and pressure'* is different to *'standard temperature and pressure'* which is normally abbreviated as **STP.**
- Standard conditions are temperature of 25°C (room temperature) and pressure of 1 atmosphere (760 mmHg) which are useful in measurement of standard values of heat changes of various chemical reactions.
- Standard temperature and pressure (STP) is temperature of 0°C (273K) and pressure of 1 atmosphere (760 mmHg) which are useful in measurement of standard volume and pressure of gases.
- **Heat change, heat absorbed** and **heat evolved;** the three should be used at the beginning of various definitions with a little care as explained below:
- **Heat change** is used for reactions which may be either endothermic or exothermic under different circumstances e.g. any chemical reaction may be either exothermic or endothermic so in defining *'heat of the reaction'* the definition must start with; *is the heat change* …….' as the change may be either positive (endothermic) or negative (exothermic).
- **Heat absorbed (**or **required)** is used for the reaction which is always endothermic e.g. *'ionisation energy'* must start with; '*is the heat absorbed* …….' It is **wrong** to start with; 'is the heat change……...' Because the word 'change' implies that the energy change may be either positive (heat absorbed) or negative (heat evolved) while the reality is that: energy change in the ionisation process **must** be positive.
- **Heat evolved** is used for the reaction which is always exothermic e.g. in combustion, heat must be evolved to the surroundings as the process is exothermic. So in defining *'combustion energy'* the definition must start with*' is the heat evolved*……'
- Definitions which must start with; '*is the heat change*…….' Implying that their values may be either positive or negative include:
  - ✓ Heat (or enthalpy) of reaction
  - ✓ Heat (or enthalpy) of solution
  - ✓ Heat (or enthalpy) of dilution
  - ✓ Electron affinity
  - ✓ Heat (or enthalpy) of transition
  - ✓ Heat (or enthalpy) of formation

However, the reader should note that for stable compounds heat of formation is negative (heat is evolved). So as most of compounds which exist are stable, in most cases heat of formation is negative.

- Definitions which bust start with; '*is the heat absorbed (or required)* ……...' implying that their values are always positive include:

- ✓ Heat (enthalpy) of atomisation or atomisation energy
- ✓ Dissociation energy
- ✓ Ionisation energy
- ✓ Second electro affinity

- Definitions which must start with *'is the heat evolved (or liberated)* ……' implying that their values are always negative include:
  - ✓ Heat (enthalpy) of combustion
  - ✓ Heat (enthalpy) of neutralisation
  - ✓ Heat (enthalpy) of hydration
  - ✓ Lattice energy
  - ✓ Heat (or enthalpy) of hydrogenation
  - ✓ First electron affinity.

- Heat and enthalpy are commonly used interchangeably as the term '**enthalpy**' stand for *heat measured at given (constant) temperature and pressure.*
- If the given temperature and pressure are 25^{o}C and 1atm respectively which are **standard conditions,** then the term *standard heat* or *standard enthalpy* are used.

Standard enthalpy of reaction

This *is the heat change when the molar quantities, represented by the equation react under standard conditions (at temperature of 25^{o}C and pressure of 760mmHg), the substance being in their normal physical state for these conditions.*

Key words to remember are:

- ✓ Heat change.
- ✓ Molar quantities.
- ✓ Standard conditions (25^{o}C and 1atm)
- ✓ Normal physical states.

Heat change for the reaction is denoted by ΔH and the standard heat change for the reaction is denoted as ΔH^{θ} whereby superscript 'ɵ' always stand for standard value.

Very important to understand that: Reactions with more negative heat of reactions (more exothermic chemical reactions) or with less positive heat of reactions (less endothermic reactions) are more thermally favoured and hence are more likely to occur. So heat of reaction is very important in determining the easiest for the reaction to occur.

- Also products of exothermic reactions are thermally more stable because have less energy than reactants.

Heat of reaction for reversible reactions

For reversible reaction it is possible to calculate heat of reaction from activation energy of forward and reverse (backward) reactions and it is given by the following equation:

$$\mathbf{\Delta H = E_{af} - E_{ab}}$$

Where:

$\mathbf{E_{af}}$ represents activation energy of forward reaction,

$\mathbf{E_{ab}}$ represents activation energy of backward reaction and

ΔH represents heat of reaction for forward reaction.

Whereby heat of reaction for backward reaction is equal in magnitude but opposite in sign to that of forward reaction,

That is;

Heat of reaction for backward reaction= −Heat of reaction for forward reaction

The two relationships can be easily deduced from energy profile diagram as follows:

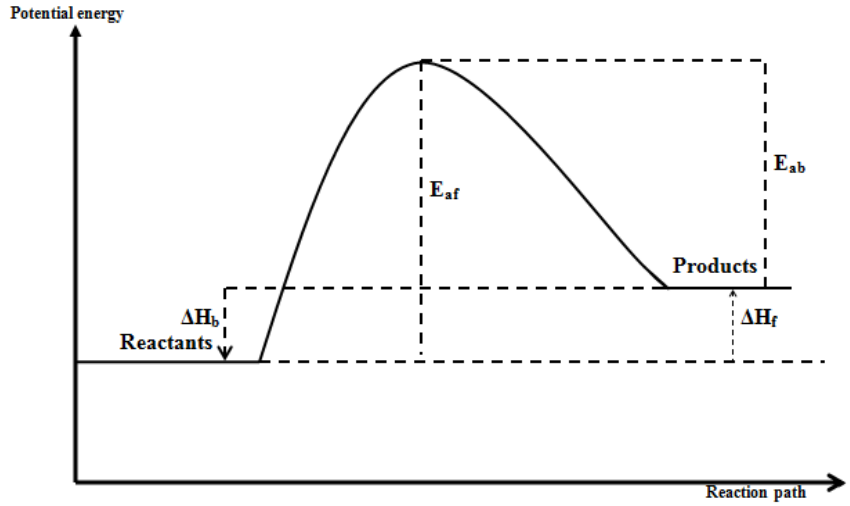


Figure 25.1 Energy profile diagram for reversible reaction

From the **figure 25.1**; it is clearly understood that:

$\Delta H_f = E_{af} - E_{ab}$---------- (i)

$\Delta H_b = E_{ab} - E_{af}$---------- (i)

From which; $\Delta H_b = E_{ab} - E_{af} = -(E_{af} - E_{ab}) = -\Delta H_f$

Where:

E_{af} and **E_{ab}** are activation energies for forward and backward reaction respectively

ΔH_f and **ΔH_b** are heat of reactions for forward and backward reactions respectively

Standard heat of formation ($\Delta H_f^{\ominus}$)

This *is the heat change which occurs when one mole of a compound is formed from its elements in their normal physical states under the standard conditions of temperature and pressure (25^{o}C and 1atm).*

Whereas the **heat of formation** *is the heat change which occurs when one mole of a compound is formed from its elements in their normal physical states measured at given conditions of temperature and pressure.*

Key words to remember are:

- ✓ Heat change
- ✓ One mole of a compound.
- ✓ Elements in their normal physical states,
- ✓ Standard conditions (for **standard** heat of formation)
- ✓ Given conditions of temperature and pressure (For heat of formation **without** the prefix **'standard'**)

The reader should understand that: normal physical states of elements are physical states of elements at standard conditions of temperature and pressure.

Heat of formation is important in determining stability of compounds. **Compounds with more negative heat of formation (highly exothermic compounds) are more stable**; while **compounds with large positive heat of formation (highly endothermic compounds) are unstable.**

Heat of formation is also important in determining heat of reactions. For a given heat chemical reactions, heat of reaction is given by the following equation:

$$\Delta H_r = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

Where: ΔH_r is the heat of reaction,

ΔH_f is the heat of formation and

$\sum$ is the summation of

With given standard values, the equation becomes:

$$\Delta H_r^\theta = \sum \Delta H_f^\theta(\text{products}) - \sum \Delta H_f^\theta \text{ (reactants)}$$

Where:

ΔH_r^θ is the standard heat of reaction.

ΔH_f^θ is the standard heat of formation.

It should be noted that: **the enthalpy of formation of an element in its natural state is zero**. For example; heat of formation of oxygen gas is zero or heat of formation solid aluminium is zero also etc.

Standard enthalpy of combustion (ΔH_c^θ)

This *is the heat evolved when one mole of an element or compound is completely burned in oxygen under standard conditions of temperature and pressure (25°C and 1atm).*

Key words to remember are:

- ✓ Heat evolved
- ✓ One mole
- ✓ Completely burned in oxygen
- ✓ Standard conditions

The term 'molar enthalpy of combustion' is commonly used in place of 'enthalpy of combustion'.

In writing a thermochemical equation to show heat of combustion, the stoichiometric coefficient of the substance (element or compound) which is burned must be one.

e.g. $2C_3H_7OH + 5O_2 \rightarrow 6CO_2 + 8H_2O \quad \Delta H \neq \Delta H_c$

The above equation is well balanced and the reaction is combustion, but since there are 2 molecules of C_3H_7OH in the equation, the heat change represented by the equation is twice the heat of combustion; i.e. $\Delta H = 2\Delta H_c$. The correct equation to show heat of combustion of C_3H_7OH is found by dividing throughout the equation by 2 giving to the following equation:

$$C_3H_7OH + 5/2O_2 \rightarrow 3CO_2 + 4H_2O \quad \Delta H = \Delta H_c$$

The thermo chemical equation to show heat of combustion of carbon is shown below;

$$C(s) + O_2(g) \rightarrow CO_2\,(g)$$

Since in burning one mole of carbon, one of mole CO_2 (compound) is formed; therefore according to the definition of the heat of formation; **heat of combustion of carbon is equal to heat of formation of CO_2**.

i.e. $\Delta H_f\,(CO_2) = \Delta H_c\,(\text{carbon})$

The thermochemical equation to show heat of combustion of hydrogen is shown below;

$$H_2(g) + ½\,O_2\,(g) \rightarrow H_2O\,(l)$$

By similar explanation to the case of combustion of carbon above;

$$\Delta H_f(H_2O) = \Delta H_c(\textbf{hydrogen gas})$$

Enthalpy of neutralisation (ΔH_n)

This *is the heat evolved when a dilute solution containing sufficient mass of acid to provide one mole of H^+ ions reacts with a dilute solution containing sufficient alkali to provide one mole of OH^- ions so as to give one mole of water, under given conditions of temperature and pressure.*

Key words to remember are:

- ✓ Heat evolved
- ✓ Dilute solution
- ✓ One mole of $H^+$and mole of OH^- (This automatically gives one mole water so it is not necessary to write one mole of water)
- ✓ Given conditions of temperature and pressure (if the given conditions are 25°C and 1 atm which are standard conditions then the enthalpy change become standard enthalpy of neutralisation)

In any neutralisation reaction the important and common change is:

$H^+(aq) + OH^-(aq) \rightarrow H_2O\ (l)$

So the heat of neutralisation reaction expresses the easiest of acid and base to react together so as to give water. If the heat of neutralisation is more negative, then the process of neutralisation in acid- base reaction is more thermally favoured (it is more likely to occur).

Among neutralisation reactions, the reaction between strong acids and strong bases have most negative heat of neutralisation because it is easiest for neutralisation to take place between strong solutions while reactions between weak acids and weak bases being relatively most difficult, have least negative heat of neutralisation.

Thus if:

(i) Strong + Strong base → salt + water $\quad \Delta H_n^\theta = -X_1 kJ/mol$

(ii) Weak acid + strong base → salt + water $\quad \Delta H_n^\theta = -X_2 kJ/mol$

(iii) Weak acid + weak base → salt + water $\quad \Delta H_n^\theta = -X_3\ kJ/mol$

Then $X_1 > X_2 > X_3$

Decrease in heat of neutralisation

Standard enthalpy of hydrogenation

This is the heat evolved when one mole of an unsaturated compound is converted to the corresponding saturated compounds by the reaction with hydrogen under standard conditions of temperature and pressure.

Key words to remember are:

- ✓ Heat evolved
- ✓ One mole of unsaturated compound
- ✓ Saturated compound
- ✓ Reaction with hydrogen
- ✓ Standard conditions

Standard enthalpy of atomisation ($\Delta H_a^\ominus$)

This *is the heat required to convert an element in its normal state into one mole of its corresponding gaseous atoms under standard conditions of temperature and pressure.*

Here *'normal state'* means the molecular state and physical state of the element at room temperature and pressure e.g. normal state of oxygen is *diatomic molecule (molecular state)* and *gas (physical state)*

Key words to remember are:

- ✓ Heat required (or absorbed)
- ✓ An element in its normal state
- ✓ One mole of gaseous atoms
- ✓ Standard conditions.

Enthalpy (heat) of atomisation is also known as **atomisation energy (A.E)**.
Examples of thermochemical equations representing atomisation energy are:

1) $1/2\ Cl_2(g) \rightarrow Cl(g) \qquad \Delta H = A.E$
2) $1/2\ O_2(g) \rightarrow O(g) \qquad \Delta H = A.E$
3) $1/2\ N_2(g) \rightarrow N(g) \qquad \Delta H = A.E$
4) $C\ (graphite) \rightarrow C\ (g) \qquad \Delta H = A.E$

The reader should note that: In atomisation of the element which is in solid state, the element **sublimes** from the solid to gas phase and hence the term 'atomisation energy' can be replaced by the term: **sublimation energy**.

Thus: **Atomisation energy = Sublimation energy for solid elements**

Hence sublimation energy can be defined as follows:

Sublimation energy *is the energy required to convert a solid element in its normal molecular state into one mole of its corresponding gaseous atoms at given conditions of temperature and pressure.*

e.g. $Al(s) \longrightarrow Al(g) \quad \Delta H = \text{Atomisation energy} = \text{Sublimation energy}$

The enthalpy of atomisation is also known as the **enthalpy of vapourisation** if it involves conversion of liquid element into corresponding gaseous atoms.
Thus enthalpy of vapourisation can be defined as follows:

Enthalpy of vapourisation *is the heat required to convert a liquid element in its normal molecular state into one mole of its corresponding gaseous atoms at given conditions of temperature and pressure.*

e.g. $Br_2(l) \longrightarrow 2Br(g) \quad \Delta H = \text{Atomisation energy} = \text{Vapourisation energy}$

Dissociation energy (D.E)

This *is the energy required to break one mole of molecules to their corresponding gaseous atoms under given conditions of temperature and pressure.*

e.g. $O_2\ (g) \rightarrow 2O\ (g) \quad \Delta H = D.E$

Key words to remember are:

- ✓ Energy required
- ✓ One mole of diatomic molecule
- ✓ Gaseous atoms
- ✓ Given conditions of temperature and pressure

Since in the dissociation of one **diatomic molecule** two gaseous atoms are formed while in the atomisation one gaseous atom only is formed then for diatomic molecule:

Dissociation energy (D.E) = 2 × Atomisation energy (A.E)

Heat (enthalpy) of solution (ΔH_{soln})

This *is the heat change when one mole of a substance (solute) dissolves in a specified amount of solvent (water) to give a solution under given conditions of temperature and pressure.*

- Usually the solvent used is water but others like alcohol or liquid ammonia may be used.

Key words to remember are:

- ✓ Heat change
- ✓ One mole of solute (substance)

- ✓ Specified amount of solvent
- ✓ Given conditions of temperature and pressure.

Heat of dilution

This *is the heat change when one mole of substance is added to so much water that further addition of water produces no further heat change under given conditions of temperature and pressure.*

When addition of more water to the solution does not produce more change in energy the solution is said to be at **infinite dilution**.
Thus: **Heat of dilution = Heat of solution at infinite dilution**.

Ionisation energy (I.E)

This *is the energy required to remove completely the most loosely bound electron each from one mole of gaseous atom or ion at given conditions of temperature and pressure.*

If an electron is removed from a gaseous neutral atom to form monopositive charged ion, the energy is then termed as the **first ionisation energy**.

$M(g) \rightarrow M^+(g) + e \qquad \Delta H = \text{First ionisation energy}$

If an electron is removed from a monopositive gaseous ion to form dipositive charged ion, the energy is then termed as the **second ionisation energy.**

$M^+(g) \rightarrow M^{2+}(g) + e \quad \Delta H = \text{Second ionisation energy.}$

Electron affinity (E.A)

This *is the energy change when electrons are added to one mole of gaseous atom or ion at given conditions of temperature pressure.*

If electrons are added to neutral gaseous atom, the energy is then termed as the **first electron affinity** and the energy is always negative.

First electron affinity *is the energy evolved when electrons are added to one mole of neutral gaseous atom to give mononegative anion at given conditions of temperature and pressure.*

e.g. $O(g) + e \rightarrow O^-(g) \quad \Delta H = \text{First electron affinity}$

If electrons are added to one mole of mononegative charge ion, the energy is then termed as the **second electron affinity** which is always positive.

Second electron affinity is the energy absorbed when electrons are added to one mole of mononegative charged ion to give dinegative charged ions under given conditions of temperature and pressure, e.g. $O^-(g) + e \rightarrow O^{2-}(g)$ ΔH = Second electron affinity

Second electron affinity is always positive (endothermic process) because extra energy is required to overcome repulsion of first added electron before adding the second electron.

Lattice energy (L.E)

Lattice energy *is the energy evolved when one mole of the solid ionic crystal is formed from its corresponding gaseous ions under given conditions of temperature and pressure.*

e.g. $Ca^{2-}(g) + O^{2-}(g) \longrightarrow CaO(s) \qquad \Delta H$ = lattice energy (L.E)

The same amount of energy evolved in forming ionic bonds of ionic crystal will be required to break the bonds.

i.e. **Lattice energy = Energy absorbed in breaking ionic bonds of solid ionic crystal**

So lattice energy is very important in determining stability of ionic compounds. Ionic compounds with more negative lattice energy have higher stability ionic and the bond between the ions (cation and anion) is stronger. Compounds with positive lattice energy are unstable and normally do not exist.

Hydration energy (H.E)

Generally, the hydration energy (or **enthalpy of hydration)** is the *heat evolved when **one mole** of **gaseous ions** is dissolved in water to give one mole of **aqueous ions** at given condition of temperature and pressure.*

In the case of hydration (crystallisation) of anhydrous salt, hydration energy may be defined as *the heat evolved when **one mole** of **anhydrous salt** reacts with a **fixed number of moles of water** to give a crystal lattice of hydrated salt under given conditions of temperature and pressure.*

Hydration energy is related to lattice energy by the following equation;

$H.E = \Delta H_{soln} - |L.E|$; where $|L.E|$ stands for positive L.E (magnitude of lattice energy).

The student should understand that:

The energy released (evolved) in forming crystal lattice by hydration is equal to the energy required to break the crystal lattice.

Hence **hydration energy is equal to the energy absorbed in breaking one mole of the crystal lattice of the hydrated salt.**

Heat of transition

This *is the heat change when one mole of one allotropic form of an element changes to another at given conditions of temperature and pressure.*

e.g. $S(\text{monoclinic}) \rightarrow S(\text{rhombic}) \quad \Delta H = \text{Heat of transition}$

$C(\text{graphite}) \rightarrow C(\text{diamond}) \quad \Delta H = \text{Heat of transition}$

CALORIMETRY

One technique we can use to measure the amount of heat involved in a chemical or physical process is known as **calorimetry**. Calorimetry is used to measure amounts of heat transferred to or from a substance. To do so, the heat is exchanged with a calibrated object called calorimeter. The temperature change measured by the calorimeter is used to derive the amount of heat transferred by the process under study. The process under study involves substance or substances undergoing chemical or physical change. We can call this process a **system** and under this context, **surroundings** will represent all other matter, including components of the measurement apparatus that serve to either provide heat to the system or absorb heat from the system.

A **calorimeter** is a device used to measure the amount of heat involved in a chemical or physical process. For example, when an exothermic reaction occurs in solution in a calorimeter, the heat produced by the reaction is absorbed by the solution, which increases its temperature. When an endothermic reaction occurs, the heat required is absorbed from the thermal energy of the solution, which decreases its temperature (Figure 25.1). The temperature change, along with the specific heat and mass of the solution, can then be used to calculate the amount of heat involved in either case.

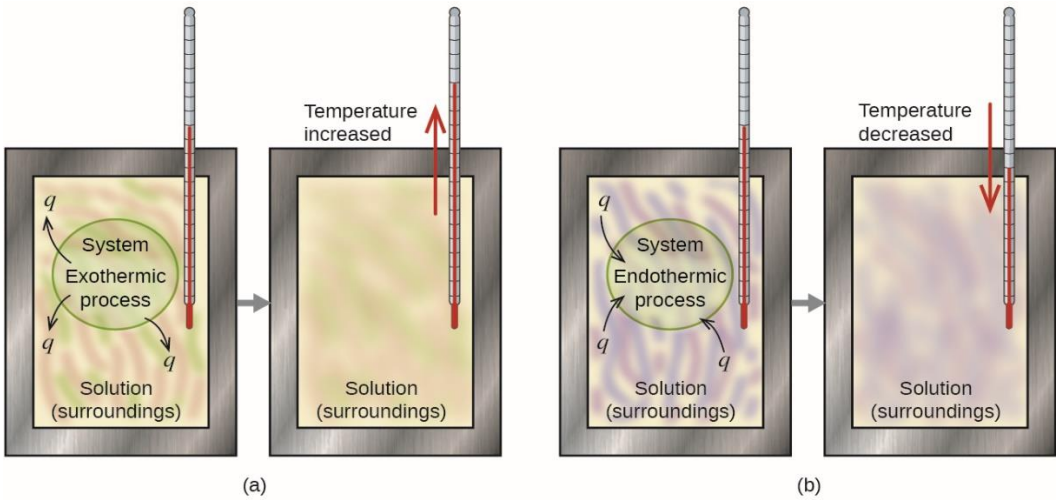


Figure 23.1 Calorimetry for exothermic and endothermic reactions.

With this calorimetric model, calorimeters should be well-insulated so that they prevent heat exchange (in most cases, heat loss) to non-system components including the calorimeter itself. This enables the accurate determination of the heat involved in chemical processes.

In normal laboratories, we often use simple calorimetric model constructed from polystyrene cups (Figure 24.2). These 'coffee cup' calorimeters are easy to use but they allow more heat exchange with the outside environment, and therefore produce less accurate energy values.

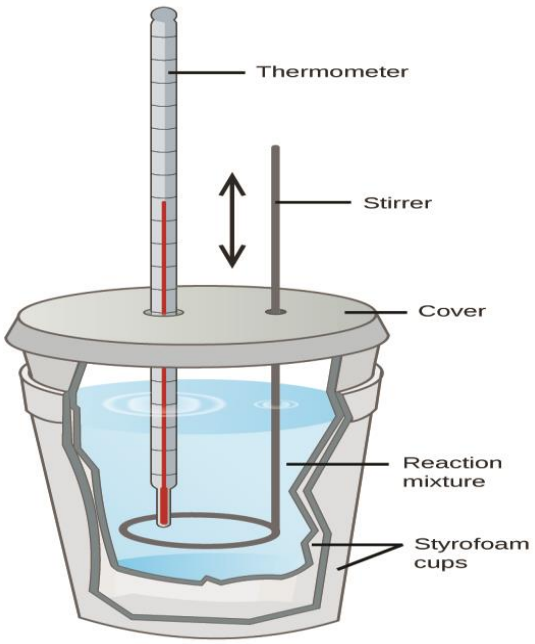


Figure 23.2 A simple calorimeter.

To have better understanding of calorimetry, we are going to use calorimetric determination of enthalpy of neutralisation as an example.

Determination of enthalpy of neutralisation

Neutralisation reactions are exothermic. So when acid and base are mixed in the calorimeter (Figure 24.2) the temperature of the vessel and its contents increases.

Then:

Heat rise in the vessel (ΔH **or** q) $= m_v C_v \Delta T$

Where: m_v is the mass of the vessel,

C_v is the specific heat capacity of the vessel and

ΔT is the rise in temperature.

Heat rise in the contents $= m_c C_c \Delta T$

Where: m_c is the mass of contents,

C_c is the specific heat capacity of contents and

ΔT is the rise in temperature.

Total heat released $= m_v C_v \Delta T + m_c C_c \Delta T = \Delta T(m_v C_v + m_c C_c)$

But from the definition; **heat of neutralisation**

=Total heat released when one mole of water is formed from acid- base reaction

Hence **Heat of neutralisation** $= \frac{\text{Total heat evolved}}{\text{Number of moles of water}} = \frac{\Delta T(m_v C_v + m_c C_c)}{nH_2O}$

You may include negative sign in the formula before $\Delta T(m_v C_v + m_c C_c)$ to insist that the reaction is exothermic and the formula for calculating the heat of neutralisation become:

$$\textbf{Heat of neutralisation} = \frac{-\Delta T(m_v C_v + m_c C_c)}{nH_2O}$$

However, in actual sense, the negative sign has already contained by the word 'evolved' of the 'heat evolved' from the definition of the heat of neutralisation.

It is better to understand that: when heat capacity is given instead of specific heat capacity;

Heat rise in the contents (or vessel) = Heat capacity × temperature rise

Example 1

125 cm^3 of 0.5M potassium hydroxide were mixed in a suitable lagged calorimeter of mass 53. 5g with 125 cm^3 of 0.5M hydrochloric acid, both being at 14°C. The temperature (after suitable correction) reached a maximum of 17.3°C. Assuming the dilute solutions to have the same specific heat capacity as water ($4.18 Jg^{-1}{}^{o}C^{-1}$) and the calorimeter to have specific heat capacity of 0.390 $Jg^{-1}{}^{o}C^{-1}$. Calculate the enthalpy of neutralisation.

Solution

Total enthalpy change $= \Delta T(m_v C_v + m_c C_c)$

Where:

ΔT is the temperature change $= (17.3 - 14)°C = 3.3°C$

m_v is the mass of the vessel (calorimeter) $= 53.5g$

C_c is the specific heat capacity of contents (solution) = $4.18 Jg^{-1}{}^{o}C^{-1}$

C_v is the specific heat capacity of the calorimeter = 0.390 $Jg^{-1}{}^{o}C^{-1}$

m_c is the mass contents (solution) = Density of solution × volume

$= 1\,g/cm^3 \times (125 + 125)\,cm^3 = 250g$

(If density of solution is not given, it is recommended to assume that the density of dilute solution is equal to that of water which is 1g/ cm^3)

Total enthalpy change = $-(53.5 \times 0.39 + 250 \times 4.18) \times 3.3$ J = -3518J

125cm^3 of 0.5MKOH contains $\frac{125}{1000} \times 0.5$mol of $OH^- = 6.25 \times 10^{-2}$mol

125cm^3 of 0.5MHCl contains $\frac{125}{1000} \times 0.5$mol of $H^+ = 6.25 \times 10^{-2}$mol

Because: OH^- and H^+ combine to give water according to the following equation:

$OH^- + H^+ \rightarrow H_2O$ from which mole ratio of H^+ (or OH^-) to H_2O is 1: 1;

Then number of moles of water formed is also 6.25×10^{-2}mol

Using; enthalpy of neutralisation $= \frac{\text{Total enthalpy rise in neutralisation}}{\text{Number of moles of water formed}}$

$= \frac{-3518\text{J}}{6.25 \times 10^{-2}\text{moles}} = -56288\text{J/mol or } -56.288\text{kJ/mol}$

(The negative sign indicate that heat energy is released to the surroundings as the reaction is exothermic)

Hence enthalpy of neutralisation is -56.288kJ/mol

Example 2

500cm^3 of 0.1M sodium hydroxide solution at 15.5°C was quickly added to 500cm^3 of 0.1M nitric acid in a calorimeter which was also at a temperature of 15.5°C. The calorimeter had a mass of 540g and a specific heat capacity of $0.39 Jg^{-1}°C^{-1}$. If the maximum temperature recorded was 16.15°C, calculate the enthalpy of neutralisation. Assume the specific heat capacity of the solution to be the same as that of water i.e. 4.2 $Jg^{-1}°C^{-1}$.

