Chapter 5a (AS-Level)

Chemical Energetics

Chemical reactions are accompanied by enthalpy changes, in the form of heat energy.

Enthalpy, given the symbol H, is the total energy content of thee reacting materials.

Enthalpy change is the change in the total energy content of the reacting materials, given the symbol ΔH ("*Delta H*").

When ΔH is negative, the reaction is exothermic; when it's positive the reaction is endothermic.

Some chemical reactions are:

- Exothermic:

  Examples:
  - Combustion of fuel
  - Respiration in our bodies
  - Reaction of metals with acids
  - Reaction of alkalis with acids
  - Reaction of quicklime with water:

    $CaO(s) + H_2O(l) \rightarrow Ca(OH)_2\ (aq) + E$

- Endothermic:

  Examples:
  - Decomposition of limestone:

    $CaCO_3(S) + E \rightarrow CaO(s) + CO_2\ (g)$
  - Photosynthesis:

    $CO_2\ (g) + H_2O + E \rightarrow$ Carbohydrates (Glucose)
  - Dissolving NH_4Cl:

    $NH_4Cl(s) + H_2O + E \rightarrow NH_4^+\ (aq) + Cl^-\ (aq)$

Energy is conserved

Energy is neither created nor destroyed, in either exothermic or endothermic reactions. In endothermic reactions, the energy is transferred to the reactants (the system) from the surroundings. In exothermic reactions it is transferred to the surroundings, all in the form of heat.

Enthalpy and Enthalpy changes

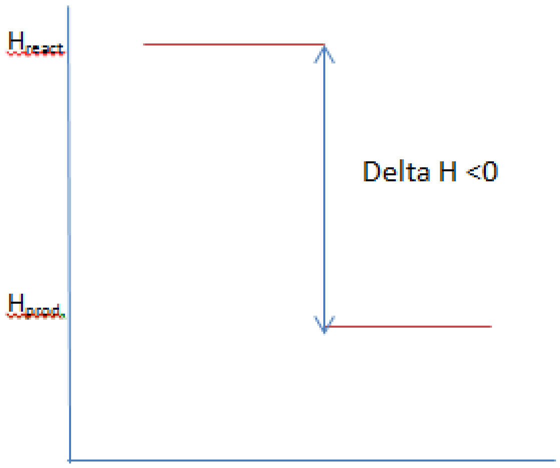
Mentioned earlier are the definitions of enthalpy and enthalpy change.