Solution

Total enthalpy change = $\Delta T(m_v C_v + m_c C_c)$

Where: $\Delta T = (16.15 - 15.5)°C = 0.65°C$, m_v = 540g,

$C_v = 0.39 Jg^{-1}°C^{-1}$, $C_c = 4.2\ Jg^{-1}°C^{-1}$ and $m_c = \rho_c V_c$

But ρ_c = 1g/cm^3 and V_c = (500 + 500)cm^3 = 1000cm^3

Then m_c = 1g/cm^3 × 1000cm^3 = 1000g

So that enthalpy change = $-(0.39 \times 540 + 4.2 \times 1000) \times 0.65\text{J} = -2866.89\text{J}$

The equation for the reaction is: $NaOH\ (aq) + HNO_3(aq) \longrightarrow NaOH(aq) + H_2O\ (l)$

From which mole ratio of NaOH (or HNO_3) to H_2O is 1:1

Thus number of moles of NaOH = number of moles of water formed

$$\frac{500}{1000} \times 0.1\text{mol} = 5 \times 10^{-2}\text{mol}$$

Using enthalpy of neutralisation = $\frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}}$

$= \frac{-2866.89\text{J}}{5 \times 10^{-2}\text{moles}} = 57337.8\ \text{J/mol or } 57.3378\text{kJ/mol}$

Hence enthalpy of neutralisation is 57.3378 kJ/mol

Example 3

Calculate the enthalpy of neutralisation of potassium hydroxide by hydrochloric acid from the following data:

250cm^3 of 0.5MKOH at 12^{o}C were mixed in a plastic beaker of negligible heat capacity with an equal volume of 0.5MHCl at the same temperature. The final temperature was 15.4^{o}C. Assume the specific heat capacity of the solution to be 4.2 $Jg^{-1}°C^{-1}$.

Solution

Total enthalpy change = $\Delta T(m_v C_v + m_c C_c)$

But $C_v = 0$ (**Plastic** beaker has negligible heat capacity)

Then: total enthalpy change = $m_c C_c \Delta T$

Where: C_c = 4.2 $Jg^{-1}°C^{-1}$

$m_c = \rho_c V_c$ = 1g/cm^3 × (250 + 250) cm^3 = 500g

$\Delta T = (15.4 - 12)°C = 3.4°C$

It follows that enthalpy change $= -500 \times 4.2 \times 3.4J = -7140J$

Using enthalpy of neutralisation = $\frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}}$

But from the equation of the reaction: $KOH\,(aq) + HCl(aq) \longrightarrow KCl\,(aq) + H_2O(l)$;

mole ratio of KOH (or HCl) to H_2O is 1:1

Thus number of moles of water produced = Number of moles of KOH

$$= \frac{250}{1000} \times 0.5\,\text{mol} = 0.125\text{mol}$$

So enthalpy of neutralisation $= \frac{-7140J}{0.125\text{moles}} = -57120J/\text{mol or } -57.12kJ/\text{mol}$

Hence enthalpy of neutralisation is $-57.12kJ/mol$.

Further worked examples in calorimetry

Example 4

40cm^3 of hydrochloric acid and with a concentration of 2moldm^{-3} were poured into a polystyrene breaker. The same volume of sodium hydroxide with the same concentration was added to the acid, the temperature rise was found to be 13.7K. Calculate the approximate enthalpy of neutralisation for the reaction.

Given that the specific heat capacity of water is $4.184 \times 10^{-3} kJg^{-1}K^{-1}$

Solution

Total enthalpy change = $\Delta T(m_v C_v + m_c C_c)$

But **polystyrene beaker** has zero heat capacity, thus $C_v = 0$

So total enthalpy change = $m_c C_c \Delta T$

But $m_c = \rho_c V_c$

Where ρ_c is the density of the contents (solution) = 1g/cm^3

V_c is the volume of contents = (40 + 40) cm^3 = 80cm^3

Then m_c = 1g/cm^3 × 80cm^3=80g

Therefore;

Total enthalpy change = $-80 \times 4.184 \times 10^{-3} \times 13.7kJ = -4.586kJ$

Equation for the reaction is:

$HCl\,(aq) + NaOH\,(aq) \longrightarrow NaCl\,(aq) + H_2O\,(l)$

From which mole ratio of HCl (or NaOH) to H_2O is 1:1

Thus number of moles of H_2O produced = number of moles HCl $= \frac{40}{1000} \times 2\text{mol} = 8 \times 10^{-2}\text{mol}$

Using enthalpy of neutralisation = $\frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}} = \frac{-4.586\text{kJ}}{8\times10^{-2}\text{moles}} = -57.325\ \text{kJ/mol}$

Hence enthalpy of neutralisation is -57.325kJ/mol.

Example 5

75cm^3 of 0.2M Lithium hydroxide solution was added to 75 cm^3 of 0.2M hydrochloric acid in a vacuum flask of water equivalent 10g. The original temperature of reactants before the reaction was 14.7°C and it rose to 16°C. Calculate the enthalpy of neutralisation under the conditions.

Given that: Specific heat capacity of solution is the same as that of water which is 4.2 $\text{Jg}^{-1}\text{°C}^{-1}$

Solution

Total enthalpy change $=$ specific heat capacity $\times$ total mass $\times$ temperature change

But mass of volume flask = 10g of water (the flask is of water equivalent 10g)

And mass of water = 1g/ $\text{cm}^3 \times (75 + 75)\ \text{cm}^3 = 150\text{g}$

Hence total mass is (150 + 10) g = 160g of water

And temperature change $= (16 - 14.7)\text{°C} = 1.3\text{°C}$

Then: Total enthalpy change $= -4.2 \times 160 \times 1.3\text{J} = -873.6\text{J}$

Using enthalpy of neutralisation = $\frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}}$

From the equation of the reaction: $LiOH(aq) + HCl\,(aq) \longrightarrow LiCl\,(aq) + H_2O\,(l)$

Mole ratio of LiOH (or HCl) to H_2O is 1:1

Thus number of moles of water produced = Number of moles of LiOH

$$= \frac{75}{1000} \times 0.2\text{mol} = 0.015\text{mol}$$

Then enthalpy of neutralisation $= \frac{-873.6\text{J}}{0.015\text{mol}} = 58240\text{J/mol or } 58.24\text{kJ/mol}$

Example 6

When 1g of graphite is burnt in excess oxygen, the energy of 32kJ is liberated. Calculate heat of combustion of the graphite.

Solution

Graphite is allotropic form of carbon whose molar mass is 12g/mol

From the definition of the heat combustion;

Heat of combustion $= \frac{\text{Heat energy liberated}}{\text{Number of moles of graphite (carbon)}}$

Using; number of moles $= \frac{\text{Given mass}}{\text{Molar mass}}$

Then; number of moles of graphite = $\frac{1}{12}\text{moles}$

Thus; heat of combustion of graphite $= \frac{-32\text{kJ}}{\frac{1}{12}\text{mol}} = -32 \times 12\text{kJ/mol} = -384\ \text{kJ/mol}$

Hence heat of combustion of graphite is -384kJ/mol.

Example 7

The combustion of 1.6g sample of methanol in a flame calorimeter result into a temperature rise of 7.8K. When a 12V supply of electricity with a current of 2A was passed through the contents of the calorimeter for 20minutes the temperature rose by 6.2K. Calculate the molar enthalpy of combustion under the conditions of this experiment.

Solution

Enthalpy change due to combustion of methanol is given by;

$\text{Enthalpy change} = \text{heat capacity} \times \text{temperature change}$

But temperature rise after combustion is 7.8K

So enthalpy change in combustion $= 7.8 \times$ heat capacity of the colourimeter

But also:

$\text{Heat change due to passage of electricity} = \text{heat capacity} \times \text{temperature rise}$

$= 6.2 \times$ heat capacity of the calorimeter

But electric energy $=$ heat change due to passage of the electricity

Then $\text{VIt} = 6.2 \times$ heat capacity of the calorimeter

Where V is the potential difference = 12V

I is the current = 2A

t is the time = 20 × 60 seconds = 1200 seconds.

And $\text{VIt} = \text{Electric energy}$

So heat capacity of the calorimeter $= \frac{\text{VIt}}{6.2} = \frac{12\times2\times1200\text{JK}^{-1}}{6.2} = 4645.1613\text{JK}^{-1}$

Thus heat capacity of the calorimeter $= 4645.1613\text{JK}^{-1}$

Then enthalpy change due to combustion $= -7.8 \times 4645.1613\text{ J} = -36232.258\text{J}$

Number of moles of methanol $\text{CH}_3\text{OH} = \frac{\text{mass of CH}_3\text{OH}}{\text{molar mass of CH}_3\text{OH}} = \frac{1.6\text{g}}{32\text{gmol}^{-1}} = 0.05\text{mol}$

Using $\text{Enthalpy of combustion} = \frac{\text{Enthalpy change}}{\text{Number of moles of the substance (CH}_3\text{OH)}}$

$= \frac{-36232.258\text{J}}{0.05\text{mol}} = -724645.16\text{ J/mol or } = -724.645\text{ kJ/mol}$

Hence the molar enthalpy of combustion of methanol is -724.645kJ/mol.

Example 8

1.5 g of ammonium nitrate (NH_4NO_3) was added to 35 g of water in a plastic beaker and stirred until the salt is dissolved. The temperature of the solution dropped from 22.7℃ to 19.4℃. Basing on the given information respond to the following:

(i) Is the process endothermic or exothermic? Explain.
(ii) Calculate the heat of solution of NH_4NO_3 in kJ/mol; given that specific heat capacity of water is 4.184J/g℃.

Solution

(i) Endothermic

Explanation

The temperature decreased from 22.7℃ to 19.4℃ suggesting that heat was absorbed from the surroundings (solution) and hence the process is endothermic.

(ii) $\text{Total heat absorbed} = \text{Heat absorbed by contents} + \text{Heat absorbed by vessel}$

But because plastic beaker does not allow the passage heat;

$\text{Heat absorbed by vessel} = 0$ (specific heat capacity of plastic beaker is negligible).

$\text{Total heat absorbed}, \Delta H = \text{Heat absorbed by contents}$

But Heat absorbed by contents $= m_c C_c \Delta T$

Where $m_c = (1.5 + 36)\text{g} = 36.5\text{ g}$

$C_c = 4.184\text{ Jg}^{-1}\text{C}^{-1}$ (Specific heat capacity of solution is equal to that of water)

$\Delta T = (22.7 - 19.4)℃ = 3.3℃$

Substituting $\Delta H = 36.5 \times 4.184 \times 3.3\text{J} = 503.9628\text{J}$

But Heat of solution,

$$\Delta H_{soln} = \frac{\text{Heat change}}{\text{Number of moles of solute } (NH_4NO_3)}$$

Then using $n = \frac{m}{M_r}$; Where $M_r\ (NH_4NO_3) = 80\text{ g/mol}$

Number of moles of $NH_4NO_3 = \frac{1.5\text{g}}{80\text{ g/mol}} = 0.01875\text{ mol}$

It follows that:

$\Delta H_{soln} = \frac{503.9628\text{J}}{0.01875\text{mol}} = 26878\text{J/mol}$

$= 26.878\text{ kJ/mol}$

Hence the heat of solution is $+26.878\text{ kJ/mol}$

Example 9

Two liquids; trichloromethane ($CHCl_3$) and ethoxyethane ($CH_3CH_2OCH_2CH_3$) form intermolecular hydrogen bonds when mixed. In a certain experiment, 0.05moles of trichloromethane and 0.3moles of ethoxyethane were weighed into the same calorimeter. When the temperature of both liquids had equalized, the liquids were mixed. The temperature increase of 5.4℃ were recorded upon mixing. Assume that the heat capacity of calorimeter is negligible, while heat capacities of trichloromethane and ethoxyethane are $0.98\text{Jg}^{-1}℃^{-1}$ and $2.28\text{Jg}^{-1}℃^{-1}$ respectively. Calculate:

(i) Heat change in this experiment.
(ii) Enthalpy change of mixing one mole of trichloromethane with excess ethoxyethane.

Solution

Using $m = nM_r$;
Mass of trichloromethane, $m_t = 0.05\text{mol} \times 119\text{gmol}^{-1} = 5.975\text{g}$

Mass of ethoxyethane, $m_e = 0.3\text{mol} \times 74\text{gmol}^{-1} = 22.2\text{g}$

Since the temperature increased, the heat change is negative (The process is exothermic)

Thus $\Delta H = -(m_t C_t \Delta T + m_e C_e \Delta T)$

Substituting; $\Delta H = -\big((5.975 \times 0.98 \times 5.4) + (22.2 \times 2.28 \times 5.4)\big)\text{J} = -304.95\text{J}$

The heat change in the experiment is the experiment is $-304.95J$

The molar enthalpy change = $\frac{\text{Heat change}}{\text{Number of moles of } CHCl_3} = \frac{-304.95J}{0.05mol} = -6099Jmol^{-1} = -6.099kJmol^{-1}$

The enthalpy change of mixing one mole of trichloromethane with excess ethoxyethane is $-6.099kJ$.

Example 10

Magnesium will displace copper from copper (II) sulphate according to the following equation:

$$CuSO_4(aq) + Mg(s) \longrightarrow Cu(s) + MgSO_4(aq)$$

When an excess of magnesium was added to $100cm^3$ of $1moldm^{-3}$ copper (II) sulphate, the temperature increased by 46.3°C. It is known that density and specific heat capacity of the solution are $1gcm^{-3}$ and $4.18Jg^{-1}°C^{-1}$ respectively. Calculate:

(i) The molar enthalpy change for the reaction.
(ii) The minimum quantity of magnesium required.
(iii) The change in temperature if only 0.8g of magnesium was added.

Solution

(i) Since the reaction accompanied with the temperature rise, it is exothermic.

Then; heat change, $\Delta H = -mc\Delta T$

But $m = \rho_{soln}V_{soln}$

Thus; $\Delta H = -\rho_{soln}V_{soln}c\Delta T$

Substituting $\Delta H = -1gcm^{-3} \times 100cm^3 \times 4.18Jg^{-1}°C^{-1} \times 46.3°C$

$= -19353.4J = -19.3534kJ$

Number of moles of $CuSO_4 = \frac{100}{100}dm^3 \times 1moldm^{-3} = 0.1mol$

Then using;

Molar enthalpy change = $\frac{\text{Heat change}}{\text{Number of moles of } CuSO_4}$

Molar enthalpy change = $\frac{-19.3534kJ}{0.1mol} = -193.534kJ/mol$

The molar enthalpy change for the reaction is $-193.534kJ/mol$

(ii) From the given equation; mole ratio of $CuSO_4$ to Mg is 1:1

Thus the minimum number of moles of Mg required is 0.1mol

Using $m = nM_r$;

Mass of $Mg = 0.1mol \times 24gmol^{-1} = 2.4g$

The minimum quantity of magnesium required is 2.4g

(iii) Number of moles of magnesium $n = \frac{0.8g}{24gmol^{-1}} = \frac{1}{30}mol$

Thus; Number of moles of $CuSO_4$ = Number of moles of $Mg = \frac{1}{30}mol$

And; Heat change = molar enthalpy change × Number of molar of $CuSO_4$

$= -193.534kJmol^{-1} \times {}^{1}/_{30}\,mol = -6.45kJ = 6450J$

From $\Delta H = -\rho_{soln}V_{soln}\,c\Delta T$

$-6450J = -1gcm^{-3} \times 100cm^3 \times 4.18Jg^{-1}°C^{-1} \times \Delta T$

From which; $\Delta T = 15.43°C$

DIGGING DEEPER EXERCISE 23

EXERCISE 23A: BINDER QUESTIONS

Question 1

Classify each of the following processes as endothermic or exothermic. In each case, indicate which has greater heat content (enthalpy), reactants or products.

(a) Combustion of natural gas
(b) Dehydrogenation of ethene
(c) Splitting of carbon dioxide into carbon and oxygen
(d) Solidification of melted wax
(e) Formation of sodium chloride (NaCl) from it elements
(f) Neutralisation of NaOH by HCl

Question 2

Predict the value ΔH_f^{θ} for the following scenarios:

(a) $Br_2(g)$ (b) $Br_2(l)$ (c) $I_2(g)$ (d) $I_2(s)$

In each case, give a reason for your prediction.

Question 3

Consider the following reaction, which occurs at standard state:

$2Cl(g) \longrightarrow Cl_2(g);\ \ \Delta H_r = -243.4kJ$

Which has the higher, more positive, enthalpy under these conditions, $Cl(g)$ or $Cl_2(g)$? Give reason(s) for your choice.

Question 4

When 100.0mL of 1.00M NaOH is added to 100.0mL of 1.00M HCl in an insulated container the temperature rises from $21.0℃$ to $27.8℃$. Calculate the enthalpy change for the neutralisation reaction. Specific heat capacity of water is $4.18JK^{-1}g^{-1}$.

Question 5

A vessel and its contents of total heat capacity $120J/K$ were heated using a methane burner. Calculate the maximum theoretical temperature rise when $0.10g$ of methane was completely burned. The standard enthalpy of combustion of methane is $-890\ kJ/mol$.

Question 6

To change the temperature of a particular calorimeter and the water it contains by one degree Celsius requires 6485Joules. The complete combustion of 1.40g of ethylene gas, C_2H_4, in the calorimeter causes a temperature rise of 10.7 degrees. Find the heat of combustion of ethylene gas.

EXERCISE 23B: REAL QUESTIONS

Question 7

The following scenarios are real life processes which involve heat change. State whether each process is endothermic or exothermic.

(i) Water is added to sodium hydroxide pellets, and the flask becomes hot.
(ii) The body metabolises glucose, producing carbon dioxide and water.
(iii) Ammonium nitrate crystals are dissolved in water, causing the solution to become cool.

Question 8

On diluting an acid, it is advised to add acid to water and not water to acid. Explain why it is so advised?

Question 9

When a human is exposed to hot water or solution with a temperature of 60℃, leads to a serious burn within a second. So care must be taken in preparing solutions of solutes that liberate heat on dissolving. Our laboratory technician, **Mr. Akilikubwa**, was preparing 500mL of 7M NaOH and he forgot to take necessary precautions during the preparation. Immediately after mixing NaOH and water at 21℃, he contacted the resulting solution to his face. Did **Mr. Akilikubwa** get burn injury?

Given that:

The heat of solution of NaOH $= -42\ \text{kJ/mol}$.

The specific heat of the solution formed $= 4.18\text{Jg}^{-1}\text{K}^{-1}$

(Assume the density of solution is equal to the density of water).

Question 10

Kipute, your lovely classmate was asked to determine the enthalpy of neutralisation by taking 100cm^3 of 0.3MNaOH and mixing it with 115cm^3 of 0.3MHNO_3 in a polystyrene beaker. If both solutions were initially at 35℃ and the temperature of the resulting solution was recorded as 39℃ and he was told to assume that there was no heat lost to the calorimeter or surroundings; but by mistake she took 100cm^3 of 0.3MNaOH and mixed 20cm^3 of distilled water in a beaker unknowingly. This led Kipute to have an error to her experimental results. Assists **Kipute** to calculate the percentage error enthalpy between the real expected and the one she calculated.

Question 11

On another day, **Kipute** performed an experiment to determine the standard molar enthalpy of neutralisation of a strong acid by a strong base. She added 50cm^3 of hydrochloric acid to $50\text{cm}^3$of sodium hydroxide solution in a polystyrene cup. The temperature rose by 6.5℃. The initial concentration of each solution was 1moldm^{-3}

(a) What result did **Kipute** get?

(Assume that the final solution has a specific heat capacity of $4.18\text{JK}^{-1}\text{g}^{-1}$ and a density of 1gcm^{-3}).

(b) When all other students in **Kipute's** class performed this experiment, the average of the results was -55kJ/mol. The accepted value for the standard molar enthalpy of neutralization of a strong acid by a strong base is -57.7kJ/mol. Explain two likely sources of experimental error that could account for the result obtained by the class.

Question 12

Mr. Akilikubwa performed an experiment that involved neutralisation reaction. He took 50cm^3 of a 0.500M solution of potassium hydroxide then mixed rapidly in a glass beaker with $50\text{cm}^3$of a 0.500M solution of hydrochloric acid. He recorded temperature as follows:

Initial temperature of each solution $=$ 19.6℃

Final temperature of the mixture $=$ 23.1℃

(a) State with a reason whether the reaction was exothermic or endothermic.
(b) Explain why the solutions were mixed rapidly.
(c) Calculate the enthalpy change in kJ/mol. Assume that the specific heat capacity of the solution is the same as that of water ($4.18\text{JK}^{-1}\text{g}^{-1}$).
(d) If **Mr. Akilikubwa** repeated experiment with an HCl concentration of 1M; state and explain what the temperature change would be.

EXERCISE 23C: HOT QUESTIONS

Question 13

Calculate amount of energy transferred when 10.00g of $N_2O(g)$ is produced by the following reaction:

$$2N_2(g) + O_2(g) \longrightarrow 2N_2O(g); \quad \Delta H = +163.2kJ$$

Question 14

Given the following reaction: $2P(s) + 3Cl_2(g) \longrightarrow 2PCl_3(g); \quad \Delta H = -574kJ$

(a) How many moles of phosphorus are needed to produce 488 kJ?

(b) How much heat is released when 122g of PCl_3 are produced?

(c) How many grams of Cl_2 are needed to produce 27.0kJ?

Question 15

When $50cm^3$ of 1M HCl is mixed rapidly with $50cm^3$ of 1M NaOH, the temperature of the resulting solution increases by 6℃. Determine the temperature change when:

(a) $100cm^3$ (instead of $50cm^3$) of each of these solutions is mixed.

(b) 2M (instead of 1M) of each solution is mixed.

Question 16

In an experiment, an excess of solid magnesium oxide was added to $50cm^3$ of 3M hydrochloric acid. The initial temperature of the solution was 21℃. After reaction, the temperature had risen to 53℃. (The specific heat capacity of water is 4.2 $JK^{-1}g^{-1}$)

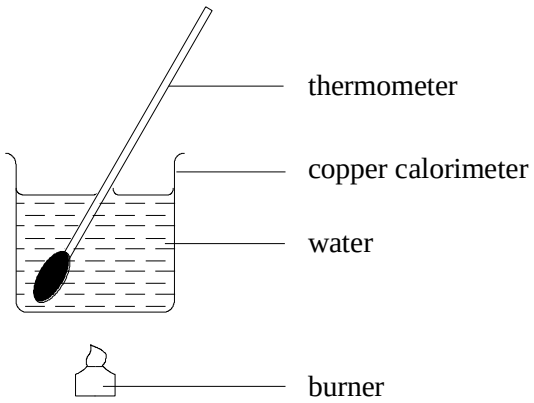
Use this information to calculate the enthalpy change for the reaction of one mole of magnesium oxide with hydrochloric acid. For your calculation you should assume that all the heat from the reaction is used to raise the temperature of 50g of water.

Question 17

An experiment was conducted to determine the enthalpy of combustion of liquid methanol. The energy obtained from burning 2.12g of methanol was used to heat 150g of water. The temperature of the water rose from 298K to 362 K. (The specific heat capacity of water is 4.18 $JK^{-1}g^{-1}$). Calculate a value for the enthalpy of combustion of liquid methanol.

Question 18

A value for the enthalpy of combustion of the alcohol C_3H_7OH was determined in the laboratory using the apparatus shown below. The following results were obtained.



Mass of water in the calorimeter $= 200\text{g}$

Initial temperature of water $= 15℃$

Final temperature $= 30℃$

Mass of alcohol burned $= 0.90\text{g}$

(a) Calculate the heat energy required to raise the temperature of the water from $15℃$ to $30℃$. The specific heat capacity of water is $4.18\ \text{JK}^{-1}\text{g}^{-1}$.
(b) Calculate the number of moles of the alcohol, C_3H_7OH, burned.
(c) Hence, calculate a value for the enthalpy of combustion of the alcohol.
(d) Give at least **two** possible reasons why your answer in (c) is not a hundred percent correct.

Chapter 25

HESS'S LAW OF CONSTANT HEAT SUMMATION

INTRODUCTION

One of the most important generalisations of thermochemistry is Hess's law. This generalisation is primarily based on the fact that enthalpy is a path independent thermodynamic function. In other words, the enthalpy change in a chemical reaction is same whether it occurs in one step or in more than one step. This may be stated in the form of Hess's law (named in honour of its discoverer, the Russian chemist, German Henry **Hess**) as follows:

"The total energy change resulting from a chemical reaction is dependent only on the initial and final state of the reactants and is independent of the route."

Thus according to the Hess's law, the standard enthalpy of reaction is the sum of algebraic sum of the standard enthalpies of reactions into which the overall reaction may be divided.

Hess's law is an application of **first law of thermodynamic** which is actually the **law of conservation of energy** which can be stated as:

Energy cannot be destroyed or created but merely changed in form or distributed in different ways.

Hess's law is also known as the **law of constant heat summation** or **second law of thermochemistry**.

To have better understanding of the concept, consider the enthalpy change from reactants **A** to products **B** via various routes as shown in **figure 25.1** below:

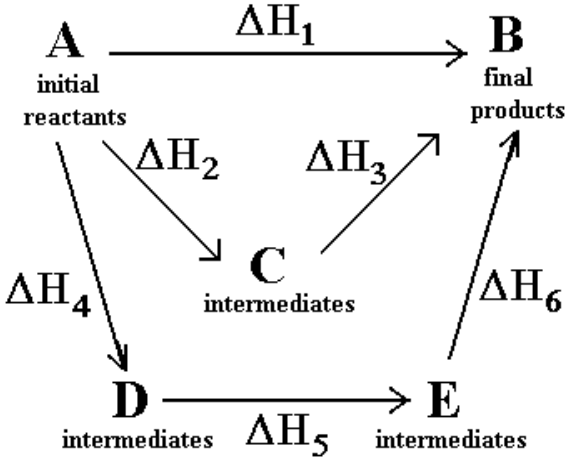


Figure 24.1 Illustration of Hess's law

From above figure:

$\Delta H_1 = \Delta H$**(A to B)**: Route 1 the most direct route with no intermediate stages.

The from Hess's law:

$\Delta H_1 = \Delta H_2 + \Delta H_3$: Route 2 involves two steps and one set of intermediates **C**.

or $\Delta H_1 = \Delta H_4 + \Delta H_5 + \Delta H_6$: Route 3 involving three steps with two sets of intermediates **D** and **E**.

So there is no limit to the complexity of the Hess's law cycle as long as A and B are constant.

METHODS OF APPLYING HESS'S LAW

In applying Hess's law, the following methods may be used:

- Hess's law cycle
- Combining thermochemical equations
- Thermochemical calculations by using enthalpy of formations
- Born-Haber cycle
- Thermochemical calculations by using bond energies

In this chapter, we are going to discuss above methods; one after another.

Hess's law cycle

Consider a process involving the conversion of reactant **A** into **B** in one step (**route 1**). The enthalpy change of the process is represented by **ΔH**. Then suppose the process is carried out in two steps involving a change from A to **B** and **C** to **B** according to **route 2** (**Figure 28.2**). If $\Delta\mathbf{H_1}$ and $\Delta\mathbf{H_2}$ are enthalpy changes from **A** to **C** and **C** to **B** respectively. Then according to Hess's law;

Enthalpy change in **route 1**= total enthalpy change in **route 2**

And hence $\Delta\mathbf{H} = \Delta\mathbf{H_1} + \Delta\mathbf{H_2}$

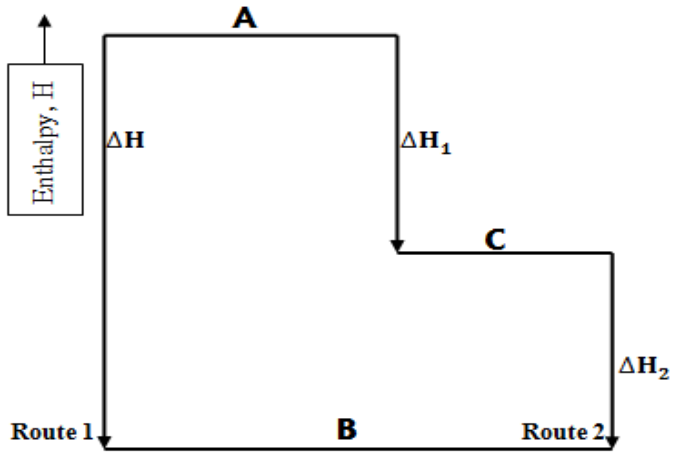


Figure 24.2 Hess's law cycle

Example 1

If the enthalpy of formation of SO_2 and enthalpy of combustion of SO_2 have been found to be -297.4kJ/mol and $-97.9\ \text{kJ/mol}$ respectively; by using Hess's law cycle, determine enthalpy of formation of SO_3.

Solution

Possible routes for forming SO_3:

Route 1: Direct formation from its constituent elements, sulphur and oxygen by one step only as per equation: $S(s) + \frac{3}{2}O_2(g) \longrightarrow SO_3(g)$

Route 2: Conversion of sulphur to SO_2 followed by further reaction with O_2 to form SO_3 as per equations: $S(s) + O_2(g) \longrightarrow SO_2(g)$

Then $SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g)$

Then the Hess's law cycle can be drawn as follows:

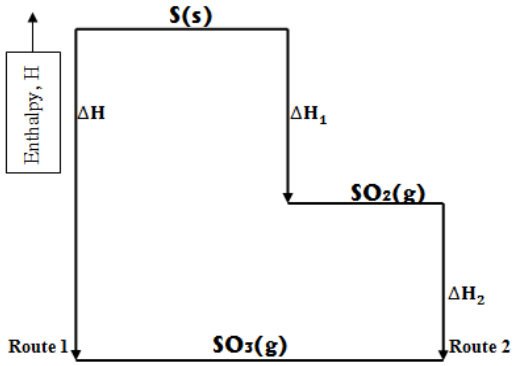


Figure 24.3 Hess's law cycle for formation of SO_3

Where: $\Delta H_1 = -297.4 kJ/mol$, $\Delta H_2 = -97.9 kJ/mol$

Then by Hess law; $\mathbf{\Delta H = \Delta H_1 + \Delta H_2}$,

Substituting $\Delta H = -297.4 + -97.9 = -395.3 kJ/mol$

Hence enthalpy of formation of SO_3 is $-395.3 kJ/mol$

Example 2

By using Hess's law, calculate enthalpy of transition of rhombic sulphur to monoclinic sulphur. Given that:

Enthalpy of combustion of monoclinic sulphur is $-296.4 kJ/mol$

Enthalpy of combustion of rhombic sulphur is $-295.1 kJ/mol$

Solution

Possible routes in formation of SO_2:

Route 1: Direct conversion of rhombic sulphur to SO_2 by one step only as per equation;

$$S(\text{rhombic}) + O_2 \longrightarrow SO_2(g)$$

Route 2: Converting rhombic sulphur to monoclinic sulphur, thereafter the monoclinic sulphur is converted to SO_2 as per equations:

$$S(\text{rhombic}) \longrightarrow S(\text{monoclinic})$$

Then $$S(\text{monoclinic}) + O_2 \longrightarrow SO_2(g)$$

So if **S(M)** stands for monoclinic sulphur and **S(R)** stands for rhombic sulphur, the Hess's law cycle for combustion of rhombic sulphur can be drawn as follows:

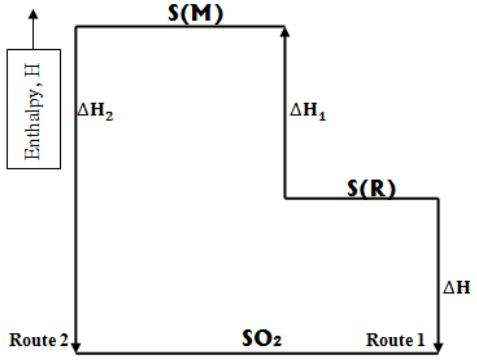


Figure 24.4 Hess's law cycle for combustion of rhombic sulphur

Where:

$\Delta\mathbf{H_1}$ = Unknown enthalpy of transition of rhombic sulphur to monoclinic sulphur

$\Delta\mathbf{H_2}$ = Enthalpy of combustion of monoclinic sulphur = -296.4kJ/mol

$\Delta\mathbf{H}$ = Enthalpy of combustion of rhombic sulphur is -295.1kJ/mol

Then by Hess's law; $\Delta\mathbf{H} = \Delta\mathbf{H_1} + \Delta\mathbf{H_2}$,

From which; $\Delta H_1 = \Delta H - \Delta H_2 = -295.1 - (-296.4) = +1.3\text{kJ/mol}$

Hence heat of transition of rhombic sulphur to monoclinic sulphur is +1.3kJ/mol

Example 3

Hydrated copper (II) sulphate can be formed by reaction between anhydrous $CuSO_4$ and water according to the following equation: $CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O(s)$

Calculate hydration enthalpy of copper (II) sulphate if enthalpies of dissolution of hydrated copper sulphate and that of anhydrous copper sulphate have been experimentally found to be $+11.70\text{kJ/mol}$ and -66.5kJ/mol respectively.

Solution

Possible routes for making solution of $CuSO_4$:

Route 1: Direct dissolving of anhydrous $CuSO_4$ in excess water by one step only as per equation: $CuSO_4(s) + \text{excess } H_2O \longrightarrow CuSO_4(aq)$

Route 2: Converting anhydrous $CuSO_4$ into crystalline $CuSO_4.5H_2O$ followed by dissolving the crystalline to give solution of $CuSO_4$ as per equations:

$$CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O(s)$$

$$CuSO_4.5H_2O(s) + aq \longrightarrow CuSO_4(aq)$$

Thus Hess's law cycle for making solution of $CuSO_4$ can be drawn as follows:

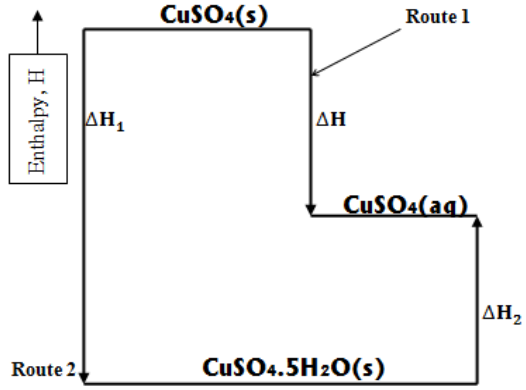


Figure 24.5 Hess's law cycle for dissolving $CuSO_4$

Where: $\Delta H_2 = 11.7\text{kJ/mol}$, $\Delta H = -66.5\text{kJ/mol}$ and ΔH_1 =?

Then by Hess law; $\Delta\mathbf{H} = \Delta\mathbf{H_1} + \Delta\mathbf{H_2}$,

From which; $\Delta H_1 = \Delta H - \Delta H_2 = -66.5 — 11.7 = -78.2\text{kJ/mol}$

Hence heat of hydration of copper (II) sulphate is -78.2kJ/mol

Combining thermochemical equations

Thermochemical equation *is a balanced stoichiometric chemical equation that includes the enthalpy change, ΔH.*

For example; $H_2(g) + ½O_2(g) \rightarrow H_2O(l); \Delta H = -285.8\text{ kJ/mol}$

$HgO\ (s) \rightarrow Hg\ (l) + ½O_2\ (g);\ \Delta H = +90.7\ kJ/mol$

In relation to thermochemical calculations, certain rules apply when using thermochemical equations:

Rule 1

ΔH is directly proportional to the quantity of a substance that reacts or is produced by a reaction.

Enthalpy is directly proportional to mass. Therefore, if you double the coefficients in an equation, then the value of ΔH is multiplied by two. For example:

$H_2(g) + ½O_2(g) \rightarrow H_2O(l);\ \Delta H = -285.8\ kJ$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(l);\ \Delta H = -571.6\ kJ$

Rule 2

ΔH for a reaction is equal in magnitude but opposite in sign to ΔH for the reverse reaction.

For example:

$HgO\ (s) \rightarrow Hg\ (l) + ½O_2\ (g);\ \Delta H = +90.7\ kJ/mol$

$Hg\ (l) + ½O_2\ (g); \rightarrow HgO\ (s);\ \Delta H = -90.7\ kJ/mol$

This law is commonly applied to phase changes, although it is true when you reverse any thermochemical reaction.

It is also known as **first law of thermochemistry** (or **first thermochemical law**). Another name is **Laplace law.**

Rule 3

ΔH is independent of the number of steps involved.

This rule is called **Hess's Law**. According to the law, ΔH for a reaction is the same whether it occurs in one step or in a series of steps provided that first reactants and final products remain the same.

So if: $\text{Reaction}(1) + \text{Reaction}(2) = \text{Reaction}(3);\ \text{then}\ \Delta H_3 = \Delta H_1 + \Delta H_2$

Good understanding of above three rules is the basis of indirect determination of enthalpy of reaction by combining thermochemical equations. And it is good to hear that all problems which are solved by Hess's law cycle can be solved by this method too**.**

Example 4

Use the following data to determine the enthalpy (ΔH^θ) of following reaction:

$NO_2(g) + \frac{7}{2}H_2(g) \longrightarrow 2H_2O(l) + NH_3(g) \quad \Delta H^\theta = ?\ kJ/mol$

Given that:

(i) $2NH_3\ (g) \longrightarrow N_2(g) + 3H_2(g) \qquad \Delta H^\theta = +92\ kJ/mol$

(ii) $\frac{1}{2}N_2(g) + 2H_2O(l) \longrightarrow NO_2(g) + 2H_2\ (g) \quad \Delta H^\theta = +170\ kJ/mol$

Solution

1) To get only one NH_3 on the right-hand side like in the required equation, equation (i) is reversed and divided by two as follows:

$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \longrightarrow NH_3(g) \quad \Delta H^\theta = -46\ kJ/mol$ ---------- **(iii)**

Notice that the sign changed on the ΔH and its numerical value was halved.

2) To get only one NO_2 on the left-hand side like in the required equation, equation (ii) is reversed as follows:

$NO_2(g) + 2H_2(g) \longrightarrow \frac{1}{2}N_2(g) + 2H_2O(l)\ \Delta H^\theta = -170\ kJ/mol$------ **(iv)**

Notice that the sign changed on the ΔH.

3) The required equation is found by taking **(iii)** + **(iv)** and cancelling terms which appear as both reactant and product as shown below:

$\cancel{\frac{1}{2}N_2}(g) + \frac{3}{2}H_2(g) + NO_2(g) + 2H_2(g) \longrightarrow NH_3(g) + \cancel{\frac{1}{2}N_2}(g) + 2H_2O(l)$

Or $NO_2(g) + \frac{7}{2}H_2(g) \longrightarrow 2H_2O(l) + NH_3(g)\ \Delta H^\theta = -46\ kJ/mol + -170\ kJ/mol$

Hence enthalpy of given reaction is $-216\ kJ/mol$

Example 5

The standard molar enthalpy of formation, ΔH_f^θ, of diborane cannot be determined directly because the compound cannot be prepared by reaction of boron and hydrogen. However, the value can be calculated. Calculate the standard enthalpy of formation of gaseous diborane (B_2H_6) using the following thermochemical information:

(a) $4B(s) + 3O_2(g) \longrightarrow 2B_2O_3(s);$ $\Delta H^\theta = -2509.1 kJ/mol$

(b) $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l);$ $\Delta H^\theta = -571.7 kJ/mol$

(c) $B_2H_6(g) + 3O_2(g) \longrightarrow B_2O_3(s) + 3H_2O(l);$ $\Delta H^\theta = -2147.5 kJ/mol$

Solution

Thermochemical equation for formation of diborane

$2B(s) + 3H_2(g) \longrightarrow B_2H_6(g);$ $\Delta H = ?$

Remember that in writing thermochemical equation for heat of formation, **one** mole of target substance (in this case diborane) must be formed.

In order to get to our formation reaction, the following should be done to equations (a), (b) and (c):

- Equation (a) is divided through by 2 so as to get 2B like in the required equation
- Equation (b) is multiplied through by 3/2 to give $3H_2$ like in the required equation
- Equation (c) is reversed to put B_2H_6 on the right-hand side like in the required equation

After above adjustments, the three equations become:

(a) $2B(s) + \frac{3}{2}O_2(g) \longrightarrow B_2O_3(s);\ \Delta H^\theta = -1254.55 kJ/mol$---------- **(i)**

(b) $3H_2(g) + \frac{3}{2}O_2(g) \longrightarrow 3H_2O(l); \Delta H^\theta = -857.55 kJ/mol$---------- **(ii)**

(c) $B_2O_3(s) + 3H_2O(l) \longrightarrow B_2H_6(g) + 3O_2(g);\ \Delta H^\theta = +2147.5 kJ/mol$---- **(iii)**

The required equation is obtained by taking (i) + (ii) + (iii) as follows:

$$2B(s) + \frac{3}{2}O_2(g) + 3H_2(g) + \frac{3}{2}O_2(g) + B_2O_3(s) + 3H_2O(l) \longrightarrow B_2O_3(s) + 3H_2O(l) + B_2H_6(g) + 3O_2(g)$$
$$2B(s) + \cancel{3O_2(g)} + 3H_2(g) + \cancel{B_2O_3(s)} + \cancel{3H_2O(l)} \longrightarrow \cancel{B_2O_3(s)} + \cancel{3H_2O(l)} + B_2H_6(g) + \cancel{3O_2(g)}$$

Whence $2B(s) + 3H_2(g) \longrightarrow B_2H_6(g)$;

And $\Delta H = (-1254.55 + -857.55 + 2147.5)kJ = +35.4kJ/mol$

Hence enthalpy of formation of diborane is $+35.4kJ/mol$

Example 6

Consider the following reaction:

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l) \quad \Delta H = -622.2\ kJ/mol$$

Given the following data, calculate the heat of reaction for the same reaction where water is a gaseous product instead of a liquid:

$$\Delta H_f \text{ for } H_2O(g) = -285.83\ kJ/mol$$
$$\Delta H_f \text{ for } H_2O(l) = -241.83\ kJ/mol$$

Solution:

Required equation:

$$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(g) \quad \Delta H = ?$$

$N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(l) \quad \Delta H = -622.2\ kJ/mol$ ------ **(i)**

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(g)\ \Delta H_f = -285.83\ kJ/mol$ ---------- **(ii)**

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\ \Delta H_f = -241.83\ kJ/mol$ ---------- **(iii)**

To get two $H_2O(g)$ on right-hand side like in the required equation, equation **(ii)** is multiplied by 2 as follows:

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)\ \Delta H_f = -571.66\ kJ/mol$ ---------- **(iv)**

To eliminate two $H_2O(l)$ from right-hand side of equation **(i)**, equation **(iii)** is reversed and multiplied by 2 as follows:

$2H_2O(l) \longrightarrow 2H_2(g) + O_2(g) \quad \Delta H = +483.66\ kJ/mol$ ---------- **(v)**

The required equation is found by taking **(i)** + **(iv)** + **(v)** and cancelling terms which appear as both reactant and product as follows:

$N_2H_4(l) + O_2(g) + \cancel{2H_2(g)} + \cancel{O_2(g)} + \cancel{2H_2O(l)} \longrightarrow N_2(g) + \cancel{2H_2O(l)} + 2H_2O(g) + \cancel{2H_2(g)} + \cancel{O_2(g)}$

Or $N_2H_4(l) + O_2(g) \longrightarrow N_2(g) + 2H_2O(g)$

And $\Delta H = (-622.2 + -571.66 + 483.66)kJ/mol = -710.2kJ/mol$

Hence if water is gaseous product, the heat of reaction would be $-710.2kJ/mol$

Thermochemical calculations by using enthalpy of formations

Hess's law can also be used for the determination of standard heat of the reaction from the knowledge of standard heats of formation of various reactants and the products. The Hess's law cycle for elements in their standard states, reactants and products can be drawn as shown in **Figure 25.6.**

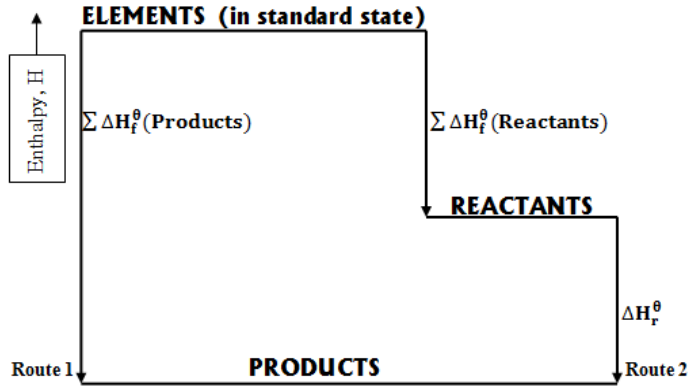


Figure 24.6 Hess's law cycle for enthalpy of reaction

Then by Hess's law:

Enthalpy change in **route 1 =** enthalpy change in **route 2**

Substituting $\sum \Delta H_f^\theta(\text{Products}) = \sum \Delta H_f^\theta(\text{Reactants}) + \Delta H_r^\theta$

From which $\boldsymbol{\Delta H_r^\theta = \sum \Delta H_f^\theta(\text{Products}) - \sum \Delta H_f^\theta(\text{Reactants})}$

The final equation is very useful in determination of enthalpy of reaction. Most of (if not all) problems which are solved by first and second method can be solved by this method (equation) and in most cases, it is the shorter method. However, the student must able to use all three methods because in some cases examiners give restriction on method to be applied in obtaining enthalpy of reaction.

Example 7

The standard enthalpy of formation of phenol is -209.3kJ/mol.

Calculate its standard enthalpy of combustion, given:

$C\,(\text{graphite}) + O_2(g) \longrightarrow CO_2(g) \qquad \Delta H^\theta = -393.5\text{kJ/mol}$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O\,(l) \qquad \Delta H^\theta = -285.9\text{kJ/mol}$

Solution

The equation for the combustion of phenol is:

$$\underset{\textbf{Phenol}}{C_6H_5OH(l)} + 7O_2(g) \longrightarrow 6CO_2(g) + 3H_2O(l)$$

And we are given with:

$\Delta H_f^\theta\,(CO_2) = -393.5\text{ kJ/mol}$, $\Delta H_f^\theta(H_2O) = -285.9\text{kJ/mol}$

$\Delta H_f^\theta\,(C_6H_5OH) = -209.3\text{kJ/mol}$

Using $\Delta H_r^\theta = \sum \Delta H_f^\theta(\text{Products}) - \sum \Delta H_f^\theta(\text{Reactants})$

Then from the equation of combustion of phenol:

$$\Delta H_c^\theta(C_6H_5OH) = 6\Delta H_f^\theta\,(CO_2) + 3\Delta H_f^\theta\,(H_2O) - \Delta H_f^\theta\,(C_6H_5OH) - 7\Delta H_f^\theta(O_2)$$

But $\Delta H_f^{\theta}(O_2) = 0$ (Heat of formation of an element in its natural state must be zero)

Then substituting given values:

$\Delta H_c^{\theta}(C_6H_5OH) = (6 \times -393.5) + (3 \times -285.9) - (-209.3)$

$\Delta H_c^{\theta}(C_6H_5OH) = -3009.4 kJ/mol$

Hence standard enthalpy of combustion of phenol is $-3009.4 kJ/mol$.

Example 8

Calculate the standard enthalpy of formation of propane, C_3H_8, from the data:

$C\ (graphite) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H^{\theta} = -393.5 kJ/mol$

$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O\ (l) \quad \Delta H^{\theta} = -285.9 kJ/mol$

The standard enthalpy of combustion of propane is $-2220 kJ/mol$

Solution

Given that:

$\Delta H_f^{\theta}(CO_2) = -393.5 kJ/mol, \quad \Delta H_f^{\theta}(H_2O) = -285.9 kJ/mol$

$C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O; \quad \Delta H_c^{\theta} = -2220 kJ/mol = \Delta H_r^{\theta}$

Using $\Delta H_r^{\theta} = \sum \Delta H_f^{\theta}(Products) - \sum \Delta H_f^{\theta}(Reactants)$

Then $\Delta H_c^{\theta}(C_3H_8) = 3\Delta H_f^{\theta}(CO_2) + 4\Delta H_f^{\theta}(H_2O) - \Delta H_f^{\theta}(C_3H_8) - 5\Delta H_f^{\theta}(O_2)$

But $\Delta H_f^{\theta}(O_2) = 0$ (Heat of formation of an element in its natural state must be zero)

So $-2220 = (3 \times -393.5) + (4 \times -285.9) - \Delta H_f^{\theta}(C_3H_8)$

From which $\Delta H_f^{\theta}(C_3H_8) = -104.1\ kJ/mol$

Hence the standard enthalpy of formation of propane is $-104.1\ kJ/mol$.

Example 9

Calculate the heat of isomerisation reaction:

$C_2H_5OH \longrightarrow CH_3 - O - CH_3$ if:

(i) Heat of formation of C_2H_5OH is $-850 kJ/mol$
(ii) Heat of combustion of $CH_3 - O - CH_3$ is $-1452 kJ/mol$
(iii) Heat of formation of CO_2 is $-395 kJ/mol$
(iv) Heat of formation of H_2O is $-284 kJ/mol$

Solution

Using $\Delta H_r = \sum \Delta H_f(Products) - \sum \Delta H_f(Reactants)$

Notice the omission of superscript 'θ' because the enthalpies given are not standard.

Thus:

Heat of isomerisation reaction $=$

$\Delta H_f(CH_3OCH_3) - \Delta H_f(C_2H_5OH) = \Delta H_f(CH_3OCH_3) - (-850) \ldots\ldots (i)$

Equation for combustion of CH_3OCH_3 is:

$CH_3OCH_3 + 3O_2 \longrightarrow 2CO_2 + 3H_2O; \quad \Delta H_c = -1452\ kJ/mol$

Then $\Delta H_c(CH_3OCH_3) = 2\Delta H_f(CO_2) + 3\Delta H_f(H_2O) - \Delta H_f(CH_3OCH_3) - 3\Delta H_f(O_2)$

But $\Delta H_f(O_2) = 0$

Substituting given values:

$-1452 = (2 \times -395) + (3 \times -284) - \Delta H_f(CH_3OCH_3)$

From which: $\Delta H_f(CH_3OCH_3) = -190 kJ/mol$ ……. (ii)

Substituting (ii) in (i) gives;

Heat of the isomerisation reaction $= -190 - (-850) = 660 kJ/mol$.

Example 10

If:

(i) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H_f = -393 kJ/mol$

(ii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$ $\Delta H_f = -286 kJ/mol$

(iii) $6C(s) + 3H_2(g) \longrightarrow C_6H_6(l)$ $\Delta H_f = +50.2 kJ/mol$

(iv) $C_2H_2(g) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + H_2O(l)$; $\Delta H_f = -1323 kJ/mol$

Calculate:

(a) The heat of formation of ethyne
(b) The heat of polymerization of ethyne to benzene.

Solution

Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

So from equation (iv);

$\Delta H_c = 2\Delta H_f(CO_2) + \Delta H_f(H_2O) - \Delta H_f(C_2H_2) - \frac{5}{2}\Delta H_f(O_2)$

But $\Delta H_f(O_2) = 0$

Then substituting given values gives: $-1323 = (2 \times -393) + -286 - \Delta H_f(C_2H_2)$

From which $\Delta H_f(C_2H_2) = 251 kJ/mol$

Hence heat of formation of ethyne is 251 kJ/mol

Equation of polymerization of ethyne to benzene is;

$3C_2H_2 \longrightarrow C_6H_6$

Ethyne **Benzene**

From which:

Heat of polymerization reaction $= \Delta H_f$ (benzene) $- 3\Delta H_f$ (ethyne)

$= 50.2 - (3 \times 251) = -702.8$ kJ/mol

Hence heat of polymerization of ethyne to benzene is $-702.8 kJ/mol$

Example 11

What is the heat of formation of NH_3 if its heat of combustion is $-379.5 kJ/mol$ and heat of formation of H_2O is $-286 kJ/mol$.

Solution

Equation for combustion of NH_3 is,

$NH_3(g) + \frac{3}{4}O_2(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2O(l)$ $\Delta H_c = -379.5 kJ/mol$

Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

Then $\Delta H_c(NH_3) = \frac{3}{2}\Delta H_f(H_2O) + \frac{1}{2}\ \Delta H_f(N_2) - ¾\ \Delta H_f(O_2) - \Delta H_f(NH_3)$

But $\Delta H_f(N_2) = 0$ and $\Delta H_f(O_2) = 0$

Substituting given values to above equation gives,

$-379.5 = \frac{3}{2} \times -286 - \Delta H_f(NH_3)$; $\Delta H_f(NH_3) = -49.5 kJ/mol$

Thus heat of formation of NH_3 is $-49.5\ kJ/mol$

Example 12

Calculate the heat of formation of anhydrous aluminium chloride (Al_2Cl_6) from the following data:

(i) $2Al(s) + 6HCl(aq) \longrightarrow 2AlCl_3(aq) + 3H_2(g)$ $\Delta H = -1003\ kJ/mol$
(ii) $H_2(g) + Cl_2(g) \longrightarrow 2HCl(g)$ $\Delta H = -184.1 kJ/mol$
(iii) $HCl(g) + aq \longrightarrow HCl(aq)$ $\Delta H = -73.2 kJ/mol$
(iv) $Al_2Cl_6(s) + aq \longrightarrow 2AlCl_3(aq)$ $\Delta H = -643.1 kJ/mol$

Hint: 2(aq) = 3(aq) = n(aq) = aq

Solution

Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

From equation (iv);

$-643.1 = 2\Delta H_f(AlCl_3(aq)) - \Delta H_f(Al_2Cl_6(s))$ ... ... (1)

From equation (iii) $-73.2 = \Delta H_f(HCl(aq)) - \Delta H_f(HCl(g))$ ... ... (2)

But from equation (ii) $2\Delta H_f(HCl(g)) = -184.1 kJ/mol$

From which $\Delta H_f(HCl(g)) = \frac{-184.1}{2} kJ/mol = -92.05 kJ/mol$

Substituting $\Delta H_f(HCl(g)) = -92.05 kJ/mol$ to (2);

$-73.2 = \Delta H_f(HCl(aq)) - (-92.05)$

$\Delta H_f(HCl(aq)) = -165.25 kJ/mol$

From equation (i);

$-1003 = 2\Delta H_f(AlCl_3(aq)) - 6\Delta H_f(HCl(aq))$

($\Delta H_f(Al) = 0$ and $\Delta H_f(H_2) = 0$)

But $\Delta H_f(HCl(aq)) = -165.25 kJ/mol$.

Therefore $-1003 = 2\Delta H_f(AlCl_3(aq)) - (6 \times -165.25)$

From which $\Delta H_f(AlCl_3(aq)) = -997.25 kJ/mol$ ... ... (3)

Substituting (3) into (1); $-643.1 = 2 \times -997.25 - \Delta H_f(Al_2Cl_6(s))$

From which $\Delta H_f(Al_2Cl_6(s)) = -1351.4 kJ/mol$.

Therefore, the heat of formation of Al_2Cl_6 is $-1351.4 kJ/mol$

Born-Haber cycle

The **Born – Haber cycle** (Named after and developed by the two German scientists Max **Born** and Fritz **Haber**) is the enthalpy diagram used in calculation of **lattice energy.** It is a system that allows for the calculation of the amount of energy released during the formation of an ionic bond.

- The cycle shows all necessary steps in the formation if ionic compounds.
- The formation of an ionic bond is actually a step wise process. After forming gaseous metallic and non-metallic atoms the following steps are involved in the process:

1. An electron is removed from the metal atom to make a positive ion in the ionisation of the metal. This value is usually positive.
2. The electron is transferred to the non-metal atom. This energy value is usually negative.
3. The ions then attract one another, forming an ionic bond.

However, it is impossible to determine the amount of energy required to make an ionic compound from its ions (**lattice energy**) in just one step.

Instead the Born-Haber cycle is used. It is a step wise process, which is based on Hess's Law.

- Below are some examples for deeper understanding of the concept.

Example 13

Calculate the lattice energy of sodium chloride from the following data: The standard enthalpy of formation of sodium chloride is -411kJ/mol, enthalpies of atomisation of sodium and chlorine are respectively $+108$ and$+121$ kJ/mol of gaseous atoms, the ionisation energy of sodium is $+$ 493 kJ/ mol and the electron affinity of chlorine is -364kJ/mol.

Solution

The following Born Haber cycle for NaCl can be drawn (not drawn to scale).

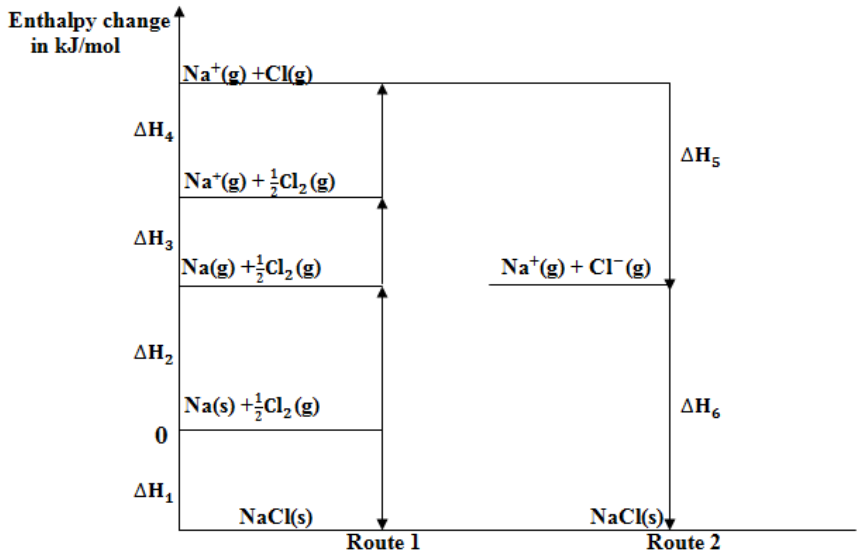


Figure 24.7 Born-Haber cycle for NaCl

Where:

ΔH_1 is the standard enthalpy of formation of sodium chloride $= -411\text{kJ/mol}$

ΔH_2 is the standard enthalpy of atomisation of sodium $= +108\text{kJ/mol}$

ΔH_3 is the ionisation energy of sodium $= +493\text{kJ/mol}$

ΔH_4 is the standard enthalpy of atomisation of chlorine $= +121\text{kJ/mol}$

ΔH_5 is the electron affinity of chlorine $= -364 kJ/mol$

ΔH_6 is the lattice energy of sodium chloride

Then by Hess's law of constant heat summation:

Enthalpy change in **Route 1**= Enthalpy change in **Route 2**

Therefore; $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

Substituting $-411 = 108 + 493 + 121 - 364 + \Delta H_6$

$\Delta H_6 = -769 kJ/mol$

The lattice energy of sodium chloride is $-769 kJ/mol$

Example 14

Calculate the lattice energy of potassium chloride from the following data:

The standard enthalpy of formation of potassium chloride $= -436 kJ/mol$

The standard enthalpy of atomisation of potassium $= +90 kJ/mol$

The standard enthalpy of atomisation of chlorine $= +121 kJ/mol$

The standard electron affinity of chlorine $= -364 kJ/mol$

The standard ionisation energy of potassium $= +420 kJ/mol$

Solution

Consider the Born- Haber cycle of formation of KCl as shown below:

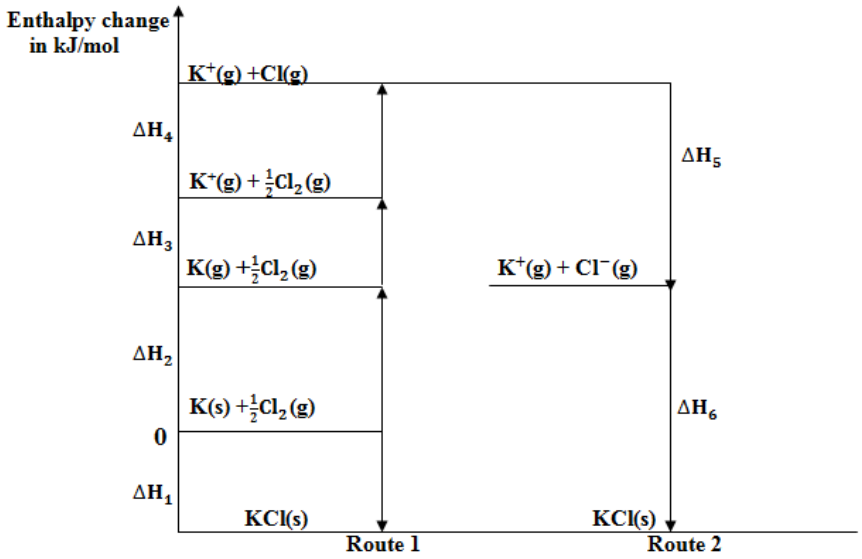


Figure 24.8 Born-Haber cycle for KCl

Where:

$\Delta H_1$is the standard enthalpy of formation of potassium chloride $= -436 kJ/mol$

ΔH_2 is the standard enthalpy of atomisation of potassium $= +90 kJ/mol$

ΔH_3 is the ionisation energy of potassium $= +420 kJ/mol$

ΔH_4 is the standard enthalpy of atomisation of chlorine $= +121 kJ/mol$

ΔH_5 is the electron affinity of chlorine $= -364 kJ/mol$

ΔH_6 is the lattice energy of potassium chloride

Then by Hess's law of constant heat summation:

Enthalpy change in **Route 1**= Enthalpy change in **Route 2**

Therefore; $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

Substituting $-436 = 90 + 420 + 121 - 364 + \Delta H_6$

$\Delta H_6 = -703 kJ/mol$

The lattice energy of potassium chloride is $-703 kJ/mol$

Example 15

For calcium, the heat of sublimation (atomisation) is $11 kJ/mol$ and the first and second ionisation potentials are $33 kJ/mol$ and $65.2 kJmol$ respectively. For Cl_2 the heat of dissociation is $13.9 kJ/mol$ and electron affinity of chlorine gaseous atom is $-20.8 kJ/mol$. The standard heat of formation of $CaCl_2$ is $-45.4 kJ/mol$

(i) Draw Born- Haber cycle for $CaCl_2$
(ii) Calculate the lattice energy for the process: $Ca^{2+}(g) + 2Cl^-(g) \rightarrow CaCl_2(s)$
(iii) If $Ca^{2+}$and Cl^-ions formed a hypothetical crystal CaCl, the lattice energy would be $+43 kJ/mol$. Use this value to calculate the heat of formation of the hypothetical CaCl.
(iv) Which one has more stable crystal lattice, $CaCl_2$ or CaCl? Give reasons.

Solution

(i) Born- Haber cycle for $CaCl_2$

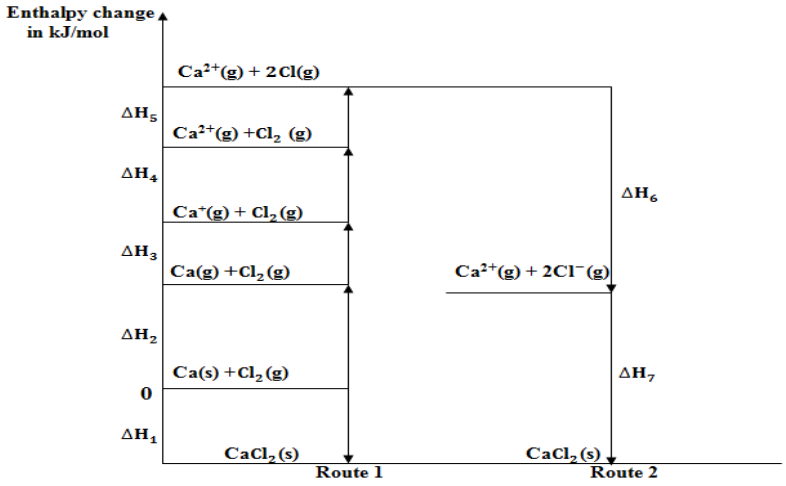


Figure 24.9 Born-Haber cycle for $CaCl_2$

Where:

ΔH_1= The standard heat of formation of $CaCl_2 = -45.4 kJ/mol$

ΔH_2= Heat of sublimation of $Ca = 11 kJ/mol$

ΔH_3= First of ionisation energy of $Ca = 33 kJ/mol$

ΔH_4 = Second ionisation energy of $Ca = 65.2 kJ/mol$

ΔH_5 = Dissociation energy of $Cl_2 = 13.9\ kJ/mol$

ΔH_6= Twice the electron affinity of chlorine $= 2 \times -20.8 = -41.6 kJ/mol$.

ΔH_7 = Lattice energy of $CaCl_2$

By Hess's law; Enthalpy change in **Route 1** = Enthalpy change in **Route 2**

Thus; $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7$

Substituting $-45.4 = 11 + 33 + 65.2 + 13.9 - 41.6 + \Delta H_7$

$\Delta H_7 = -126.9 kJ/mol$

(ii) So lattice energy for the process; $Ca^{2+}(g)+2Cl^{-}(g) \rightarrow CaCl_2(s)$ is $-126.9 kJ/mol$

(iii)When Ca^{+} and Cl^{-} forms a hypothetical crystal CaCl:

- There is not second ionisation energy of Ca, so ΔH_4 is ignored
- Dissociation energy of Cl_2 is replaced by its atomisation energy as only one atom is required, such that $A.E = ½D.E$
- Twice the electron affinity of chlorine is replaced by simply electron affinity (for one atom only) because unlike $CaCl_2$ which need two atoms of chlorine during its formation, CaCl needs one atom only.

So electron affinity of chlorine is $-20.8 kJ/mol$

Thus using: $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_5 + \Delta H_6 + \Delta H_7$ (with above modifications)

Where:

ΔH_1 = Heat of formation of CaCl

ΔH_2 = Heat of sublimation of Ca $= 11 kJ/mol$

ΔH_3 = First of ionisation energy of Ca $= 33 kJ/mol$

ΔH_5 = Atomisation energy of chlorine $= ½ D.E = ½ \times 13.9 = 6.95 kJ/mol$

ΔH_6 = Electron affinity of chlorine $= -20.8 kJ/mol$

ΔH_7 = Lattice energy of CaCl $= +43 kJ/mol$

Then $\Delta H_1 = 11 + 33 + 6.95 - 20.8 + 43 = 73.15 kJ/mol$

The heat of formation of hypothetical CaCl is $73.15 kJ/mol$

(iv) $CaCl_2$ has more stable crystal lattice than CaCl.

Reasons:

1) $CaCl_2$ has more negative heat of formation ($CaCl_2$ has negative value while CaCl has positive heat of formation)
2) $CaCl_2$ has more negative lattice energy ($CaCl_2$ has negative value while CaCl has positive lattice energy)

Example 16

Carefully study the information given below:

Atomisation energy of Ca $= +177 kJmol$

First ionisation energy of Ca $= +590 kJ/mol$

Second ionisation energy of Ca $= +1110$ kJ/mol

Heat of atomisation of oxygen $= +249 kJ/mol$

First electron affinity of oxygen $= -149 kJ/mol$

Second electron affinity of oxygen $= +790 kJ/mol$

Heat of formation of CaO $= -636 kJ/mol$

From this information draw a fully labelled Born Haber diagram for CaO and calculate the lattice energy of CaO.

Born – Heber cycle for CaO

Before drawing Born – Heber cycle, it is important to determine the amount of total electron affinity (First electron affinity + second electron affinity)

- This enables us to understand whether the electron affinity is positive or negative; thus knowing the direction of the cycle with respect electron affinity whether is upward (for positive total) or downward (for negative total)

Total electron affinity of oxygen = First electron affinity + Second electron affinity

$$= (-149 + 790)\ \text{kJ/mol} = +641\ \text{kJ/mol}$$

(On your own draw the Born Heber cycle of CaO without determining this, i.e. by indicating separately first and second electron affinity of the oxygen).

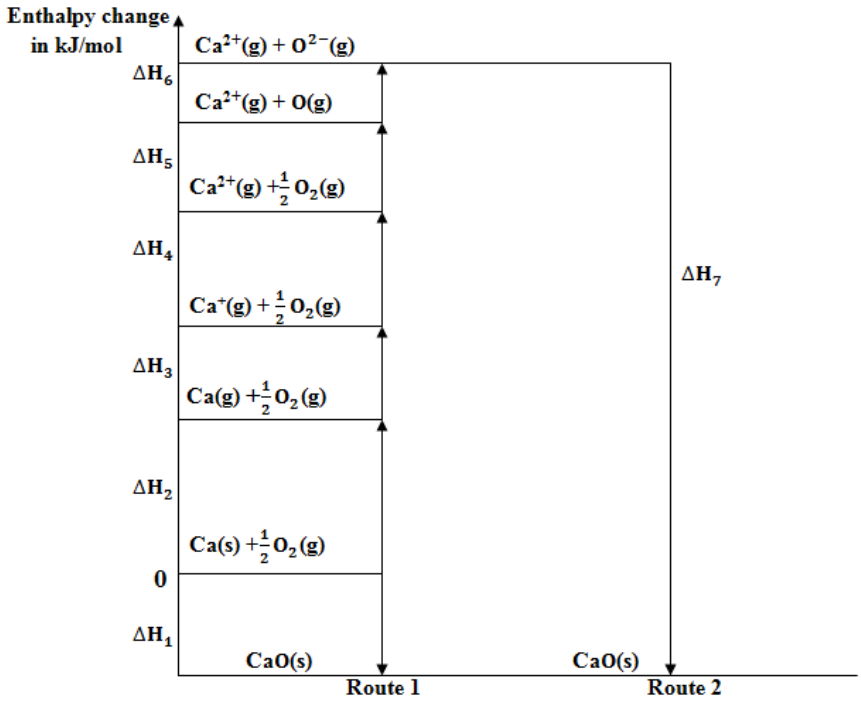


Figure 24.10 Born-Haber cycle for CaO

Where:

ΔH_1 = Heat of formation of $CaO = -636\ \text{kJ/mol}$

ΔH_2 = Atomisation energy of $Ca = +177\text{kJ/mol}$

ΔH_3 = First ionisation energy of $Ca = +590\text{kJ/mol}$

ΔH_4 = Second ionisation energy of $Ca = +1110\text{kJ/mol}$

ΔH_5 = Heat of atomisation of oxygen $= +249\text{kJ/mol}$

ΔH_6= Total electron affinity oxygen $= +641\text{kJ/mol}$

ΔH_7 = Lattice energy of CaO.

By the Hess's law:

Enthalpy change in **Route 1**= Enthalpy change in **Route 2.**

$$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7$$

Substituting $-636 = 177 + 590 + 1110 + 249 + 641 + \Delta H_7$

$$\Delta H_7 = -3403\text{kJ/mol}$$

So lattice energy for CaO is -3403kJ/mol

Thermochemical calculations by using bond energies

For better understanding of this method, we must firstly understand the term, bond energy. The term, bond energy is closely related to another term, bond dissociation energy. Good understanding of the two terms (bond dissociation energy and bond energy) is crucial in understanding thermochemical calculations by using bond energies.

Bond dissociation energy versus bond energy

When a bond breaks, energy is absorbed. So the process of bond breaking is endothermic process.

The energy required to break the bond is termed as **bond dissociation energy** (or **bond dissociation enthalpy**).
As an example to bond dissociation enthalpy (**BDE**); to break up 1 mole of gaseous hydrogen chloride molecules into separate gaseous hydrogen and chlorine atoms takes 432 kJ. The $+432\ \text{kJmol}^{-1}$ is then known as the bond dissociation energy for the H−Cl bond.

By definition; **Bond dissociation energy (enthalpy)** *is the energy (enthalpy) required (absorbed) per mole of a gaseous compound to break homolytically a particular covalent bond to produce gaseous fragments.*

Being homolytic (in breaking the bond each atom takes one electron from the two bonded electrons), the bond dissociation energy of hydrogen chloride represents energy absorbed in the following process:

$$\text{H} - \text{Cl(g)} \longrightarrow \text{H}^{\bullet}\text{(g)} + \text{Cl}^{\bullet}\text{(g)};\ \Delta\text{H} = \text{Bond dissociation energy}$$

And **not** in the following process:

$$\text{H} - \text{Cl(g)} \longrightarrow \text{H}^{+}\text{(g)} + \text{Cl}^{-}\text{(g)};\ \Delta\text{H} \neq \text{Bond dissociation energy}$$

We have seen the example of bond dissociation in the simple molecule with two atoms only (diatomic molecule) where there is only one bond; ***what if there is more complex molecule where there are more than two covalent bonds?***

To understand this, consider two cases of water molecule (H_2O) and methane molecule (CH_4).

For H_2O:

Here water has two $\text{O} - \text{H}$ covalent bonds and the two bonds break in steps.

An $\text{HO} - \text{H}$ bond of a water molecule ($\text{H} - \text{O} - \text{H}$) has 498kJ/mol of bond dissociation energy, and 430kJ/mol is needed to break the remaining $\text{O} - \text{H}$ bond as per following equations:

First step: $\text{HO} - \text{H} \longrightarrow \text{HO}^{\bullet} + \text{H}^{\bullet};\ \Delta\text{H} = 498\ \text{kJ/mol}$
Water

Second step: $\text{H} - \text{O}^{\bullet} \longrightarrow \text{O}^{\bullet\bullet} + \text{H}^{\bullet};\ \Delta\text{H} = 430\text{kJ/mol}$

A little bit confusion!

The same kinds of $\text{O} - \text{H}$ bonds in the same molecule of water have different bond dissociation energy!
If we want to mention the value of bond dissociation energy for O-H bond what is its real value?

To answer above question, the **bond energy term** was introduced. It is an average of all bond dissociation energies of the same kind present in the molecule.

Thus for $\text{O} - \text{H}$ bond; **Bond energy** $= \frac{498+430}{2} = 464\text{kJ/mol}$

Bond energy is also termed as **mean bond energy** or **average bond energy** (Although in most cases the prefix 'mean' or 'average' is dropped to remain with simply 'bond energy')

For CH_4:

In the same way for removing successive hydrogen atoms from methane the bond dissociation energies are $423\ \text{kJ/mol}$ for breaking $\text{CH}_3 - \text{H}$ bond, $480\ \text{kJ/mol}$ for breaking $\text{CH}_2 - \text{H}$ bond, $425\ \text{kJ/mol}$ for breaking $\text{CH} - \text{H}$ bond and finally $335\ \text{kJ/mol}$ for breaking $\text{C} - \text{H}$ bond.

$$\text{CH}_4\text{(g)} \rightarrow \text{CH}_3\text{(g)} \quad + \quad \text{H(g)}\ \ \Delta\text{H} = \ 423\ \text{kJ/mol}$$

$CH_3(g) \rightarrow CH_2(g) \quad + \quad H(g)\ \Delta H = \ 480\ kJ/mol$

$CH_2(g) \rightarrow CH\ (g) \quad + \quad H(g)\ \ \Delta H = \ 425\ kJ/mol$

$CH(g) \rightarrow C\ (g) \quad + \quad H(g)\ \ \Delta H = \ 335\ kJ/mol$

Thus for $C-H$ bond;

Bond energy $= \frac{423+480+425+335}{4} = 416 kJ/mol$ (By approximation)

Notice that none of the $C-H$ bond dissociation energy is 416kJ/mol.

So the following conclusion can be made on the use of two terms; bond dissociation energy and dissociation energy:

In a **diatomic molecule** (a molecule with two atoms only. The two atoms may be the same like in Cl_2 or different like in HCl) only one bond breaks per molecule and such that there is only one figure of the bond dissociation energy and hence for diatomic molecule;

Bond dissociation energy = Bond energy

For a molecule with more than one bond, an average must be found as the bond dissociation energies are always different and hence for a **polyatomic molecule** (a molecule with more than two atoms);

Bond dissociation energy = Bond energy

By definition; **bond energy (enthalpy)** *is the average energy (enthalpy) required to dissociate bonds of the same type in 1 mole of a given gaseous compound.*

Very important to note!

The reader should note the importance of use of word **'gaseous'** in both definition of bond dissociation energy and bond energy. You can only use bond energies directly if everything you are working with is in the gas state.

You cannot use bond energies to do calculations directly from substances starting in the liquid or solid state.

If you have liquid or solid present, you need an extra energy term to work out the enthalpy change when you convert them to gas. That term is the atomisation energy (enthalpy of atomisation) or more specific; **sublimation energy** for converting solid to gas or **vapourisation energy** for converting liquid to gas.

Significance of bond energy

When bond breaks heat energy is absorbed from the surroundings (endothermic process) while when a new bond is formed heat energy is evolved to the surroundings (exothermic process). So there are two main information which can be deduced from the bond energy which are:

1. It gives amount of energy required to break the bond thus determining stability of the bond

A bond with greater amount of energy is more stable and therefore the compound containing those bonds is more stable too.

2. It gives amount of energy released during the formation of the bond

Amount of energy released when a new bond is formed is numerically equal (but opposite in sign) to the amount of bond energy of the bond.

For Example, If $C-H$ bond energy is 416kJ/mol it means that:

- The process of breaking $C-H$ bond requires the energy of 416kJ/mol by average.
- During formation of $C-H$ bond, the average energy of 416kJ/mol is released to surroundings.

Being aware of that two information, enthalpy of reaction can be determined from bond energies as discussed in the next section.

In summary:

- Bond energy explain the stability of covalent bond and compound.
- Bond energy enables indirect determination (calculation) of heat of reaction.

It should be understood that:

Bond energy which applies for covalent bond is equivalent to lattice energy which applies for ionic bond. Bond energy gives the strength of covalent bond while lattice energy gives the strength the ionic bond.

Example 17

It takes 1656kJ/mol to break all bonds in methane (CH_4) and $4006\ \text{kJmol}^{-1}$ to break all bonds in propane, C_3H_8. Based on these data calculate the average bond energy of the $C-C$ bond?

Solution

Methane has **four** $C-H$ bonds

So bond energy of $C-H=\frac{\text{Total energy for dissociating all four bonds}}{4}=\frac{1656}{4}=414\text{kJ/mol}$

Propane (C_3H_8) has **eight** $C-H$ bonds and **two** $C-C$ (On your own write the structure of propane to deduce this fact).

So total bond energies in propane = $8(C-H)+2(C-C)=4006$

Substituting $(8\times 414)+2(C-C)=4006;\ C-C=\frac{694}{2}=347\text{kJ/mol}$

Hence the average bond energy for $C-C$ bond is 347kJ/mol.

Relationship between bond energies and heat of reaction

In chemical reactions, bonds are broken in the reactants and are formed in the products. The difference between the total energy absorbed in breaking the bonds and the total energy released in formation of bonds of products results to heat of the reaction.

Thus if: $\sum \mathbf{B.E(reactants)}$ represents summation of bond energies in reactants side,

$\sum \mathbf{B.E(products)}$ represents summation of bond energies in products side,

Then $\Delta \mathbf{H_r}=\sum \mathbf{B.E(reactants)}-\sum \mathbf{B.E(products)}$

Example 18

Calculate the standard enthalpy of the reaction: $CH_2=CH_2+H_2(g)\longrightarrow CH_3CH_3(g)$

Mean standard bond enthalpies are (in kJ/mol)

$C-H=416, C=C=612, C-C=348, H-H=436$

Solution

In reactants side there are:

One $C=C$, four $C-H$, one $H-H$

In products side there are:

One $C-C$, six $C-H$

Using $\Delta H_r=\sum \text{B.E(reactants)}-\sum \text{B.E(products)}$

$=(C=C)+4(C-H)+(H-H)-(C-C)-6(C-H)$

$=(C=C)+(H-H)-2(C-H)-(C-C)$ (By combining like terms)

$=612+436-(2\times 416)-348=-132\text{kJ/mol}$

So the standard enthalpy of the reaction is -132kJ/mol.

Example 19

Calculate the enthalpy of hydrogenation of propyne from the following bond energies;

Bond	Bond energy in kJ/mol
$C \equiv C$	837
$C = C$	611
$C - C$	347
$C - H$	414
$H - H$	437

Solution

The balanced equation for hydrogenation of propyne is:

$CH_3C \equiv CH(g) + 2H_2(g) \longrightarrow CH_3CH_2CH_3(g)$

In reaction side, there are: Four $C - H$, two $H - H$, One $C - C$, One $C \equiv C$

In products side, there are; Two $C - C$, eight $C - H$

Using: $\Delta H_r = \sum B.E(\text{reactants}) - \sum B.E(\text{products})$

$= 4(C - H) + 2(H - H) + (C - C) + (C \equiv C) - 2(C - C) - 8(C - H)$

$= 2(H - H) + (C \equiv C) - (C - C) - 4(C - H)$ (By combining like terms)

$= (2 \times 437) + 837 - 347 - (4 \times 414) = -292\ \text{kJ/mol}$

So the enthalpy of hydrogenation of propyne is -292kJ/mol.

Example 20

Given that, average bond energies; $(C - H) = 413\text{kJ/mol}, (C - C) = 348\text{kJ/mol}$, $(O - H) = 463\text{kJ/mol}$. Atomisation energy of hydrogen and oxygen are 217kJ/mol and $247\ \text{kJ/mol}$ respectively. The enthalpy of formation of gaseous C_2H_5OH is -235.4kJ/mol and atomisation energy of carbon is 716.7kJ/mol. Calculate the $C - O$ bond energy.

Solution

An equation to show formation of C_5H_5OH is: $2C(s) + 3H_2(g) + \frac{1}{2}O_2(g) \longrightarrow C_2H_5OH(g)$

In reactants side:

- $2 \times 716.7 = 1433.4\text{kJ/mol}$ are absorbed in atomizing 2moles of carbon atoms so as to form 2 moles of gaseous carbon atoms.
- $6 \times 217 = 1302\text{kJ/mol}$ are absorbed in atomizing 6 moles of hydrogen atoms so as to form 6 moles of gaseous hydrogen atoms.
- 247kJ/mol is absorbed in atomizing 1 mole of oxygen atom so as to form one mole of gaseous oxygen atom.

Thus the total energy absorbed in reactants side is: $(1433.4 + 1302 + 247)\ \text{kJ} = 2982.4\text{kJ}$

In products side:

- $5 \times 413 = 2065\text{kJ}$ are released in forming 5 moles of $C - H$ bonds.
- 348 kJ are released in forming 1 mole of $C - C$ bond.
- 463kJ are released in forming 1 mole of $O - H$ bond.
- Unknown energy is released in forming 1 mole $C - O$ bond

Total energy released in products side $= 2065 + 348 \times 463 + (C - O) = 2876 + (C - O)$

Thus the total energy released in products side is $2876 + (C - O)$

Using: $\Delta H_r = \sum B.E(\text{reactants}) - \sum B.E(\text{products})$

But in this question: Heat reaction = Heat of formation of C_2H_5OH

Then: $-235.4 = 2982.4 - 2876 - (C - O);\ C - O = 341.8\text{kJ/mol}$

The bond energy of $C - O$ bond is 341.8kJmol.

Example 21

The heats of combustion of methane, carbon and hydrogen are 890kJ/mol, 393kJ/mol and 285.8kJ/mol respectively. The heat of sublimation of carbon is 720kJ/mol and heat of dissociation of hydrogen molecule is 431kJ/mol. Calculate the $C - H$ bond energy in methane.

Solution

Very important to note that: Heat of combustion **must be negative** because combustion is exothermic. So in calculation we **must** use values which include negative signs (In some cases signs of thermochemical values are deliberately ignored because are yet contained in their definitions e.g. heat of combustion is the heat evolved ……So someone may consider the negative sign has been contained in the word **'evolved'** thus making unnecessary to include the sign in the value of heat of combustion. However, it is not allowed to ignore the sign in calculations).

Equation for combustion of methane is:

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g) \qquad \Delta H_c = -890\text{kJ/mol}$

But $\Delta H_c(\text{Carbon}) = \Delta H_f(CO_2) = -393\text{kJ/mol}$

$\Delta H_c\ (\text{Hydrogen gas}) = \Delta H_f(H_2O) = -285.8\text{kJ/mol}$

And $\Delta H_f(O_2) = 0$

Using $\Delta H_r = \sum \Delta H_f(\text{Products}) - \sum \Delta H_f(\text{Reactants})$

Then: $\Delta H_c(CH_4) = \Delta H_f(CO_2) + 2\Delta H_f(H_2O) - \Delta H_f(CH_4)$

$-890 = -393 + (2 \times -285.8) - \Delta H_f(CH_4)$

$\Delta H_f(CH_4) = -74.6\text{kJ/mol}$

Thermochemical equation to show formation of methane: $C\ (s) + 2H_2(g) \longrightarrow CH_4(g)$

In the reactants side:

- 720kJ/mol is absorbed in sublimating (atomizing) carbon atoms so as to form one mole of gaseous carbon atoms.
- $2 \times 431 = 862\text{kJ/mol}$ is absorbed in dissociating 2 moles of hydrogen molecules so as form 4 moles of gaseous atoms.

In the products side:

- Unknown energy is released in forming four $(C - H)$ bonds.

Using $\Delta H_r = \sum B.E(\text{reactants}) - \sum B.E(\text{products})$

But in this problem; Heat of reaction = Heat of formation of CH_4.

Then $-74.6 = 720 + 862 - 4(C - H);\ 4(C - H) = 1656.6\text{kJ/mol}$

From which $(C - H) = \frac{1656.6}{4} = 414.15\text{kJ/mol}$

Hence bond energy of $C - H$ bond is 414.15kJ/mol.

APPLICATIONS OF HESS'S LAW

The main significance of Hess's law is to allow the enthalpy change (ΔH) for a reaction to be calculated even when it cannot be measured directly. This is accomplished by performing basic algebraic operations based on the chemical equation of reactions using previously determined values for the enthalpies of formation.

Hess's law of constant heat summation is useful in the determination of enthalpies of the following:

1. Enthalpy of formation

There are a large number of compounds such as methane, benzene, ethane, ethyne which cannot be directly synthesized from their elements. Hence, their enthalpy of formation cannot be determined by the calorimetric method.
Other compounds like carbon monoxide, CO, and nitrogen monoxide, NO, are very unstable intermediates (as they are easily oxidised by oxygen into CO_2 and NO_2 respectively) such that even though they can be synthesized from their constituent elements (C and O for CO_2 or N and O_2 for NO), it is very difficult to control the amount of oxygen so as to prevent their further oxidation.
In case of such substances the enthalpy of formation can be determined by an indirect method based upon Hess's law as done in the **example 8**, **10(a)** etc.

2. Enthalpy of transition

Transition implies *the conversion of one allotropic form of a substance to another*.

For example, change of graphite to diamond, red phosphorus to yellow phosphorus and rhombic sulphur to monoclinic sulphur.
Such reactions have so small enthalpy change accompanying them that cannot be measured directly. However, Hess's law is quite helpful in determining the enthalpy of transition as done in the **example**

3. Enthalpy of reaction

Some reactions are too slow to measure their enthalpy of reaction directly. Hess's law enables indirect measurement of enthalpy of these reactions from the knowledge of standard enthalpy of formation of various reactants and the products as done in the example **9**, **10(b)** etc.

4. Enthalpy of hydration of anhydrous salt

Hydration means the conversion of an anhydrous salt into its hydrate by combining with specific number of moles of water.
Direct measurement of enthalpy of hydration is not possible. However, the use of Hess's law makes it possible as done in the **example 3**.

5. Lattice enthalpy

Lattice energies of ionic substances are always indirectly determined by Hess's law through construction of Born-Haber cycles if the electron affinity to form the anion is known (Born-Haber cycle will be discussed in the next chapter).

6. Electron affinity

Electron affinities can also be indirectly determined by using Born-Haber cycle with theoretical lattice energy.

DIGGING DEEPER EXERCISE 24

EXERCISE 24A: BINDER QUESTIONS

Question 1

Given the following data:

$SrO(s) + CO_2(g) \longrightarrow SrCO_3(s);\ \Delta H = -234 kJ/mol$

$2SrO(s) \longrightarrow 2Sr(s) + O_2(g);\ \Delta H = +1184 kJ/mol$

$2SrCO_3(s) \longrightarrow 2Sr(s) + 2C(s) + 3O_2(g);\ +2440 kJ/mol$

Find the ΔH of the following reaction: $C(s) + O_2(g) \longrightarrow CO_2(g)$

Question 2

What is the standard enthalpy of reaction for the reduction of iron (II) oxide by carbon monoxide?

$$FeO(s) + CO(g) \longrightarrow Fe(s) + CO_2(g);$$

Given the following information:

$3Fe_2O_3(s) + CO(g) \longrightarrow 2Fe_3O_4(s) + CO_2(g);\ \Delta H = -48.26\ kJ/mol$

$Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g);\ \Delta H = -23.44\ kJ/mol$

$Fe_3O_4(s) + CO(g) \longrightarrow 3FeO(s) + CO_2(g);\ \Delta H = +21.79\ kJ/mol$

Question 3

From a consideration of the following reactions, calculate ΔH_f^θ for ethane, $C_2H_6(g)$.

$CH_3CHO(g) + 2H_2(g) \longrightarrow C_2H_6(g) + H_2O(l);\ \Delta H^\theta = -204 kJ/mol$

$2H_2(g) + O_2(g) \longrightarrow 2H_2O(g);\ \Delta H^\theta = -484 kJ/mol$

$2C_2H_5OH(l) + O_2(g) \longrightarrow 2CH_3CHO(g) + 2H_2O(l);\ \Delta H^\theta = -348 kJ/mol$

$H_2O(l) \longrightarrow H_2O(g);\ \Delta H^\theta = 44 kJ/mol$

$2C_2H_5OH(l) \longrightarrow 4C(s) + 6H_2(g) + O_2(g);\ \Delta H^\theta = 555 kJ/mol$

Question 4

If the heat of combustion data for diamond and graphite is $-395.4\ kJ/mol$ and $-393.5\ kJ/mol$ respectively; calculate the heat of transition of diamond to graphite.

Question 5

Some standard enthalpy change of combustion values are listed below:

Substance	**ΔH^θ/ kJmol^{-1}**
C (graphite)	–393.5
$H_2(g)$	–285.8
ethane $C_2H_6(g)$	–1560.0

(a) Write thermochemical equation for the standard enthalpy change of combustion of ethane

(b) Use the data to calculate the standard enthalpy change of formation of ethane. Draw Hess's law cycle as part of your answer.

Question 6

(a) What name is given to the enthalpy change of the following reaction?

$$K^+(g) + Br^-(g) \longrightarrow KBr(s)$$

(b) Use the following data to construct a fully-labelled energy diagram and use it to calculate the enthalpy change in (a).

	$\Delta H^\theta/kJmol^{-1}$
$Br_2(l) \longrightarrow 2Br(g)$	$+224$
$Br(g) + e \longrightarrow Br^-(g)$	-348
$K(s) + \frac{1}{2}Br_2(l) \longrightarrow KBr(s)$	-392
$K(s) \longrightarrow K(g)$	$+90$
$K(g) \longrightarrow K^+(g) + e$	$+424$

Question 7

The following data relate to lithium chloride.

Standard molar enthalpy change of solution is $-37kJ/mol$.

Lattice enthalpy is $-846\ kJ/mol$.

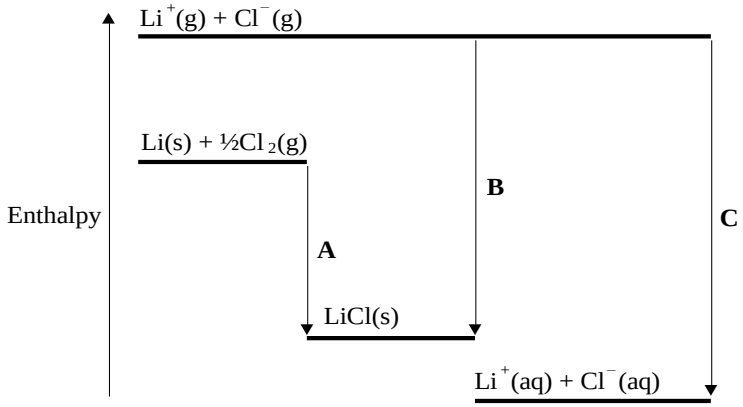


Figure 24.11 Enthalpy diagram for question 7

(a) Give the name of each of the changes **A** and **B**.
(b) Calculate the value of the enthalpy change represented by **C** and suggest the name(s) of the enthalpy change(s).

Question 8

Hydrogenation of double and triple bonds is an important industrial process. Calculate (in kJ/mol) the standard enthalpy change ΔH for the hydrogenation of ethyne (acetylene) to ethane:

$$H - C \equiv C - H(g) + 2H_2(g) \longrightarrow H_3C - CH_3(g)$$

Bond enthalpies (in kJ/mol): $C - C\ (347);\ C \equiv C\ (839);\ C - H\ (413);\ H - H\ (432)$

Question 9

Under suitable conditions decane $(C_{10}H_{22})$ can undergo cracking to give butane (C_4H_{10}) and cyclopropane (C_3H_6) as per equation: $C_{10}H_{22} \longrightarrow C_4H_{10} + 2C_3H_6$

Assuming bonds broken and formed only, what is the enthalpy change for the above reaction?

Question 10

Calculate the bond energy of the $Cl - F$ bond using the following data:

$$Cl_2 + F_2 \longrightarrow 2ClF;\ \Delta H = -108\ kJ/mol$$

Bond enthalpies (in kJ/mol): $Cl - Cl\ (239);\ F - F\ (159)$

EXERCISE 24B: REAL QUESTIONS

Question 11

Born-Haber cycle is an important tool that helps us to indirectly determine lattice energy of compounds. This is because direct determination of lattice energy through experiment is impossible. However, lattice energy determined by the Born-Haber cycle are not realised in practice for most compounds.

(i) Why direct determination of lattice energy by calorimetry is impossible?
(ii) Explain why lattice energy of most ionic compounds cannot be precisely determined by Born-Haber cycle?
(iii) Which compounds can Born-Haber cycle used to determine their lattice energy more accurate?

Question 12

Calculations of heat of reaction from bond energy is very simple method of applying Hess's law. However, when we come to real life, chemists prefer heat of formation to the bond energy. Give two reasons to support chemists' decision.

Question 13

Practically it is possible to convert one allotropic form of an element to another allotropic form; as an example, diamond can be converted to graphite under suitable conditions. However, we cannot measure heat change in these kind of reactions, why?

Question 14

Blue crystals of hydrated copper (II) sulphate can be formed by reaction between anhydrous $CuSO_4$ and water according to the following equation: $CuSO_4(s) + 5H_2O \longrightarrow CuSO_4.5H_2O(s)$. However, we cannot apply calorimetry to determine the enthalpy change for this reaction.

(i) Why the calorimetric method is not applicable?
(ii) Give any two methods which can be applied to determine the enthalpy of the above reaction.

Question 15

Alkynes such as ethyne, $H-C\equiv C-H$, are unsaturated compounds and undergo addition reactions in a similar fashion to alkenes. Under suitable conditions, ethyne will react with water, and the reaction might be expected to be;

$$H-C\equiv C-H + H_2O \longrightarrow \underset{\textbf{Ethenol}}{H_2C=CH-OH}$$

Using the bond enthalpies given below, suggest why in real life, the product of this reaction is not ethenol, but its structural isomer ethanal, CH_3CHO.

$$\Delta H/\text{kJ mol}^{-1}: \quad C\text{–}H\ 412, C=C\ 612, C\text{–}O\ 360, C=O\ 743, O\text{–}H\ 463$$

$$C\text{–}C\ 348, C\equiv C\ 837$$

EXERCISE 24C: HOT QUESTIONS

Question 16

The magnesium ions in seawater are mainly associated with chloride ions.

(a) Use the following ΔH_f^θ values to calculate a value for the ΔH^θ of the following reaction:

$$MgCl_2(s) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)$$

Species	ΔH_f^θ in kJ/mol
$MgCl_2(s)$	-641
$Mg^{2+}(aq)$	-467
$Cl^-(aq)$	-167

(b) Use your answer to explain why $MgCl_2$ is very soluble in water.

Question 17

(a) Cyclohexene, C_6H_{10}, contains one $C=C$ double bond in its molecule, of the type found in ethene. It reacts with hydrogen to form cyclohexane, C_6H_{12}, as follows:

$$C_6H_{10} + H_2 \longrightarrow C_6H_{12}$$

Calculate ΔH for this reaction, given that the enthalpies of formation of cyclohexene and cyclohexane are $-36 kJ/mol$ and $-156 kJ/mol$ respectively.

(b) Benzene undergoes a similar reaction with hydrogen to form cyclohexane:

$$C_6H_6 + H_2 \longrightarrow C_6H_{12}$$

Predict the value of ΔH for this reaction, assuming that benzene contains three $C=C$ double bonds of the type found in ethene.

(c) The actual value of ΔH for the reaction in (c) is $-207 kJ/mol$. What can you deduce from this about the stability of the benzene ring? Use an enthalpy diagram to illustrate your answer.

Question 18

(a) Using the data provided, construct a Born-Haber cycle for magnesium chloride, $MgCl_2$, and from it determine the electron affinity of chlorine.

	$\Delta H/kJmol^{-1}$
Enthalpy of atomisation of chlorine	+122
Enthalpy of atomisation of magnesium	+148
First ionisation energy of magnesium	+738
Second ionisation energy of magnesium	+1451
Lattice enthalpy of magnesium chloride	–2526
Enthalpy of formation of magnesium chloride	–641

(b) The theoretically calculated value for the lattice enthalpy of magnesium chloride is –2326kJ/mol. Explain the difference between the theoretically calculated value and the experimental value given in the data in (a), in terms of the bonding of magnesium chloride.

Question 19

A Born-Haber cycle for the formation of calcium oxide is shown below.

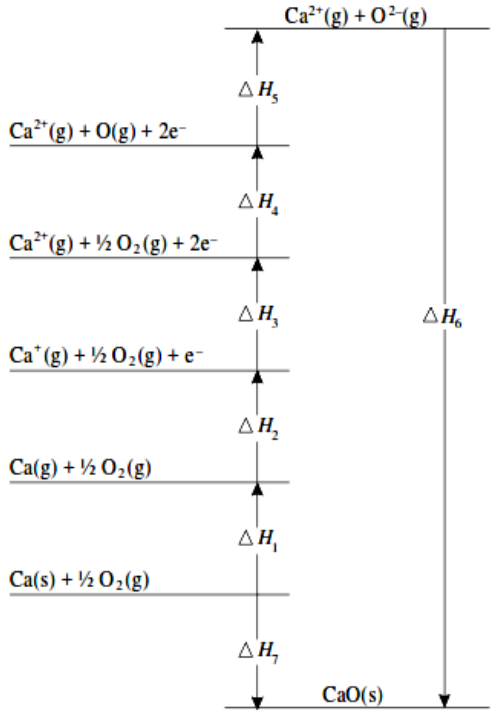


Figure 24.12 Born Haber cycle for question 19

Data $\Delta H/kJmol^{-1}$:

$$\Delta H_1 = +193;\ \Delta H_2 = 590;\ \Delta H_3 = +1150;\ \Delta H_4 = +248;\ \Delta H_6 = -3513;\ \Delta H_7 = -635.$$

(a) Identify the change which represents the lattice enthalpy of CaO.
(b) What enthalpy change does the value of ΔH_2 represent?
(c) Use the data above to calculate ΔH_5
(d) Use this value of ΔH_5 to calculate the first electron affinity of oxygen, given that the second electron affinity of oxygen is $+844\ kJ/mol$.

Question 20

A Born–Haber cycle for the formation of calcium sulphide is shown below. The cycle includes enthalpy changes for all Steps except Step **F**. (The cycle is not drawn to scale.)

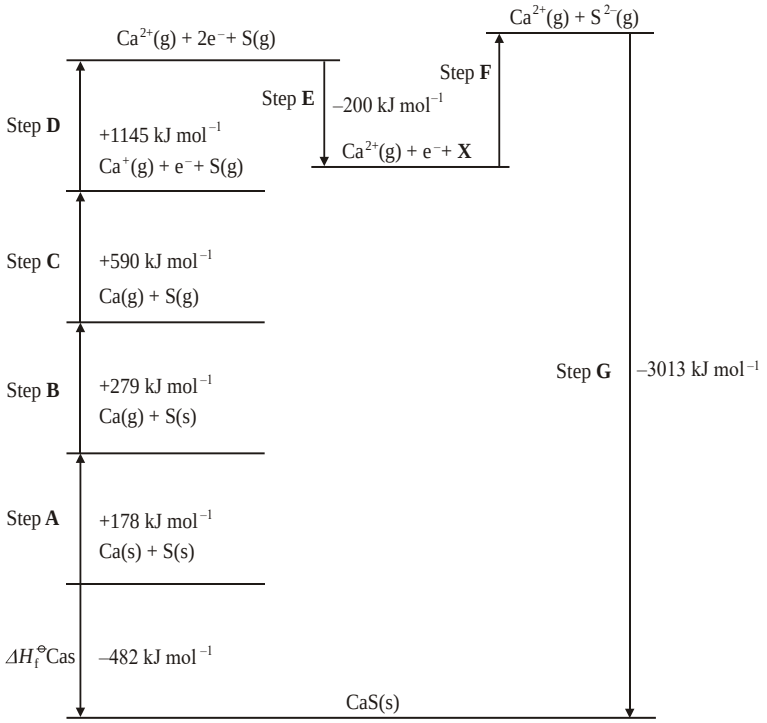


Figure 24.13 Born Haber cycle for question 20

(a) Identify the species **X** formed in Step **E**.
(b) Suggest why Step **F** is an endothermic process.
(c) Name the enthalpy change for each of the following steps.
  (i) Step **B**
  (ii) Step **D**
  (iii) Step **F**
(d) Explain why the enthalpy change for Step **D** is larger than that for Step **C**.
(e) Use the data shown in the cycle to calculate a value for the enthalpy change for Step **F**.

Question 21

(a) (i) Construct a Born-Haber cycle for the formation of calcium chloride, $CaCl_2$, from its elements. Name each step in the cycle and mark on the cycle each species involved together with its state symbol.

(ii) When calcium reacts with chlorine under normal laboratory conditions, $CaCl_2$ is formed not CaCl. Identify the stages in the Born-Haber cycle for the formation of CaCl which differ from those in the cycle for the formation of $CaCl_2$.

(b) (i) Use the data given below to calculate the standard enthalpy of solution of $CaCl_2$. Draw appropriate cycle as part of your solution.

Lattice dissociation enthalpy of $CaCl_2$ = +2255kJ mol^{-1}

Hydration enthalpy of calcium ions = –1650 kJ mol^{-1}

Hydration enthalpy of chloride ions = –384 kJ mol^{-1}

(ii) Using your answer to part (b)(i), deduce how the solubility of $CaCl_2$ changes as temperature is increased. Explain your answer.

Question 22

(a) Given the following standard enthalpies of combustion, ΔH_f^{θ},

$$C(s) = -393kJ/mol; H_2(g) = -285.6kJ/mol; C_2H_6(g) = -1560kJ/mol$$

Calculate standard enthalpy of formation of ethane

(b) Given the following bond enthalpies (bond energies) in kJ/mol:

$$C-H\ 412;\ C-C\ 347;\ O-H\ 464;\ O=O\ 498;$$

$$C=O\ 805\ (\text{for } CO_2 \text{ only});\ C-O\ 358$$

(i) Calculate the enthalpy of combustion of ethane assuming all species are gaseous.
(ii) Why in (i) do you not get the value of $-1560kJ/mol$?

Question 23

(a) Given that:

$$C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H^{\theta} = -393kJ/mol$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow H_2O(l);\ \Delta H^{\theta} = -285.6kJ/mol$$

$$6C(s) + 6H_2(g) \longrightarrow C_6H_{12}(l);\ \Delta H^{\theta} = -156kJ/mol$$

Calculate the standard enthalpy of combustion of cyclohexane.

(b) Given the following bond enthalpies in kJ/mol;

$$C-H\ 412;\ C-C\ 347;\ O-H\ 464;\ O=O\ 498;$$

$$C=O\ 805\ (\text{for } CO_2 \text{ only});\ C-O\ 358$$

Calculate theoretical enthalpy of combustion of cyclohexane, assuming all reactants and products are gases.

(c) If the enthalpy of vapourisation of water is $+40.7kJ/mol$ and the enthalpy of vapourisation of cyclohexane is $+30.0\ kJ/mol$, from your answer to (b), **recalculate** the enthalpy of combustion of cyclohexane.
(d) Compare and comment on your answers to (a), (b) and (c).

EXAMINATION QUESTIONS FOR PART SEVEN

Question 1

(a) State whether the following quantities are exothermic or endothermic.
  (i) Ionisation energy for lithium
  (ii) Electron affinity for iodine
  (iii) Electron affinity for oxygen leading to O^- and O^{2-}

(b) When a 6.5g sample of solid NaOH dissolves in $100cm^3$ of water in a coffee-cup calorimeter, the temperature rises from 21.6°C to 37.8°C. Calculate the enthalpy of solution of NaOH. (Assume the specific heat of the solution formed is $4.18Jg^{-1}K^{-1}$).

Question 2

(a) With one exception, the standard heats of formation of Mg(s), $I_2(s)$, $N_2(g)$, $NO_2(g)$, $Br_2(l)$, $Cl_2(g)$, Cu(s) and $O_2(g)$ are identical. What is the exception? Explain.

(b) For the reaction $CO(g) + NO_2(g) \rightleftharpoons CO_2(g) + NO(g)$ the amounts of activation energy for the forward and reverse reaction are known to be $32\ kJmol^{-1}$ and $82.1kJmol^{-1}$ respectively;
  (i) Calculate the heat of reaction.
  (ii) Draw the energy profile (i.e. potential energy) diagram for this system indicating the heat of reaction and the activation energy for forward and backward reaction.

Question 3

(a) The Standard enthalpy changes of formation of $MgCl, MgCl_2, MgCl_3$ are $-110kJ/mol$, $-650kJ/Mol$ and $+4000kJ/mol$ respectively. How do you compare the energetic stabilities of MgCl(s), $MgCl_2(s)$ and $MgCl_3(s)$ with respect to their constituent elements?

(b) When 15.3g of sodium nitrate was dissolved in water in a calorimeter, the temperature fell from 25°C to 21.56°C. If the heat capacity of the solution and the calorimeter is 1071 J/°C, what is the enthalpy of solution of sodium nitrate?

Question 4

(a) Given the hypothetical compounds have the lattice energies as tabulated below:

Hypothetical compound	XN	XO_2	X_2C	XS_3
Lattice energy (kJ/mol)	-700	-195.3	-630	-912

Arrange the compounds in order of increasing of their stabilities.

(b) Ethanol, which is used as a fuel, burns in air according to the equation shown below;

$$C_2H_5OH(1) + 3O_2(g) \longrightarrow 3H_2O(g) + 2CO_2(g) + \text{heat}$$

In an experiment to determine the heat value of ethanol, the heat produced by an ethanol burner was used to heat $200cm^3$ of water. The following result were obtained:

Initial mass of lamp + ethanol =56.69g

Final mass of lamp +ethanol =56.46g

Initial temperature of water =25.00℃

Final temperature of water =31.24℃

(i) Assuming there were no heat loss, calculate the heat value of ethanol.

(ii) If the experiment was carried out at standard temperature and pressure (STP), what volume of carbon dioxide gas was produced?

(C = 12, H = 1, 0 =16; specific heat capacity of water, c = 4.18kJ/kg K; molar volume of gas at STP = $22.41dm^3/mol$)

Question 5

(a) Why is it important to give the physical state of a substance in thermochemical reaction?
(b) The standard molar enthalpy changes of neutralisation for some aqueous neutralisation reactions are given below.

	Acid	**Base**	$\Delta H/kJmol^{-1}$
1.	HCl	NaOH	-57.1
2.	HCl	KOH	-57.2
3.	HNO_3	NaOH	-57.3
4.	HF	NaOH	-68.6
5.	HCl	NH_3	-52.2
6.	CH_3COOH	NaOH	-55.2
7.	HCN	NH_3	-5.4

Account qualitative for:

(i) The similarities of values in 1, 2 and 3.
(ii) The differences between the values 5, 6 and those in 1, 2 and 3.
(iii) Very high negative values in 4 and the low negative in 7.

Question 6

(a) Identify each heat change by name and classify each change as exothermic or endothermic for the following:
(i) $C_2H_5OH(l) \longrightarrow C_2H_5OH(g)$
(ii) $NaNO_3(s) + 20kJ/mol \longrightarrow NaNO_3(aq)$
(iii) $NaCl(s) \rightarrow NaCl(l)$
(iv) $1mol\ HF(g) \longrightarrow 1mol\ HF(l)$
(v) $1mol\ H_2O\ (l) \longrightarrow 1mol\ H_2O\ (s)$

(b) When 1g of anhydrous copper (II) sulphate ($CuSO_4$) was dissolved in large amount of water, $0.418kJ$ of heat was liberated. When 5g of copper (II) sulphate pentahydrate crystalline salt ($CuSO_4.5H_2O$) were dissolved in a large amount of water, $0.230kJ$ of heat were absorbed. From this data, calculate the heat change in the following reaction:

$$CuSO_4(s) + 5H_2O\ (l) \longrightarrow CuSO_4.5H_2O(s);\quad \Delta H = \mathbf{Z}kJ/mol$$

Question 7

(a) Consider the following statement, *"The more negative the value of heat of formation, the more stable the compound."* Is this statement true or false? Explain.
(b) $100cm^3$ of $1.00moldm^{-3}$ sodium hydroxide solution and $100cm^3$ of $1.00moldm^{-3}$ ethanoic acid are mixed in a calorimeter. All the three were at the same temperature. The heat capacity of the calorimeter was $90J/K$ and the rise in temperature was $5.3K$. Calculate the standard enthalpy of neutralisation (specific heat capacity of solution is $4.2Jg^{-1}K^{-1}$).

Question 8

(a) Sodium hydroxide dissolves in water according to the following equation:

$$NaOH(s) + H_2O(l) \longrightarrow Na^+(aq) + OH^-(aq) + 44kJ$$

Would this process increase or decrease the temperature of the water? Explain.

(b) $100cm^3$ of $1MKOH$ and $100cm^3$ of $1MHCl$ were mixed in a calorimeter. The temperature rise was 6.25 K. The heat capacity of calorimeter was $95J/K$ and specific heat capacity of the solution mixture was 4.2 $J/K/g$. Calculate the standard enthalpy of neutralisation.

Question 9

(a) Why the enthalpy of neutralization involving strong acid and strong base is higher compared to those involving strong acid and weak base or weak acid and strong base?

(b) $100cm^3$ of 0.5M ethanoic acid solution were mixed with $100cm^3$ of 0.5M sodium hydroxide solution in a plastic beaker of negligible heat capacity. The original temperature of reactions was 18.2°C and the final corrected temperature was 21.45°C. Calculate the enthalpy of neutralisation of ethanoic acid by sodium hydroxide under these conditions. Assume the specific of the solution to be that of water, i.e. 4.2 $Jg^{-1}°C^{-1}$.

Question 10

(a) During chemical reactions, bonds are broken (reactants) and formed (products), and the overall process may be exothermic or endothermic. Compare bond strengths in reactants and products if the overall reaction is:
   (i) Exothermic
   (ii) Endothermic

(b) $50cm^3$ of sodium hydroxide solution of concentration $0.400moldm^{-3}$ required 20.00 cm^3 of sulphuric acid of concentration 0.500 $moldm^{-3}$ for neutralisation. A temperature rise of 3.9˚C was observed if both solution and container were initially at the same temperature. Calculate the standard enthalpy of neutralisation of sodium hydroxide with sulphuric acid (the specific heat capacity of all solution is $4.2Jg^{-1}K^{-1}$and assume no heat passes to the container).

Question 11

25 cm^3 of 1.00 $moldm^{-3}$ hydrochloric acid, at 298K was added to 50 cm^3 of 1.00 $moldm^{-3}$ sodium hydroxide also initially at 298K, in a polystyrene cup calorimeter. The specific heat capacity of water is $4.2Jg^{-1}K^{-1}$ and the density of water is $1.00g/mL$.

(i) Calculate the value for standard enthalpy change for the reaction. If the temperature was raised by 4.6K.
(ii) What assumptions have to be made in order to carry this calculation?

Question 12

(a) A sprit burner containing ethanol is weighed and then used to heat up copper calorimeter containing $200cm^3$ of cold water and then reweighed. The results recorded are:

Decrease in mass of ethanol $= 0.4g$

Rise in temperature of water $= 10℃$

Specific heat capacity of water $= 4.2\ J/gK$

Heat capacity of calorimeter is negligible.

Use these results to calculate the heat of combustion of ethanol.

(b) Calculate the enthalpy change of solution of magnesium hydroxide, using the following data:

Energy or enthalpy change	Value / $kJmol^{-1}$
Lattice energy of $Mg(OH)_2(s)$	-2842
$\Delta_{hyd}(Mg^{2+}(aq))$	-1920
$\Delta_{hyd}(OH^-(aq))$	-460

Question 13

(a) Given the standard enthalpy of combustion (ΔH_c^θ) of the following substances:

$$\text{Hydrogen, } \Delta H_c^\theta = -286 \text{kJ/mol}$$

$$\text{Carbon, } \Delta H_c^\theta = -394 \text{kJ/mol}$$

$$\text{Methane, } \Delta H_c^\theta = -890 \text{kJ/mol}$$

$$\text{Ethene, } \Delta H_c^\theta = -1390 \text{kJ/mol}$$

Given that heat of formation of ethanol is -276kJ/mol; calculate in kJ/mol the heat change:

(i) Of formation of methane.
(ii) Of formation of ethene.
(iii) For the reaction $CH_2 = CH_2(g) + H_2O(l) \longrightarrow CH_3CH_2OH(l)$
(iv) Of combustion of 4.48dm^3 of ethene.

(b) By using Hess's law, calculate the standard enthalpy of formation of methane (CH_4) given that its standard heat enthalpy of combustion is 895.5 kJ/mol, the standard enthalpy of combustion of carbon graphite is 395.5 kJ/mol and the enthalpy of formation of water is 285.9 kJ/mol.

Question 14

(a) The decomposition of baking soda is represented by the following thermochemical equation:

$$2NaHCO_3(s) + 129\text{kJ} \longrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(l)$$

(i) Is this reaction exothermic or endothermic?
(ii) What is the heat of reaction (ΔH) value for this reaction?
(iii) Calculate the amount of heat required to decompose 2.24 mol of baking soda.

(b) Calculate the heat of formation of N_2O_5 from the following data of energy cycle.
(i) $NO(g) + \frac{1}{2}O_2(g) \longrightarrow NO_2(g); \quad \Delta H = -57.05 \text{kJ/mol.}$
(ii) $4NO_2(g) + O_2(g) \longrightarrow 2N_2O_5(g); \quad \Delta H = -110.2 \text{ kJ/mol.}$
(iii) $N_2(g) + O_2(g) \longrightarrow 2NO(g); \quad \Delta H = 130 \text{ kJ/mol.}$

Question 15

(a) The standard heat of formation of methane, carbon dioxide and water are $-76.2, -394.8$ and -241.6 kJ/mol, respectively. Calculate the amount of heat evolved by burning 1m^3 of methane measured at s.t.p.

(b) 5.93g of CH_3CHO is combusted in 9.29L of oxygen gas measured at 25°C and 1atm. How much heat is produced? Given that:

$$\Delta H_f^\theta(CH_3CHO) = -166 \text{kJ/mol}$$

$$\Delta H_f^\theta(H_2O) = -284 \text{kJ/mol}$$

$$\Delta H_f^\theta(CO_2) = -395 \text{kJ/mol}$$

Question 16

The following data gives the energies liberated when lg of each substance burned in excess oxygen. Use it to calculate the standard enthalpy of formation of ethene.

Substance	**Energy liberated (kJ)**
Graphite	32
Hydrogen	143
Ethene	50

Question 17

Calculate the standard of enthalpy of formation of ethyne (acetylene) from the following data:

- 2g of carbon burned in excess oxygen liberated 66.1kJ
- 2 g of hydrogen burned in excess oxygen liberated 284kJ
- 2g of ethyne burned in excess of oxygen liberated 99.5 kJ

Question 18

(a) Study carefully the information in the following table and then answer the questions that follow:

Process	ΔH^{θ}**(kJ/mol)**
$Na(s) \longrightarrow Na(g)$	$+108$
$\frac{1}{2}Cl_2(g) \longrightarrow Cl(g)$	$+121$
$Na(g) \longrightarrow Na^+(g) + e$	$+496$
$Cl(g) + e \longrightarrow Cl^-(g)$	-349
$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$	$+787$
$NaCl(s) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$	$+4$

(i) Calculate the standard enthalpy change for the process :

$$2Cl(g) \longrightarrow Cl_2(g)$$

(ii) Calculate the standard enthalpy change for the process:

$$Na(s) + \frac{1}{2}Cl_2(g) \longrightarrow Na^+(g) + Cl^-(g)$$

(iii) Compare the difference between enthalpy change for the processes:
$NaCl(s) \longrightarrow Na^+(g) + Cl^-(g)$ and $NaCl(s) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$ and then comment on the difference.

(b) Calculate the enthalpy of formation of carbon disulphide given that the enthalpy of combustion of:

$\text{Carbon disulphide} = -1072\ \text{kJ/mol.}$

$\text{Carbon} = -393.5\ \text{kJ/mol.}$

$\text{Rhombic sulphur} = -296.1\ \text{kJ/mol.}$

Question 19

(a) Some enthalpy change data are shown in the table below:

Process	**Enthalpy change** $(\mathbf{kJ/mol})$
$AgI(s) \longrightarrow Ag^+(aq) + I^-(aq)$	$+112$
$Ag^+(g) \longrightarrow Ag^+(aq)$	-464
$I^-(g) \longrightarrow I^-(aq)$	-293

(i) Use the data in above table to calculate the lattice energy of silver iodide.
(ii) A calculation of the lattice energy of silver iodide based on a perfect ionic model gives a smaller numerical value than the value calculated in (i) above. Explain this difference.

(b) Hydrogen chloride gas dissolves in water to form hydrochloric acid. Use standard enthalpies of formation shown below to calculate ΔH^{θ} of this reaction at 298K.

Standard enthalpies of formation at 298K in kJ/mol

HCl(g)	-92.3
$H^+(aq)$	0
$Cl^-(aq)$	-167.2

Question 20

(a) Anhydrous magnesium chloride, $MgCl_2$, can absorb water to form the hydrated salt, $MgCl_2.4H_2O$.

$$MgCl_2(s) + 4H_2O(l) \longrightarrow MgCl_2.4H_2O(s)$$

(i) Suggest **one** reason why the enthalpy change for this reaction cannot be determined directly by calorimetry.

(ii) Some enthalpies of solution are shown in the table below:

Salt	**Enthalpy of solution (kJ/mol)**
$MgCl_2(s)$	-155
$MgCl_2.4H_2O(s)$	-39

Calculate the enthalpy change for the absorption of water by $MgCl_2(s)$ to form $MgCl_2.4H_2O(s)$.

(b) Given that the enthalpies of combustion of ethane, ethene and hydrogen are $-1323, -1429$ and -242 kJ/mol respectively. Calculate the enthalpy of hydrogenation of ethene.

Question 21

Enthalpies of combustion of some substances are given below:

Substance	$\Delta H/kJmol^{-1}$
Hydrogen	-242
Benzene	-3302
Cyclohexene	-3746
Cyclohexane	-3940

Calculate the enthalpy of hydrogenation of benzene and cyclohexene.

Question 22

(a) What does the first law of thermodynamics say?

(b) Draw a well labelled Born Haber cycle for calcium fluoride and calculate atomisation energy of fluorine.

Heat of formation of calcium fluoride $= -860$ kJ/mol

Atomisation energy of calcium $= +174$ kJ/mol

First ionisation energy of calcium $= 550$ kJ/mol

Second ionisation energy of calcium $= +1000$ kJ/mol

Electron affinity of fluorine $= -363$ kJ/mol

Lattice energy of calcium fluoride $= -2100$ kJ/mol

Question 23

Values of energy terms appearing in the Born Haber cycle for KCl are given below. The sign of each term has been deliberately omitted.

Enthalpy of atomisation of potassium is 353.2 kJ/mol

Dissociation enthalpy of chlorine gas is 507.5 kJ/mol

Ionisation enthalpy of potassium atom is 748 kJ/mol

Electron affinity of chlorine atom is 1488.1kJ/mol

Lattice energy of potassium chloride is 2900.9kJ/mol.

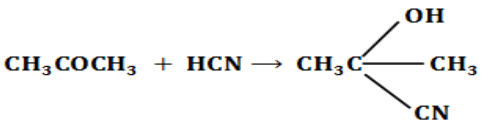
Assign either +ve or –ve sign to each energy term and calculate the enthalpy of formation of KCl(s).

Question 24

The following are mean standard bond enthalpies

$$\begin{aligned} C=O \ \Delta H &= 743\ kJ/mol \\ C-H \ \Delta H &= 412\ kJ/mol \\ C-O \ \Delta H &= 360\ kJ/mol \\ C-C \ \Delta H &= 348\ kJ/mol \\ H-O \ \Delta H &= 463\ kJ/mol \end{aligned}$$

Using above information, calculate the standard enthalpy change of the reaction;



Question 25

Using bond energies:

$$\begin{aligned} C=C &\quad 610 kJmol^{-1} \\ C-C &\quad 345\ kJ\ mol^{-1} \\ C-H &\quad 415\ kJ\ mol^{-1} \\ H-H &\quad 435\ kJ\ mol^{-1} \end{aligned}$$

And, assuming that the bonding between the carbon atoms of benzene consists of alternate double and single covalent bonds, predict a value for standard enthalpy of hydrogenation of benzene and comment on difference between this value and the experimentally determined value of approximately $-210 kJ/mol$.

Question 26

Benzene has a standard enthalpy of formation of $83 kJ/mol$.

Calculate the standard enthalpy of formation from the following data.

Mean standard bond enthalpies are

$$\begin{aligned} C-C &= 348 kJ/mol \\ C=C &= 615 kJ/mol \\ C-H &= 412\ kJ/mol \end{aligned}$$

ΔH^{θ} for vapourisation of carbon $= 715\ kJ/mol$

ΔH^{θ} for atomisation of hydrogen $= 217.5\ kJ/mol$.

Compare the experimental value and the theoretical value for ΔH_f^{θ}

Question 27

(i) What are the four factors affecting the quantity of heat evolved or absorbed during a physical or chemical transformation?

(ii) Using the following information and the fact that the average $C-H$ bond energy is $414 kJ/mol$, estimate the standard enthalpy of formation of methane (CH_4).

$$\begin{aligned} C(s) &\longrightarrow C(g); \quad \Delta H = 716 kJ \\ 2H_2(g) &\longrightarrow 4H(g); \ \Delta H = 872.8 kJ \end{aligned}$$

Question 28

(a) What does each of the following terms implies?
   (i) Heat of dilution
   (ii) Heat of solution

   What is the relation between the two terms?

(b) The reaction between peroxide and hydrazine is; $2H_2O_2 + N_2H_2 \longrightarrow 4H_2O + N_2$

   Use the values of bonds energies given below, calculate:

The enthalpy change for the above reaction in the gas phase

Bond	$O-H$	$N-H$	$N-N$	$O-O$	$N\equiv N$
Bond energy (kJ/mol)	463	391	159	143	945

Question 29

(a) State the types of enthalpies in each of the following thermochemical equations:
(i) $AgI(s)+H_2O(l) \longrightarrow Ag^+(aq) + I^-(aq)$ $\Delta H = +112kJ/mol$
(ii) $Na(s) \longrightarrow Na(g)$ $\Delta H^\theta = +108kJ/mol$
(iii) $Cl(g) + e \longrightarrow Cl^-(g)$ $\Delta H = -349kJ/mol$
(iv) $NaOH(aq) + HCl(aq) \longrightarrow NaCl + H_2O$ $\Delta H^\theta = -57kJ/mol$

(b) The table below lists a number of mean bond enthalpies values.

Bond	**Mean bond Enthalpy / kJ/mol^{-1}**
$C-C$	348
$C=C$	612
$C-H$	413
$O-H$	463

(i) Given that the enthalpy of combustion to form carbon dioxide and water (steam) is $-2102kJ/mol$ for propane and $-1977kJ/mol$ for propene, determine the enthalpy change for the oxidation of 1 mole of propane to propene and steam.

$$C_3H_8(g) + \tfrac{1}{2}O_2(g) \longrightarrow C_3H_6(g) + H_2O(g)$$

(ii) Use the mean bond enthalpies in the table above together with your answer in part (i) to calculate the bond enthalpy for the O = O bond in oxygen molecule.

Question 30

(a) Explain briefly what is wrong with each of the following definitions:
(i) **Standard enthalpy of combustion:** *Is the heat change when one mole of an element or compound is completely burned in oxygen under standard conditions of temperature and pressure.*
(ii) **Enthalpy of neutralisation:** *Is the heat evolved when dilute solutions of acid and base react to give water under given conditions of temperature and pressure.*
(iii) **Standard enthalpy of hydrogenation:** *Is the heat evolved when an unsaturated compound is converted to the corresponding saturated compound by the reaction with one mole of hydrogen under standard conditions of temperature and pressure.*
(iv) **Ionisation energy:** *Is the energy required to remove completely any valence electron each from one mole of gaseous atom or ion at given conditions of temperature and pressure.*

(b) The heat combustion of carbon and hydrogen are $393.5\ kJ/mol$ and $286\ kJ/mol$ respectively. The enthalpy of sublimation of carbon is 720kJ/mol and dissociation energy of hydrogen is $432\ kJ/mol$. Calculate the mean $C-C$ bond energy of cyclopropane given the enthalpy of combustion of cyclopropane to be $2091\ kJ/mol$; the mean $C-H$ bond energy is $414\ kJ/mol$.

ANSWERS TO DIGGING DEEPER EXERCISES

EXERCISE 23

1. (a) Exothermic, reactants (b) Endothermic, products (c) Endothermic, products

(d) Exothermic, reactants (e) Exothermic, reactants (f) Exothermic, reactants

2.

(a) $\Delta H_f^{\theta}(Br_2(g)) > 0$; Elemental bromine is liquid at standard conditions; to convert it to gas heat must be added.

(b) $\Delta H_f^{\theta}(Br_2(l)) = 0$; Diatomic liquid state is the pure elemental form of bromine.

(c) $\Delta H_f^{\theta}(I_2(g)) > 0$; Elemental iodine is solid at standard conditions; to convert it to gas, heat must be added.

(d) $\Delta H_f^{\theta}(I_2(s)) = 0$; Diatomic solid state is the pure elemental form of iodine.

3. Cl(g) has higher (more positive) enthalpy.

Reason:

The enthalpy of reaction, ΔH_r, is $\Delta H_f(\text{product}) - \Delta H_f(\text{reactant})$.The change being negative means reactant is at a higher potential than the product. When the reaction occurs, heat is released, stabilising the system and the system moves to a lower energy potential.

4. -56.848kJ/mol **5.** 46.4K (or °C) **6.** -1390kJ/mol

7.

(i) Exothermic
(ii) Exothermic
(iii) Endothermic

8. Diluting a concentrated acid with water is a highly exothermic process. So, when water is added to concentrated acid, large amount of heat is liberated which changes some water to steam explosively which can splash the acid and even the glass apparatus may break due to excessive heating.

9. From the definition of heat of solution;

Heat of solution of NaOH, $\Delta H_{soln} = \frac{\text{Heat change},\Delta H}{\text{Number of moles of NaOH},n}$

From which; $\Delta H = n \times \Delta H_{soln} = V_{soln} \times [NaOH] \times \Delta H_{soln} = \frac{500}{1000}L \times 7 mol L^{-1} \times -42000 J mol^{-1} = -147000 J$

But also; heat change, $\Delta H = -mc\Delta T$ (negative sign is introduced because the process is exothermic)

Where $m = \rho_{soln} V_{soln}$

Thus; $\Delta H = -\rho_{soln} V_{soln} c\Delta T$ (where ΔT represents temperature that increased in making the solution)

It follows that: $-\rho_{soln} V_{soln} c\Delta T = -147000 J$

Substituting $\Delta H = -1 gcm^{-3} \times 500 cm^3 \times 4.18 Jg^{-1}°C^{-1} \times \Delta T = -147000 J$

From which, $\Delta T = 70°C$

Thus the temperature of the solution $=$ Initial temperature $+ \Delta T = (21 + 70)°C = 91°C$ which is far above the temperature required to cause the burn injury and hence Mr. Akilikubwa got serious burn injury.

10. Reaction equation: $NaOH + HNO_3 \rightarrow NaNO_3 + H_2O$

Incorrect determination:

$n_{NaOH} = \frac{100}{1000} \cancel{dm^3} \times 0.3 \text{ mol} \cancel{dm^{-3}} = 0.03 mol$

$n_{HNO_3} = \frac{115}{1000} \cancel{dm^3} \times 0.305 \text{ mol} \cancel{dm^{-3}} = 0.030575 mol$

Since $n_{HNO_3} > n_{NaOH}$ and the mole ratio of the reaction equation is 1:1, HNO_3 was in excess and limited reactant is NaOH.

Thus $n_{NaOH} = n_{H_2O}$ produced $= 0.03 mol$

Using $\Delta H = mc\Delta T$; Where $m = \rho V$ and

Heat released in the reaction, $\Delta H = -\rho VC\Delta T$

Where: $\rho = 1 gcm^{-3}$; $V = (100 + 115)cm^3 = 215 cm^3$; $C = 4.2 Jg^{-1}C^{-1}$; $\Delta T = (39 - 35)°C = 4°C$

Then $\Delta H = -1 \cancel{gcm^{-3}} \times 215 \cancel{cm^3} \times 4.24.2 Jg \cancel{^{-1}C^{-1}} \times 4 \cancel{^{o}C} = -43612 J = -3.612 kJ$

Then using $\Delta H_n = \frac{\Delta H}{n_{H_2O}} = \frac{-3.612 kJ}{0.03 \text{ mol}} = -120.4 \text{ kJ/mol}$

Hence incorrectly determined enthalpy of neutralisation is -120.4 kJ/mol.

Correct determination:

Adding water to the container with NaOH does not change the number of moles of NaOH (n_{NaOH})

So n_{NaOH} and hence n_{H_2O} produced remained to be 0.03 mol. The only variable that will change is, V

That is correct $V = (100 + 115 + 20)\text{cm}^3 = 235\text{cm}^3$

(The temperature rise of 4℃ occurred in 235cm^3 of solution and not in 215cm^3).

Correct $\Delta H = -1\cancel{\text{gcm}^{-3}} \times 235\cancel{\text{cm}^3} \times 4.2\text{J}\cancel{\text{g}^{-1}\text{C}^{-1}} \times 4\,\cancel{^oC} = -3948\text{J} = -3.948\text{kJ}.$

Then correct $\Delta H_n = -\frac{3.948\text{kJ}}{0.03\text{ mol}} = -131.6\text{kJ/mol}$

Absolute error $= (131.6 - 120.4) = 11.2\text{kJ/mol}$

Percentage error $= \left(\frac{\text{Absolute error}}{\text{Real value}}\right) \times 100\% = \frac{11.2}{131.6} \times 100\% = 8.5\%$

Hence the percentage error is 8.5%

11. (a) -54.3kJ/mol

(b) The two possible reasons which made the determined value of enthalpy of neutralisation to be smaller than the actual value are:

1) **Heat loss to the surroundings** (to calorimeter wall, to air or to thermometer) due to imperfections of calorimeter or mixing the two solutions slowly, causing an underestimation of the heat released which in turn makes the enthalpy to appear smaller than the actual value.
2) **Incomplete mixing** due to incomplete transfer of acid or base from graduated cylinder or spattering of some of the acid or base leading to overestimation of amount of water produced and hence the enthalpy appears to be smaller than the actual value

12. (a) Exothermic because the temperature increases confirming that heat was released in the process.

(b) To make all the heat is given out rapidly so that heat loss becomes as small as possible.

(c) -58.5kJ/mol

(d) Since the number of moles of each reactant is the same and both are used up in the reaction (there is no limiting reagent) doubling the concentration of HCl would not change the temperature because it would become the excess reagent and KOH the limiting reagent.

13. 18.54kJ is absorbed. **14.** (a) 1.7mol (b) 255kJ (c) 10g

15. The temperature change is directly proportional to the molarity of the substance. Therefore:

Even though the volume has doubled, the molarity of acid and alkali has remained the same so the temperature rise remains to be 6℃.
When the concentration is doubled, the temperature change doubles, and hence the temperature rise and become 12℃.

16. -90kJ **17.** -605.7kJ/mol

18. (a) 12.6kJ (b) 0.015mol (c) -840kJ/mol

(d) 1. Heat lost to surroundings 2. Heat absorbed by the apparatus due to its heat capacity 3. Incomplete combustion.

EXERCISE 24

1. -394kJ/mol **2.** -10.94kJ/mol **3.** -83.5kJ/mol **4.** -1.9kJ/mol

5. (a) $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l);\ \Delta H_c^\theta = -1560\text{kJ/mol}$

Don't forget to include **state symbols** and the **value of enthalpy change** whenever you are asked to give thermochemical equation.

(b) 84.4kJ/mol

6. (a) Lattice enthalpy/energy (b) -670kJmol^{-1}

7. (a) **A** is enthalpy of formation, **B** is lattice enthalpy (b) -883kJ/mol; Hydration (or solvation) enthalpy.

8. -296kJ/mol **9.** 0 **10.** 253kJ/mol

11.

(i) It is impossible to get isolated constituent ions of a compound which would then combine and measure amount of heat evolved.
(ii) This is due to presence of covalent characters in ionic compounds.

Explanation:

Calculations of lattice energy by Born-Haber cycle assumes the bonds in the compounds are hundred percent ionic while in reality there are some covalent characters which go together with a degree of polarisation of the ionic bonds. The covalent nature makes the bond to be stronger than the prediction made by the lattice energy.

(iii) **Strongly** ionic compounds like halides of alkali metals, for example; KCl and NaF.

12. Using bond energy to calculate heat of reaction is the least accurate method for determining heat of reactions due to the following reasons:

1) The bond energy values are given as average values and hence their calculations just give estimations of heat of reactions.
2) The calculation from bond energy is for gaseous reactants and products only hence the calculated heat of reactions that involve solids and liquids will be even less accurate.

13. Such transition reactions have so small heat change accompanying them that cannot be measured directly.

14.

(i) It is difficult to control hydration of anhydrous copper (II) sulphate. Any attempt to form hydrated copper (II) sulphate by mixing anhydrous copper (II) sulphate and water in the calorimeter will give a solution of copper (II) sulphate instead of hydrated copper (II) sulphate.

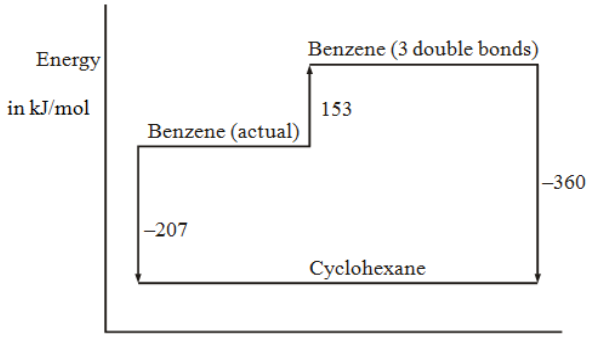
(ii) Methods which can be applied are:
1) Hess's law cycle method.
2) Combining thermochemical equation method.

15. Hint: Calculate enthalpy of reaction when ethenol is formed and when ethanal is formed and you will find that in forming ethanal the reaction is more exothermic and hence more thermodynamically favoured.

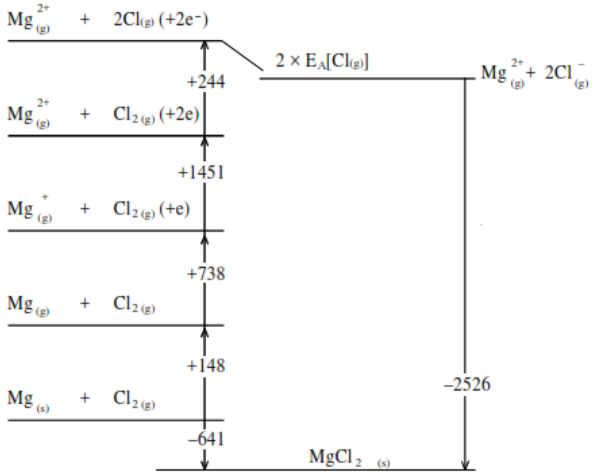
16. (a) -160kJ/mol (b) Highly exothermic enthalpy change of solution.

17. (a) -120kJ/mol (b) $3\times(-120\text{kJ/mol}) = -360\text{kJ/mol}$ (c) Benzene is more stable because unlike in cyclohexene where π bond is localised, π bonds in benzene are stabilised by delocalisation of the electrons through mesomerism and the difference between actual and calculated value amounted to +153kJ/mol is the energy required to break mesomerism/resonance before doing addition of hydrogen atoms.

Illustration



18. (a)



E.A$= -348\text{kJ/mol}$

(b) Theoretical value assumes the compound is 100% ionic while in reality the compound has some covalent character which corresponds to its degree of polarisation. So the difference is due to presence of covalent bond character because Mg^{2+} polarises Cl^-.

19. (a) ΔH_6 (b) First ionisation energy of calcium (c) +697kJ/mol (d) -147kJ/mol

20. (a) $S^-(g)$ (b) Before the addition of second electron, energy is absorbed to overcome repulsion of the first electron in step **E**. (For more detail refer to the book for Inorganic chemistry in the series) (c) (i) Atomisation enthalpy of S (ii) Second ionisation enthalpy of Ca (iii) Second electron affinity of S (d) To remove second electron in step **D** requires more energy because fewer electrons which remain after removing first electron in step **C** experience weaker screening effect **OR** simply fewer remaining electrons are more strongly attracted nearer to nucleus (due to decreased repulsion) and stronger nuclear attractive force per electron (Again you may refer to the Inorganic book in the series for more discussion) (e) $+539\text{kJ/mol}$

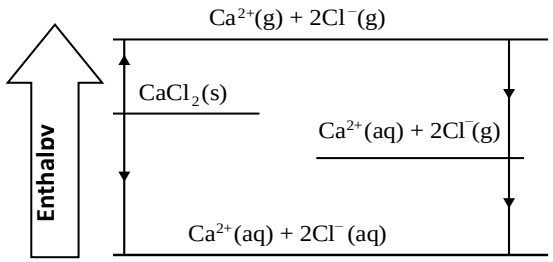
21. (a) (ii)

Second ionisation energy is required for formation of $CaCl_2$ while only first ionisation energy is required for CaCl.

Dissociation energy of $Cl_2$is required for formation of $CaCl_2$ while a half of the dissociation energy is required for CaCl.

Twice the electron affinity of Cl is required for formation of $CaCl_2$ while only single electron affinity is required for CaCl.

(b) (i)



Use above cycle to get enthalpy of solution of $CaCl_2 = -163kJ/mol$

(ii) Decrease. **Reason:** Dissolving $CaCl_2$ is exothermic (as negative sign of its enthalpy of solution obtained in (i) suggests), so according to Le-Chatelier's principle when temperature is increased the position of equilibrium shifts to the left by forming more undissolved $CaCl_2$.

22. (a) $-82.8kJ/mol$ (b) (i) $-1442kJ/mol$ (ii) The bigger source of error is that the calculation in (i) does **not** take into account the enthalpy of vapourisation of water. Extra energy would be released from the condensation of water, giving a more exothermic value which is closer to $-1560\ kJ/mol$.

Digging deeper!

Since the enthalpy of vapourisation of water is $40.7kJ/mol$, $3 \times 40.7kJ$ would be released when the water condenses, giving an enthalpy of combustion of $-1442 - (3 \times 40.7) = -1564\ kJ/mol$, which is very close to the standard value.

23. (a) $-3915.6kJ/mol$ (b) $-3720kJ/mol$ (c) $-3934.2kJ/mol$ **Hint**: To correct value obtained in (b); cyclohexane being at reactants side, apply (add to the answer obtained in (b)) its **endothermic** enthalpy of vapourisation for one mole while for water which is at products side, apply its **exothermic** enthalpy of condensation for six moles keeping in the mind that the enthalpy of condensation is of equal magnitude but opposite in sign to the enthalpy of vapourisation.

(d)

- Apart from (a) none of the answers can be considered as a standard enthalpy values at 298K/1atm, since bond enthalpy calculations can only involve gaseous species and the fact that bond energies are based on average values for similar molecules.
- The value of $-3720\ kJ/mol$, ignoring state changes, has an error of $195.6\ kJ/mol$ compared to the standard enthalpy value based on standard enthalpy changes calculated in (a).
- When corrections are applied to take into account state changes with respect to 298K/1atm, the error is reduced to $18.6\ kJ/mol$, which implies there are not bad results from average bond enthalpies in organic molecules.

SOLUTIONS TO EXAMINATION QUESTIONS

Question 1

(a)

(i) Endothermic
(ii) Exothermic (common electron affinity of iodine is the one which involve the formation of I^- which is first electron affinity).
(iii) The electron affinity leading to O^- is first electron affinity which is **exothermic**. The electron affinity leading to O^{2-} is second electron affinity which is **endothermic**.

(b) Since the reaction was accompanied with an increase in temperature, it was exothermic.
Thus $\Delta H = -mc\Delta T$; where $m = m_{NaOH} + m_{H_2O} = 6.5g + (1gcm^{-3} \times 100cm^3) = 106.5g$

Then $\Delta H = -106.5g \times 4.18Jg^{-1}K^{-1} \times (37.8 - 21.6)K = -7211.754J$

Using; $\Delta H_{soln} = \frac{\Delta H}{n_{NaOH}}$; where $n_{NaOH} = \frac{6.5g}{40gmol^{-1}} = 0.1625mol$

Then $\Delta H_{soln} = \frac{-7211.754J}{0.1625mol} = -44380J/mol$ or $-44.38kJ/mol$

The enthalpy of solution is $-44.38kJ/mol$.

Question 2

(a) $NO_2(g)$

Explanation

All the substances are in their elemental states, thus their standard heats of formation is zero, with the exception of $NO_2(g)$, which is a compound.

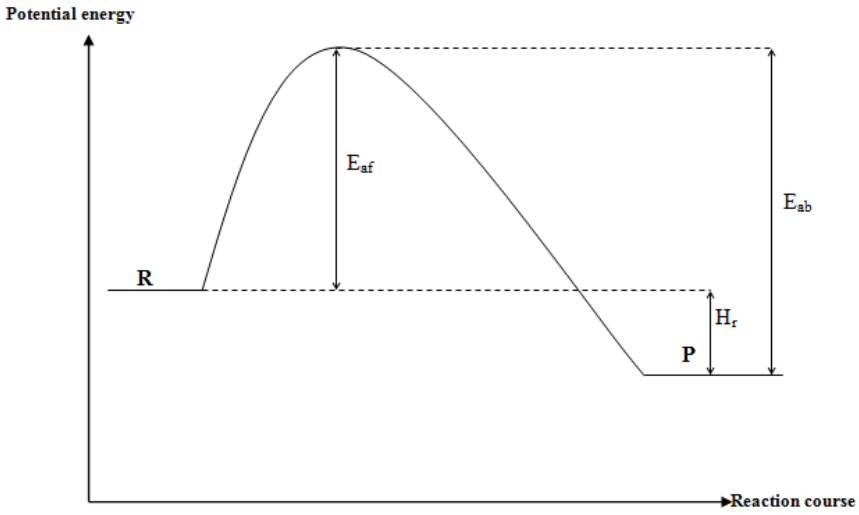
(b)(i) For reversible reaction

Heat of reaction = Activation energy of forward reaction – Activation energy for backward reaction

$= (32 - 82.1)kJ/mol = -50.1\ kJ/mol$

Hence heat reactions $-50.1kJ/mol$.

(ii)



Where **R** is the reactants $(CO(g) + NO_2(g))$

P is the products $(CO_2(g) + NO(g))$

E_{af} is the activation energy for forward reaction.

E_{ab} is the activation energy for backward reaction.

H_r is the heat of reaction

Question 3

(a) $MgCl_2$ is most stable among given elements as it has most negative heat of formation followed by MgCl which is more stable, than $MgCl_3$. $MgCl_3$ having most positive heat of formation among given compounds is least stable.
(b) Since the reaction was accompanied with a decrease in temperature, it was endothermic.
Thus ΔH = Heat capacity $\times \Delta T = 1071J/℃ \times (25 - 21.56)℃ = 3684.24J$

Using; $\Delta H_{soln} = \frac{\Delta H}{n_{NaNO_3}}$; where $n_{NaNO_3} = \frac{15.3g}{85gmol^{-1}} = 0.18mol$

Then $\Delta H_{soln} = \frac{+3684.24J}{0.18mol} = +20468J/mol \text{ or } +20.468kJ/mol$

The enthalpy of solution is $+20.468kJ/mol$.

Question 4

(a) Compound with more negative lattice energy is more stable so the order becomes:

$XO_2 < X_2C < XN < XS_3$

$\xrightarrow{\text{Increase of their stabilities}}$

(b) Using $\Delta H = mC\Delta T = \rho VC\Delta T$ ($m = \rho V$)

$\rho_{water} = 1kgdm^{-3}, V = 200cm^3 = 0.2dm^3$ $C = 4.18kJkg^{-1}K^{-1}$

$\Delta T = (31.24 - 25)℃ = 6.24℃$

$\Delta H = 1\cancel{kg\,dm^{-3}} \times 0.2\cancel{dm^3} \times 4.18kJ\cancel{kg^{-1}}\cancel{K^{-1}} \times 6.24\cancel{K} = 5.21664kJ$

The heat value of ethanol is 5.21664kJ.

Mass of ethanol burnt $= (56.69 - 56.46)g = 0.23g$

Number of males of ethanol burnt $= \frac{0.23g}{46gmol^{-1}} = 0.005mol \left(n = \frac{M}{Mr}\right)$

From the given equation of ethanol combustion mole ratio of ethanol to CO_2 is 1:2

Thus number of moles of CO_2 produced = (2×0.005) mol =0.01mol

Used $n = \frac{V}{GMV} = \frac{V}{22.4L/mol}$; $V = n \times 22.4L/mol$

$V = 0.01\cancel{mol} \times 22.4L/\cancel{mol} = 0.224L$

Volume of CO_2 produced was 0.224L

Question 5

(a) Change in the physical state is always accompanied with an energy change.

(b)

(i) The solutions involved are all strong acids and strong bases which are essentially full ionised. So in each case the same process: $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ is taking place and hence values become similar.

(ii) In 5 and 6 the process involved the absorption of energy when weak base (NH_3) and weak acid (CH_3COOH) respectively, are dissolved in their respectively reaction solutions and hence their value become low.

(iii) The large negative value in 4 indicates that although HF is a relatively weak acid; as it dissociated the small F^- (Fluoride ions) has a large exothermic (negative) enthalpy of hydration which overweighs that factor (of weak acidic strength).

Low value in 7 because both NH_3 and HCN are weak base and weak acid respectively; such that both absorb energy in being dissociated as the neutralisation proceed.

Question 6

(a)

(i) Heat of vapourisation; endothermic
(ii) Heat of solution; endothermic
(iii) Heat of fusion; endothermic
(iv) **Molar** heat of condensation; exothermic
(v) **Molar** heat of solidification; exothermic

(b) Number of moles in 1g of anhydrous $CuSO_4 = \frac{1g}{159.5gmol^{-1}} = \frac{2}{319}mol$

Thus heat evolved when the anhydrous salt is dissolved in large amount of water in kJ/mol is $\frac{0.418kJ}{\frac{2}{319}mol} = \frac{0.418\times319}{2}kJmol^{-1}$

$= 66.671kJmol^{-1}$

Number of moles in 5g of $CuSO_4.5H_2O = \frac{5g}{249.5gmol^{-1}} = \frac{10}{499}mol$

Thus heat absorbed when the hydrated salt is dissolved in large amount of water in kJ/mol

$= \frac{0.23kJ}{\frac{10}{499}mol} = \frac{0.23\times499}{10}kJmol^{-1} = 11.477kJmol^{-1}$

When anhydrous copper (II) sulphate ($CuSO_4$) is dissolved **in large amount of water**, the following reactions occur:

Firstly $CuSO_4\ (s) + 5H_2O(l) \longrightarrow CuSO_4.5H_2O(s);\ \Delta H = \mathbf{Z}kJ/mol.$

Then $CuSO_4.5H_2O(s) + aq \rightarrow [Cu(OH)_4]SO_4(aq);\ \Delta H = +11.477kJ/mol.$

Blue solution

But when the anhydrous salt is dissolved **in large amount of water**, 66.671kJ/mol is evolved.

Then – 66.671 = **Z** + 11.477; $\mathbf{Z} = -78.148$

Hence the heat change for the given reaction is $-78.148kJ/mol.$

Question 7

(a) True

Explanation

Since stability implies lower energy; the greater amount of heat released in forming a compound, the more stable is the compound relative to its elements whose heat of formations are always zero.

$$\text{Heat rise in calorimeter} = \text{heat capacity of calorimeer} \times \text{temperature rise}$$
$$= 90 \times 5.3 = 477J$$

(b) Heat rise in the solution $= MC\Delta T = \rho VC\Delta T = 1 \times (100 + 100) \times 4.2 \times 5.3 = 4452J$

Total heat evolved in the neutralisation $= -(477 + 4452) = -4929J$

Equation for the reaction: $NaOH\ (aq) + CH_3COOH(aq) \longrightarrow CH_3COONa(aq) + H_2O(l)$

From stoichiometric ratio of above equation;

Number of moles of water formed $= \frac{100}{1000} \times 1 \text{ moles} = 0.1 \text{ moles}$

$$\text{Enthalpy of neutralisation} = \frac{\text{Total heat evolved}}{\text{Number of moles of water}}$$
$$= \frac{-4929}{0.1} = -49290J/mol = 49.29kJ/mol$$

Hence the standard enthalpy of neutralisation is $-49.29kJ/mol.$

Question 8

(a) Increase

Explanation:

In the equation, heat is produced in the product side as one of the products and thus the process is exothermic. Being exothermic, the process release heat to the surroundings including water causing the temperature of water to increase.

(b) Number of moles of water formed = $\frac{100}{1000}$mol = 0.1mol

Heat rise in calorimeter = Heat capacity × temperature rise = $95 \times 6.25\text{J} = 593.75\text{J}$

Heat rise in solution = $\rho VC\Delta T = 1 \times (100 + 100) \times 4.2 \times 6.25\text{J} = 5250\text{J}$

Total heat evolved in combustion = $-(593.75 + 5250)\text{J} = -5843.75\text{J}$

Enthalpy of neutralisation = $\frac{\text{Total heat evolved}}{\text{Number of moles of water}} = \frac{-5843.75}{0.1}\text{Jmol}^{-1}\text{or } 58.4375\text{kJmol}^{-1}$

Hence the standard enthalpy of neutralisation is -58.4375kJ/mol

Question 9

(a) Because both strong acid and strong base ionises completely (to give $H^+$and OH^- respectively) it easier for neutralisation reaction to take place between them than if one of them would be weak as weak acid and base tend to ionise only partially. Easier for $H^+$and OH^- to combine means more heat is evolved and hence greater enthalpy of neutralisation between strong acid and strong base.

(b) Total enthalpy change = $\Delta T(m_v C_v + m_c C_c)$

But $C_v = 0$; so total enthalpy change = $m_c C_c \Delta T$

But $m_c = \rho_c V_c$ = 1g/cm^3× (100 + 100)cm^3 = 200g and $\Delta T = (21.45 - 18.2)℃ = 3.25℃$

Total enthalpy change = $-200 \times 4.2 \times 3.25\text{J} = -2730\text{J}$

Using enthalpy of neutralisation = $\frac{\text{Total enthalpy change}}{\text{Number of moles of water produced}}$

From the equation for the reaction:

CH_3COOH (aq) + NaOH(aq)⟶CH_3COONa (aq) + H_2O (l)

Number of moles of water produced = Number of moles of CH_3COOH

$= \frac{100}{1000} \times 0.5 \text{ moles} = 0.05\text{moles}$

Enthalpy of neutralisation = $\frac{-2730\text{J}}{0.05\text{mol}} = -54600\text{kJ/mol or } -54.6\text{kJ/mol}$

Hence enthalpy of neutralisation is -54.6kJ/mol.

Question 10

(a)

(i) Reactants have weaker bonds than products.
(ii) Reactants have stronger bonds than products.

(b) Equation for the reaction

$2NaOH\ (aq) + H_2SO_4(aq) \rightarrow Na_2SO_4 + 2H_2O(l)$

$\frac{50}{1000} \times 0.4\text{mol}$ $\frac{20}{1000} \times 0.5\text{mol}$ 0.02mol

$= 0.02\text{moles}$ $= 0.01\text{mol}$

Number of moles of water formed in the reaction is 0.02 moles.

Heat evolved in neutralisation reaction = $-mC\Delta T = \rho VC\Delta T$

Assuming density of solution = density of water = gcm^{-3}

Then the heat evolved = $-1 \times (50 + 20) \times 4.2 \times 3.9\text{ J} = -1146.6\text{ J}$.

Standard enthalpy of neutralisation = $\frac{\text{Heat evolved}}{\text{Number of moles of water formed}}$

$= \frac{-1146.6}{0.02} = 57330\text{J/mol} - 57.33\text{kJ/mol}$

Hence the standard enthalpy of neutralisation is -57.33kJ/mol.

Question 11

Hydrochloric acid and sodium hydroxide reacts according to the following equation:

$$HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O\ (l);$$

Initially:

Number of moles of HCl(aq) was $\frac{25}{1000} \times 1\text{mol} = 0.025\text{mol}$.

Number of moles of NaOH(aq) was $\frac{50}{1000} \times 1\text{mol} = 0.05\text{mol}$

From the equation of reaction, moles ratio of HCl to NaOH is 1:1

So NaOH (aq) present in excess and HCl (aq) is the **limited reactant** which predicts amount of water formed in the reaction.

Mole ratio of number of moles of HCl(aq) to water is 1:1

So number of moles of water formed was also 0.025 moles.

Then since the reaction is neutralisation reaction;

It follows that: standard enthalpy change for the reaction = standard enthalpy for neutralisation.

But Standard enthalpy of neutralisation $= \frac{\text{Heat evolved}}{\text{Number of moles of water formed}}$

$$= \frac{mC\Delta T}{nH_2O} = \frac{\rho VC\Delta T}{nH_2O} = \frac{-1 \times (25+50) \times 4.2 \times 4.6}{0.025} = -57960 J/mol \text{ or } -57.96 kJ/mol$$

Hence the standard enthalpy for the reaction is -57.96kJ/mol

Assumptions made are:

1) Polystyrene cup calorimeter has negligible heat capacity; that is no heat passes to the cup.
2) There is no volume change in mixing two solutions: that is $V_{mixture} = V_{acid} + V_{base}$
3) Enthalpy of solution is negligible, i.e. the temperature change results from neutralisation reaction only.

Question 12

(a) Heat evolved in combustion $= -mC\Delta T$

But $m = \rho V$

Then, heat evolved in combustion $= -\rho VC\Delta T$.

But density of water $1 gcm^{-3}$, $V = 200\ cm^3$, $C = 4.2\ Jg^{-1}K^{-1}$, $\Delta T = 10^{\circ}C$

So heat evolved in combustion $= -1 \times 200 \times 4.2 \times 10 J = -8400 J$

Heat of combustion of ethanol = $\frac{\text{Heat evolved in combustion}}{\text{Number of moles of ethanol reacted}}$

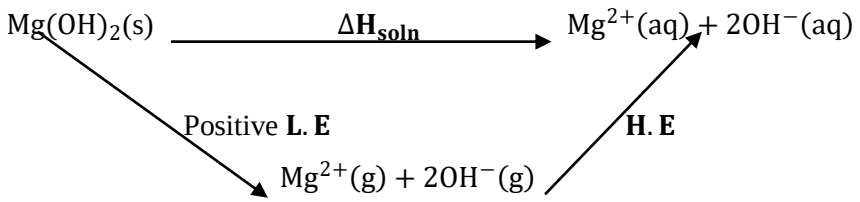
But mass of ethanol reacted = decrease in mass of ethanol $= 0.4g$

So number of moles of ethanol reacted $= \frac{0.4}{46} mol = \frac{1}{115} mol$

Therefore, heat of combustion of ethanol $= -8400 \times 115\ J/mol = -966000 J/mol$ or $-966 kJ/mol$

Hence the heat of combustion of ethanol is $-966 kJ/mol$.

(b)



$\Delta H_{soln} = \text{Positive L. E} + \text{H. E}$

Where $\text{L. E} = -2842 kJ/mol$

and $\text{H. E} = \Delta_{hyd}(Mg^{2+}(aq)) + 2\Delta_{hyd}(OH^-(aq))$

$= -1920 kJ/mol + 2 \times -460 kJ/mol = -2840 kJ/mol$

Thus $\Delta H_{soln} = 2842 kJ/mol - 2840 kJ/mol = 2 kJ/mol$.

Question 13

(a)

(i) Methane undergoes combustion according to the following equation:

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$; $\Delta H_c^{\theta} = -890 kJ/mol$

From which; $\Delta H_c^{\theta} = 2\Delta H_f^{\theta}(H_2O) + \Delta H_f^{\theta}(CO_2) - 2\Delta H_f^{\theta}(O_2) - \Delta H_f^{\theta}(CH_4)$

But $\Delta H_f^{\theta}(O_2) = 0, \Delta H_f^{\theta}(CO_2) = \Delta H_c^{\theta}(C) = -394 kJ/mol, \Delta H_f^{\theta}(H_2O) = \Delta H_c^{\theta}(H_2) = -286 kJ/mol$

Then $-890 kJ/mol = (2 \times -286 kJ/mol) + (-394 kJ/mol) - \Delta H_f^{\theta}(CH_4)$

From which $\Delta H_f^{\theta}(CH_4) = -76 kJ/mol$

(ii) Ethene undergoes combustion according to the following equation:

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l)$; $\Delta H_c^\theta = -1390 kJ/mol$

From which; $\Delta H_c^\theta = 2\Delta H_f^\theta(H_2O) + 2\Delta H_f^\theta(CO_2) - 3\Delta H_f^\theta(O_2) - \Delta H_f^\theta(C_2H_4)$

But $\Delta H_f^\theta(O_2) = 0, \Delta H_f^\theta(CO_2) = \Delta H_c^\theta(C) = -394 kJ/mol, \Delta H_f^\theta(H_2O) = \Delta H_c^\theta(H_2) = -286 kJ/mol$

Then $-1390 kJ/mol = (2 \times -286 kJ/mol) + (2 \times -394 kJ/mol) - \Delta H_f^\theta(C_2H_4)$

From which $\Delta H_f^\theta(C_2H_4) = +30 kJ/mol$

(iii) $\Delta H_r^\theta = \Delta H_f^\theta(CH_3CH_2OH) - \Delta H_f^\theta(H_2O) - \Delta H_f^\theta(C_2H_4)$

$= -276 kJ/mol - (-286 kJ/mol) - 30 kJ/mol = -20 kJ/mol$

(iv) From ideal gas equation; $n = \frac{PV}{RT}$; Where P = 1atm and T = 298K (standard conditions)

$$n_{ethene} = \frac{1\cancel{atm} \times 4.48\cancel{dm^3}}{0.082\cancel{atm\,dm^3}mol^{-1}\cancel{K^{-1}} \times 298\cancel{K}} = 0.183 mol$$

Then $\Delta H = n_{ethene} \times \Delta H_c^\theta(ethene) = 0.183\cancel{mol} \times (-1390 kJ/\cancel{mol}) = -254.37 kJ$

Hence the heat change is approximately $-254 kJ$

(b) Given that:

$\Delta H_c^\theta = \Delta H_f^\theta(CO_2) = -395.5 kJ/mol$ (Heat of Combustion is the heat evolved so it must be negative even if it is deliberately omitted)

$\Delta H_f^\theta(H_2O) = -285.9 kJ/mol$ (Here $\Delta H_f^\theta(H_2O) = \Delta H_c^\theta(H_2)$, so it must be negative too.

$\Delta H_c^\theta(CH_4) = -895.5 kJ/mol$ (Again the negative sign must be included)

An equation to show the combustion of CH_4:

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

From Hess's law of constant heat summation, it can be shown that:

$$\Delta H_r^\theta = \sum \Delta H_f^\theta(Products) - \sum \Delta H_f^\theta(Reactants)$$

Thus $\Delta H_c^\theta(CH_4) = \Delta H_f^\theta(CO_2) + 2\Delta H_f^\theta(H_2O) - \Delta H_f^\theta(CH_4) - 2\Delta H_f^\theta(O_2)$

But $\Delta H_f^\theta(O_2)$ (Heat of formation of an element in its normal state is zero)

So $-895.5 = -395.5 + (2 \times -285.9) - \Delta H_f^\theta(CH_4)$; $\Delta H_f^\theta(CH_4) = -71.8$ kJ/mol

Hence the standard enthalpy of formation of methane is $-71.8 kJ/mol$.

Question 14

(a)

(i) Endothermic

(ii) $\Delta H = +129 kJ$

(iii) From the stoichiometry of the equation;

2 mol of baking soda requires 129kJ (for its decomposition)

Thus 2.24 mol of it requires $\frac{2.24 mol}{2 mol} \times 129 kJ = 144.48 kJ$

The amount of heat required is 144.48kJ

(b) From (iii)

$\Delta H = 130 = 2H_f(NO) - H_f(N_2) - H_f(O_2)$ (Here exceptionally, heat of combustion of N_2 is positive due to its inert character. So high energy is absorbed in breaking $N \equiv N$ of N_2)

But $H_f(N_2) = 0$ and $H_f(O_2) = 0$

Then $H_f(NO) = \frac{130}{2} = 65 kJ/mol$

From (i); $\Delta H = -57.05 = H_f(NO_2) - ½H_f(O_2) - H_f(NO$

But $H_f(O_2) = 0$

Then $-57.05 = H_f(NO_2) - 65$; $H_f(NO_2) = 7.95$ kJ/mol

From (ii); $\Delta H = -110.2 = 2H_f(N_2O_5) - 4H_f(NO_2) - H_f(O_2)$

But $H_f(O_2) = 0$ and $H_f(NO_2) = 7.95$ kJ/mol

Then $-110.2 = 2H_f(N_2O_5) - (4 \times 7.95)$

From which $H_f(N_2O_5) = -39.2$ kJ/mol

Hence heat of formation of N_2O_5 is $-39.2 kJ/mol$.

Question 15

(a) Equation for combustion of methane (CH_4)

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$; $\Delta H_c^\theta = ?$

$\Delta H_c^\theta = \Delta H_f^\theta(CO_2) + 2\Delta H_f^\theta(H_2O) - \Delta H_f^\theta(CH_4) - 2\Delta H_f^\theta(O_2)$

But $\Delta H_f^\theta(O_2) = 0$

Then $\Delta H_c^\theta = -394.8 + (2 \times -241.6) + 76.2 = -801.8\ kJ/mol$

Thus $\Delta H_c^\theta(CH_4) = -801.8\ kJ/mol$

At s. t. p: $T = 273K, P = 1\ atm$

And we are given with volume of methane $= 1m^3 = 10^3 dm^3$

Assuming methane gas behaves as ideal gas, then;

$PV = nRT$ or $n = \frac{PV}{RT} = \frac{1 \times 10^3}{0.082 \times 273} = 44.67mol$

But enthalpy of combustion $= \frac{\text{Heat evolved}}{\text{Number of moles of substance burnt}}$

From which, heat evolved in burning methane $= \Delta H_c^\theta(CH_4) \times$ number of moles of CH_4

$= -801.8kJ/mol \times 44.67\ mol = -35816.4kJ$

The amount of heat evolved by burning given amount of methane is $35816.4kJ$.

(b) The given compound undergoes the combustion according to the following equation:

$$CH_3CHO\ (l) + \frac{5}{2}O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l);\ \Delta H_c^\theta = ?$$

Using $\Delta H_r^\theta = \sum \Delta H_f^\theta(\text{Products}) - \sum \Delta H_f^\theta(\text{Reactants})$

Then $\Delta H_c^\theta(CH_3CHO) = 2\Delta H_f^\theta(CO_2) + 2\Delta H_f^\theta(H_2O) - \Delta H_f^\theta(CH_3CHO)$ $(\Delta H_f^\theta(O_2) = 0)$

Substituting $\Delta H_c^\theta(CH_3CHO) = (-395kJ/mol \times 2) + (-284kJ/mol \times 2) - (-166kJ/mol) = -1192kJ/mol$

Then $n_{CH_3CHO} = \frac{5.93g}{44gmol^{-1}} = 0.1348mol$

And $n_{O_2} = \frac{PV}{RT} = \frac{1atm \times 9.29L}{0.082atmLmol^{-1}K^{-1} \times 298K} = 0.38mol$

From the above equation of combustion, 1 mol of CH_3CHO reacts with $\frac{5}{2}$ mol of O_2.

Thus $0.1348mol$ of CH_3CHO reacts with $\frac{5}{2} \times 0.1348mol = 0.337mol$ of O_2 which is smaller than the given amount of O_2 and hence the oxygen was in excess (as expected) and CH_3CHO was limited reactant.

The limited is the one that determine the amount of heat change (in this case heat released) in the reaction because it is entirely consumed in the reaction.

Using $\Delta H_c^\theta(CH_3CHO) = \frac{\Delta H}{n_{CH_3CHO}}$

From which; $\Delta H = \Delta H_c^\theta(CH_3CHO) \times n_{CH_3CHO} = -1192kJ/mol \times 0.1348mol = -160.7kJ$

The amount of heat produced is approximately $161kJ$.

Question 16

Number of moles in 1g of graphite (carbon) = $\frac{1}{12}mol$

Thus enthalpy of combustion of carbon $= -32 \times 12kJ/mol = -384kJ/mol = \Delta H_f^\theta(CO_2)$

Number of moles in 1g of hydrogen = $\frac{1}{2}mol$

Thus enthalpy of combustion of hydrogen $= -143 \times 2 = -286kJ/mol = \Delta H_f^\theta(H_2O)$

Number of moles in 1g of ethene $(C_2H_4) = \frac{1}{28}mol$

Thus enthalpy of combustion of ethene $= -50 \times 28 = -1400kJ/mol$

Equation to show combustion of ethene:

$C_2H_4 + 3O_2 \longrightarrow 2CO_2 + 2H_2O \quad \Delta H_c = -1400kJmol^{-1}$

Using $\Delta H_r^\theta = \sum \Delta H_f^\theta(\text{Products}) - \sum \Delta H_f^\theta(\text{Reactants})$;

$\Delta H_c(C_2H_4) = 2\Delta H_f^\theta(CO_2) + 2\Delta H_f^\theta(H_2O) - \Delta H_f^\theta(C_2H_4)$

Substituting $-1400 = (2 \times -384) + (2 \times -286) - \Delta H_f^\theta(C_2H_4)$;

From which $\Delta H_f^\theta(C_2H_4) = 60kJ/mol$

Hence the standard enthalpy of formation of ethene is $60kJ/mol$.

Question 17

Using enthalpy of combustion $= \frac{\text{Enthalpy evolved}}{\text{Number of moles of substance burned}}$

Number of moles in 2g of carbon $= \frac{2}{12}\text{mol} = \frac{1}{6}\text{mol}$

Thus enthalpy of combustion of carbon $= -66.1 \times 6\ \text{kJ/mol} = -396.6\text{kJ/mol}$

Number of moles in 2g of hydrogen $= \frac{2}{2}\text{mol} = 1\text{mol}$

Thus enthalpy of combustion of hydrogen $= \frac{-284}{1}\text{kJmol}^{-1} = -284\text{kJmol}^{-1}$

Number of moles in 2g of ethyne $(C_2H_2) = \frac{2}{26}\text{mol} = \frac{1}{13}\text{mol}$

Thus enthalpy of combustion of ethyne $= -99.5 \times 13\ \text{kJ/mol} = -1293.5\ \text{kJ/mol}$

Equation to show combustion of ethyne:

$C_2H_2 + \frac{5}{2}O_2 \longrightarrow 2CO_2 + H_2O \quad \Delta H_c = -1293.5\text{kJmol}^{-1}$

$\Delta H_c = -1293.5 = 2\Delta H_f(CO_2) + \Delta H_f(H_2O) - \Delta H_f(C_2H_2)$

Then $-1293.5 = (2 \times -396.6) + -284 - \Delta H_f(C_2H_2); \Delta H_f(C_2H_2) = 216.3\text{kJ/mol}$

Hence heat of formation of ethyne is 216.3kJ/mol

Question 18

(a)

(i) Given:

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g);\ \Delta H^\theta = +121\text{kJ/mol} \ldots\ldots (i)$

Reversing (i) gives;

$Cl(g) \rightarrow \frac{1}{2}Cl_2(g);\ \Delta H^\theta = +121\text{kJ/mol} \ldots\ldots (ii)$

Taking $2 \times$ (ii) gives;

$2Cl(g) \rightarrow Cl_2(g)\Delta H^\theta = 2 \times -121\text{kJ/mol} = -242\text{kJ/mol}$

The standard enthalpy change for the given process is -242kJ/mol

(ii) Given;

$Na(s) \rightarrow Na(g);\ \Delta H^\theta = +108\text{kJ/mol} \ldots\ldots (i)$

$Na(g) \rightarrow Na^+(g) + e;\ \Delta H^\theta = +496\text{kJ/mol} \ldots\ldots (ii)$

$\frac{1}{2}Cl_2(g) \rightarrow Cl(g);\ \Delta H^\theta = +121\text{kJ/mol} \ldots\ldots (iii)$

$Cl(g) + e \rightarrow Cl^-(g);\ \Delta H^\theta = -349\text{kJ/mol} \ldots\ldots (iv)$

Taking (i)+(ii)+(iii)+(iv) gives;

$$Na(s) + Na(g) + \frac{1}{2}Cl_2(g) + Cl(g) + e^- \rightarrow Na(g) + Na^+(g) + e + Cl(g) + Cl^-(g)\Delta H^\theta = (108 + 496 + 121 - 349)\text{kJ/mol}$$

Cancelling like terms which appear as both reactants and products gives;

$Na(s) + \frac{1}{2}Cl_2(g) \rightarrow Na^+(g) + Cl^-(g);\ \Delta H^\theta = +376\ \text{kJ/mol}$

The enthalpy change for the given process is $+376\ \text{kJ/mol}$.

Comparison:

(iii) The enthalpy change of the process, $NaCl(s) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$

is **less endothermic** than that of the process $NaCl(s) \rightarrow Na^+(g) + Cl^-(g)$

Comment:

The process, $NaCl(s) + H_2O(i) \rightarrow Na^+(aq) + Cl^-(aq)$ involves hydration of ions which is exothermic and hence the overall process becomes less endothermic with the hydration energy amounted to $-783\ \text{kJ/mol}$ $(4\text{kJ/mol} - 787\text{kJ/mol})$ accounting for the difference in enthalpy change of the two processes.

(b) Given that:

$\Delta H_c(\text{carbon}) = -393.5\ \text{kJ/mol} = \Delta H_f(CO_2)$

$\Delta H_c(\text{sulphur}) = -296.1\text{kJ/mol} = \Delta H_f(SO_2)$

Equation to show combustion of carbon disulphide

$CS_2 + 3O_2 \rightarrow CO_2 + 2SO_2; \quad \Delta H = -1072\ \text{kJ/mol}$

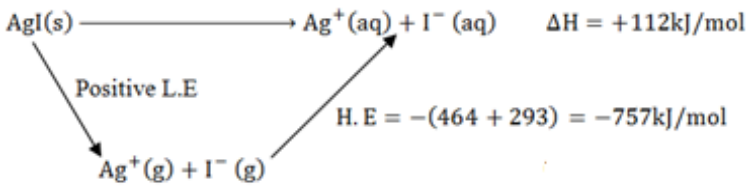
$\Delta H = -1072 = \Delta H_f(CO_2) + 2\Delta H_f(SO_2) - \Delta H_f(CS_2) = -393.5 + (2 \times -296.1) - \Delta H_f(CS_2)$

$\Delta H_f\ (CS_2) =\ 86.3\ kJ/mol$

Hence the enthalpy of formation of carbon disulphide is $86.3kJ/mol$.

Question 19

(a)



By Hess's law:

$\Delta H = \text{Positive L. E} + \text{H. E}$

Substituting $+112\ kJ/mol = \text{Positive L. E} + (-757kJ/mol)$

From which positive L.E = $+869kJ/mol$

The lattice energy of silver iodide is $-869kJ/mol$

Alternative solution:

Given that:

$AgI(s) \rightarrow Ag^+(aq) + I^-(aq);\ \Delta H = +112kJ/mol$ ... ... (i)

$Ag^+(g) \rightarrow Ag^+(aq);\quad \Delta H = -464kJ/mol$ ... ... (ii)

$I(g) \rightarrow I^-(aq)\quad \Delta H = -293kJ/mol$ ... ... (iii)

Reversing (i) gives;

$Ag^+(aq) + I^-(aq) \rightarrow AgI(s);\ \Delta H = -112kJ/mol$ ... ... (iv)

Taking (ii)+(iii)+(iv) and cancelling like terms which appear as both reactants and products gives;

$Ag^+(aq) + I^-(g) \rightarrow AgI(s) \Delta H = -(464 + 293 + 112)kJ/mol$

Hence the lattice of silver iodide is $-869kJ/mol$

Having high degree of polarisation, AgI is highly covalent in character and therefore practically bonds are stronger than predicted.

(b) $HCl(g) + (aq) \longrightarrow H^+(aq) + Cl^-(aq);\quad H^\theta = ?$

$H^\theta = \Delta H_f^\theta(H^+) + \Delta H_f^\theta(Cl^-) - \Delta H_f^\theta(HCl);\ \Delta H^\theta = 0 - 167.2 + 92.3 = -74.9kJ/mol$

Hence ΔH^θ for this reaction is $-74.9kJ/mol$.

Question 20

(a)

(i) Practically it is impossible to prevent dissolving of the crystals in water thus the obtained enthalpy change will always accompany enthalpy of solution of the dissolved part of the crystals.

(ii) Consider the formation of $Mg^{2+}(aq)$ and $Cl^-(aq)$ from anhydrous $MgCl_2(s)$ and H_2O by the following possible routes:

Route 1: Direct route.

$MgCl_2(s) + H_2O\ (excess) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)\quad \Delta H = -155kJ/mol$

Route 2: Indirect route under the following steps:

Step 1: $MgCl_2(s) + 4H_2O(l) \longrightarrow MgCl_2.4H_2O(s)\quad \Delta H = \Delta H_1$

Step 2: $MgCl_2.4H_2O(s) + H_2O\ (excess) \longrightarrow Mg^{2+}(aq) + 2Cl^-(aq)\ \Delta H_2 = -39kJ/mol$

Then from Hess's law:

Enthalpy change in route 1 = Enthalpy change in route 2

$\Delta H = \Delta H_1 + \Delta H_2$

Substituting $-155kJ/mol = \Delta H_1 + -39kJ/mol;\quad \Delta H_1 = -116kJ/mol$

The enthalpy change is $-116kJ/mol$

(b) An equation for combustion of ethane is;

(i) $C_2H_6 + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O;\quad \Delta H = -1323kJ/mol$

An equation for combustion of ethene is;

(ii) $C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O;\ \Delta H = -1429kJ/mol$

An equation for combustion of hydrogen is:

(iii) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O; \quad \Delta H = -242\text{kJ/mol}$

An equation for hydrogenation of ethene is:

(iv) $C_2H_4 + H_2 \rightarrow C_2H_6; \quad \Delta H = ?$

From (iii) $\Delta H = \Delta H_f(H_2O) = -242\text{kJ/mol}$

From (i) $\Delta H = -1323 = 3\Delta H_f(H_2O) + 2\Delta H_f(CO_2) - \Delta H_f(C_2H_6) - \frac{7}{2}\Delta H_f(O_2)$

Where $\Delta H_f(O_2) = 0$ and $\Delta H_f(H_2O) = -242\text{kJ/mol}$.

So $2\Delta H_f(CO_2) = \Delta H_f(C_2H_6) - 597$ ……(1)

From (ii) $\Delta H = -1429 = 2\Delta H_f(CO_2) + 2\Delta H_f(H_2O) - \Delta H_f(C_2H_4) - 3\Delta H_f(H_2O)$

Where $\Delta H_f(O_2) = 0$ and $\Delta H_f(H_2O) = -242\text{kJ/mol}$

So $2\Delta H_f(CO_2) = \Delta H_f(C_2H_4) - 945$ ……(2)

Equating (1) and (2) gives;

$\Delta H_f(C_2H_6) - 597 = \Delta H_f(C_2H_4) - 945$

$\Delta H_f(C_2H_6) - \Delta H_f(C_2H_4) = -348\text{ kJ/mol}$

But from (iv);

$\Delta H_f(C_2H_6) - \Delta H_f(C_2H_4) =$ Heat of hydrogenation of ethene; where $\Delta H_f(H_2) = 0$.

Hence heat of hydrogenation of ethene is -348 kJ/mol.

Question 21

Equation to show combustion of benzene:

(i) $C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O; \quad \Delta H = -3302\text{kJ/mol}$

Benzene

Equation to show combustion of cyclohexene

(ii) $C_6H_{10} + \frac{17}{2}O_2 \longrightarrow 6CO_2 + 5H_2O; \quad \Delta H = -3746\text{ kJ/mol}$

Cyclohexene

Equation to show combustion of cyclohexane

(iii) $C_6H_{12} + 9O_2 \longrightarrow 6CO_2 + 6H_2O; \quad \Delta H = -3940\text{kJ/mol}$

Cyclohexane

From (i)

$\Delta H = -3302 = 6\Delta H_f(CO_2) + 3\Delta H_f(H_2O) - \Delta H_f(C_6H_6)$ ……(1)

From (iii) $\Delta H = -3940 = 6\Delta H_f(CO_2) + 6\Delta H_f(H_2O) - \Delta H_f(C_6H_{12})$ ……(2)

(1) – (2) gives: $638 = \Delta H_f(C_6H_{12}) - \Delta H_f(C_6H_6) - 3\Delta H_f(H_2O)$

But it is given that: $\Delta H_c(\text{hydrogen}) = -242\text{kJ/mol} = \Delta H_f(H_2O)$

Then $638 = \Delta H_f(C_6H_{12}) - \Delta H_f(C_6H_6) - (3 \times -242)$

From which $\Delta H_f(C_6H_{12}) - \Delta H_f(C_6H_6) = -88\text{kJ/mol}$

But from the equation of hydrogenation of benzene:

$$C_6H_6 + 3H_2 \longrightarrow C_6H_{12}$$

Benzene cyclohexane

From which, heat of hydrogenation of benzene = $\Delta H_f(C_6H_{12}) - \Delta H_f(C_6H_6)$.

Hence heat of hydrogenation of benzene is -88kJ/mol.

From (ii)

$\Delta H = -3746 = 6\Delta H_f(CO_2) + 5\Delta H_f(H_2O) - \Delta H_f(C_6H_{10})$ ……(3)

Taking (3) – (2) gives;

$194 = \Delta H_f(C_6H_{12}) - \Delta H_f(C_6H_{10}) - \Delta H_f(H_2O)$

But $\Delta H_f(H_2O) = -242\text{ kJ/mol}$

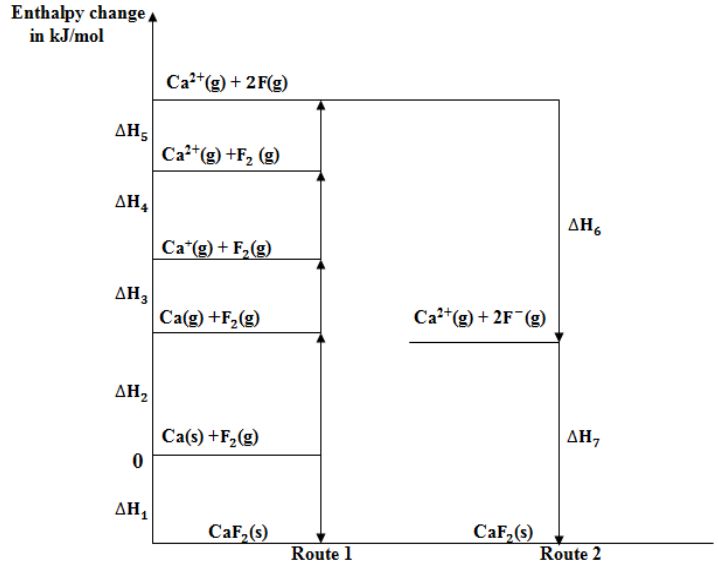
Then $\Delta H_f(C_6H_{12}) - \Delta H_f(C_6H_{10}) = -48\text{kJ/mol}$.

But from equation of hydrogenation of cyclohexene, $C_6H_{10} + H_2 \longrightarrow C_6H_{12}$

From which; enthalpy of hydrogenation of cyclohexene = $\Delta H_f(C_6H_{12}) - \Delta H_f(C_6H_{10})$

Hence enthalpy of hydrogenation of cyclohexene is -48 kJ/mol.

Question 22



Where:

ΔH_1 is the heat of formation of calcium fluoride $= -860\ \text{kJ/mol}$

$\Delta H_2$is the atomisation energy of calcium $= +174\ \text{kJ/mol}$

$\Delta H_3$is the first ionisation energy of calcium $= +550\ \text{kJ/mol}$

ΔH_4 is the second ionisation energy of calcium $= +1000\ \text{kJ/mol}$

ΔH_5 is the dissociation energy of fluorine gas

$\Delta H_6$is the twice election affinity of fluorine $= 2 \times -363 = -726\ \text{kJ/mol}$

ΔH_7 is the lattice energy of calcium fluoride $= -2100\ \text{kJ/mol}$

By Hess's law of constant heat summation: $\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6 + \Delta H_7$

$-860 = 174 + 550 + 1000 + \Delta H_5 - 726 - 2100;\ \Delta H_5 = 242\ \text{kJ/mol}$

Thus dissociation energy of fluorine gas is 242kJ/mol.

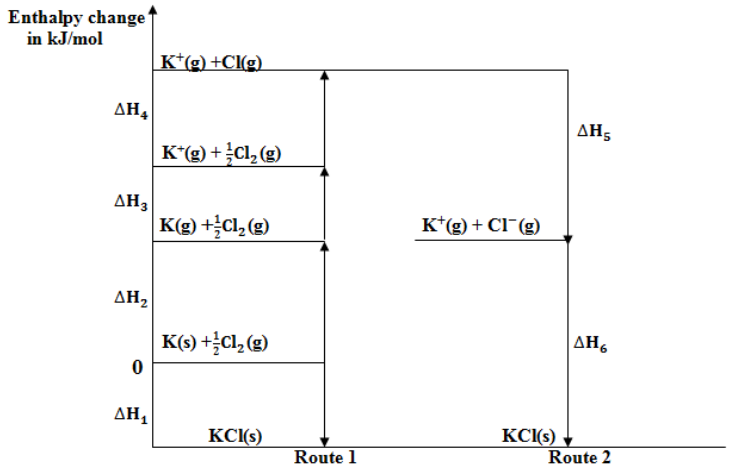
But atomisation energy $= \frac{\text{Dissociation energy}}{2} = \frac{242}{2} = 121\text{kJ/mol}$

Hence the atomisation energy of fluorine is 121kJ/mol.

Question 23

Enthalpy	Amount
Enthalpy of atomisation of potassium	+353.2 kJ/mol
Dissociation of enthalpy of chlorine gas	+507.5 kJ/mol
Ionisation enthalpy of potassium atom	+748 kJ/mol
Electron affinity of chlorine atom	−1488.1 kJ/mol
Lattice energy of potassium chloride	−2900.9 kJ/mol

Born-Haber cycle for KCl



Where:

ΔH_1 is enthalpy of formation of KCl(s)

ΔH_2 is the enthalpy of atomisation of potassium $= +353.2\text{kJ/mol}$

ΔH_3 is the ionisation enthalpy of potassium atom $= +748\text{kJ/mol}$

ΔH_4 is the atomisation enthalpy of chlorine $= ½ \times 507.5\ \text{kJ/mol} = 253.75\text{kJ/mol}$

ΔH_5 is the electron affinity of chlorine atom $= -1488.1\text{kJ/mol}$

ΔH_6 is the lattice energy of potassium chloride $= -2900.9\text{kJ/mol}$.

By Hess's law of constant Heat Summation

$\Delta H_1 = \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 + \Delta H_6$

$\Delta H_1 = (353.2 + 748 + 253.75 - 1488.1 - 2900.9)\text{kJ/mol}$

$\Delta H_1 = -3034.05\text{kJ/mol}$

Hence the enthalpy of formation of KCl(s) is -3034.05kJ/mol.

Question 24

Enthalpy for the reaction = total bond energy of reactants – total bond energy of products

$= 6(C-H) + 2(C-C) + (C=O) + (C-H) + (C\equiv N) - 6(C-H) - 3(C-C) - (C-O) - (O-H) - (C\equiv N)$

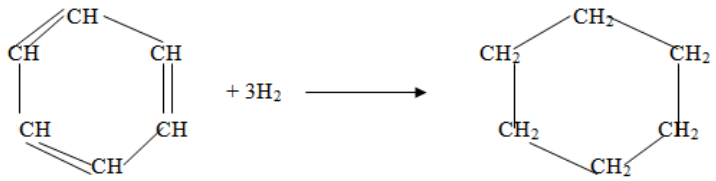
$= (C=O) + (C-H) - (C-O) - (O-H) - (C-C)$

$= 743 + 412 - 360 - 463 - 348 = -16\text{kJ/mol}$

Hence the standard enthalpy change for the reaction is -80kJ/mol.

Question 25

Equation to show hydrogenation of benzene



Benzene Cyclohexane

Using $\Delta H_r = \sum \text{B.E(reactants)} - \sum \text{B.E(products)}$

$= 3(C-C) + 3(C=C) + 6(C-H) + 3(H-H) - 6(C-C) - 12(C-H)$

$= 3(C=C) + 3(H-H) - 3(C-C) - 6(C-H)$

$= (3 \times 610) + (3 \times 435) - (3 \times 345) - (6 \times 415) = -390\ \text{kJ/mol}$

Hence standard enthalpy of hydrogenation of benzene is -390kJ/mol.

Comment:

Experimentally determined value is lower (less negative) than the calculated heat of hydrogenation because π electrons (electron in pi bond) are delocalized throughout the benzene ring in mesomerism. So extra energy amounted to 180 kJ/mol **(resonance energy**) is required to break the resonance of electrons before adding hydrogen atoms.

Question 26

Equation to show formation of benzene: $6C + 3H_2 \longrightarrow C_6H_6$

Energy absorbed in vapourising 6 carbon atoms $= 6 \times 715 = 4290$ kJ/mol

Energy absorbed in atomizing 6 hydrogen atoms $= 6 \times 217.5 = 1305$ kJ/mol

Total energy absorbed in the reactant side $= (4290 + 1305)$ kJ/mol $= 5595$ kJ/mol.

Total energy evolved in the product side

$= 3(C-C) + 3(C=C) + 6(C-H)$

$= (3 \times 348) + 3 \times 615) + (6 \times 412) = 5361$ kJ/mol.

Enthalpy or reaction (formation of benzene from its elements)

= Total energy absorbed in the reactant side – total energy evolved in product side

$= (5595 - 5361)$ kJ/mol $= 234$kJ/mol

The standard enthalpy of formation of benzene from the given data is 234kJ/mol.

The experimental value is lower (less positive) than the theoretical one because practically structure of benzene is stabilized by mesomerism (resonation of electrons) and the energy difference between experimental and theoretical value amounted to151 kJ/mol is the resonance energy in benzene.

Question 27

(a) The factors are:

1) Amount of reactants and products.
2) Physical state of reactants and products.
3) Temperature of the reaction.
4) Specific heat capacity of the container and substances involved in the transformation.

(b) An equation to show formation of methane: $C(s) + 2H_2(g) \longrightarrow CH_4(g)$

Total energy absorbed in the reactant side $= 716 + 872.8 = 1588.8$ kJ/mol

Total energy evolved in the product side $= 4(C-H) = 4 \times 414 = 1656$kJ/mol

Head of reaction = total energy absorbed in reactant side – total energy evolved in the product side

$= (1588.8 - 1656)$ kJ/mol $= -67.2$kJ/mol

Hence heat of formation of methane is -67.2kJ/mol.

Question 28

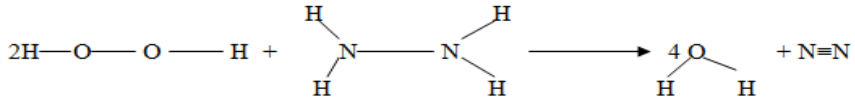
(a) (i) Heat of solution is the **heat change** when **one mole of solute** is added to so much water that further addition **of water produces no further heat change under given conditions of temperature and pressure.**

(ii) Heat of solution is the **heat change** when **one mole of a solute** dissolves in **specified amount of water** to give a solution under **given conditions of temperature and pressure.**

Relation:

When the solution is diluted to infinite dilution, heat of solution becomes equal to heat of dilution.

(b) Rewriting the given chemical reaction in structural formulae;



$\Delta H_r = \sum$ B. E(reactants) $- \sum$ B. E(products)

$= 4(O-H) + 2(O-O) + 4(N-H) + N-N - 8(O-H) - (N \equiv N)$

$= 2(O-O) + 4(N-H) + (N-N) - 4(O-H) - (N \equiv N).$

$= 2 \times 143 + (4 \times 391) + 159 - (4 \times 463) - 945 = -788$kJ/mol

Hence the enthalpy for the reaction is -788kJ/mol.

Question 29

(a)

(i) Enthalpy of solution
(ii) Atomisation energy
(iii) First electron affinity
(iv) Enthalpy of neutralisation

(b) Equation for combustion of propane:

(i) $C_3H_8 + 5\ O_2(g) \longrightarrow 3CO_2 + 4H_2O;\ \Delta H = -2102 kJ/mol$

Equation for combustion of propene

(ii) $C_3H_6 + \frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O;\ \Delta H = -1977 kJ/mol$

From (i)

$\Delta H = -2102 = 4\Delta H_f(H_2O) + 3\Delta H_f(CO_2) - \Delta H_f(C_3H_8) \ldots\ldots\ldots\ldots (1)$

From (ii)

$\Delta H = -1977 = 3\Delta H_f(H_2O) + 3\Delta H_f(CO_2) - \Delta H_f(C_3H_6) \ldots\ldots\ldots\ldots (2)$

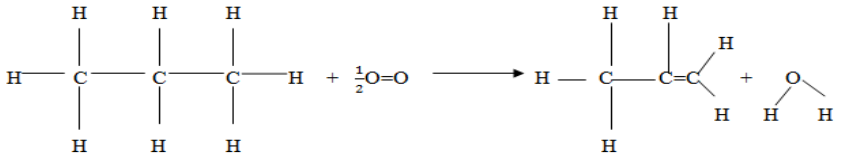
$-$ (2) gives: $\Delta H_f(C_3H_6) - \Delta H_f(C_3H_8) + \Delta H_f(H_2O) = 125\ kJ/mol$

But $\Delta H_f(C_3H_6) + \Delta H_f(H_2O) - \Delta H_f(C_3H_8)$ = Enthalpy change for the oxidation of propane to propene and steam according to the equation:

$C_3H_8(g) + ½O_2(g) \rightarrow C_3H_6(g) + H_2O(g)$

Hence the enthalpy change for the oxidation is $-125 kJ/mol$.

An equation for oxidation of propane into propene:



Then using $\Delta H_r = \sum B.E(reactants) - \sum B.E(products)$

$= 8(C-H) + 2(C-C) + ½(O=O) - 6(C-H) - (C-C) - (C=C) - 2(O-H)$

$= 2(C-H) + (C-C) + ½(O=O) - (C=C) - 2(O-H)$

Thus;

$$-125 = (2 \times 413) + 348 + ½(O=O) - 612 - (2 \times 463)$$

From which: $(O=O) = 478 kJ/mol$.

Question 30

(a)

(i) It is wrong to use the phrase "heat change" instead of "heat evolved".

Explanation

Using the word "change" which actually may be positive or negative change, implies that the combustion may be either endothermic or exothermic which is not correct because combustions are commonly exothermic.

(ii) It is wrong to exclude the phrase "one mole" (of water) in the definition.

Explanation

The amount of heat evolved in the neutralisation reaction depends on the amount of acid and base reacted and hence the amount of water produced. To make the data uniform enthalpy of neutralisation is always given per one mole of water.

(iii) It is wrong to state "one mole of hydrogen" instead of "one mole of unsaturated compound".

Explanation

Enthalpy of hydrogenation is always given per one mole of the compound that has undergone complete hydrogenation. One mole of compound like alkyne need two moles of H_2 for its complete combustion, so defining the enthalpy of hydrogenation in terms of one mole of H_2 will correspond to 0.5 mole of the alkyne which is not correct.

(iv) It is wrong to give a definition with an idea that "any valence electron" is removed during ionisation instead of the idea of an electron which is least tightly (most loosely) held by nuclear attractive force.

(b) Given that:

ΔH_c (carbon) $= -393.5$ kJ/mol $= \Delta H_f(CO_2)$

ΔH_c (hydrogen) $= -286$ kJ/mol $= \Delta H_f(H_2O)$

$\Delta H_c(C_3H_6) = -2091$ kJ/mol.

(Heat of combustion is the heat evolved, so the negative sign must be included in calculations although they are given as positive values).

Equation for combustion for cyclopropane:

$$C_3H_6 + \frac{9}{2}O_2 \longrightarrow 3CO_2 + 3H_2O;\ \Delta H = -2091 \text{kJ/mol}$$

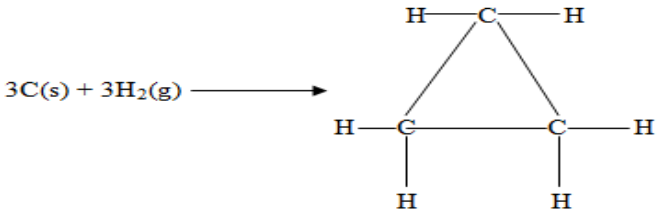
Cyclopropane

$$\Delta H_c(C_3H_6) = 3\Delta H_f(CO_2) + 3\Delta H_f(H_2O) - \Delta H_f(C_3H_6) - \frac{9}{2}\Delta H_f(O_2)$$

But $\Delta H_f(O_2) = 0$

So $-2091 = (3 \times -393.5) + (3 \times -286) - \Delta H_f(C_3H_6)$; $\Delta H_f(C_3H_6) = 52.5$ kJ. mol

Equation to show formation of cyclopropane from its elements:



Total energy absorbed in reactants side

$=$ energy of sublimating three carbon atoms $+$ energy for dissociating three H_2

$= (3 \times 720) + (3 \times 432) = 3456$ kJ/mol

Total energy evolved in product side $= -6(C-H) - 3(C-C)$

Thus heat of formation of cyclopropane $= 3456 - 6(C-H) - 3(C-C)$

So $52.5 = 3456 - (6 \times 414) - 3(C-C)$

From which the mean $C-C$ bond energy is 306.5kJ/mol.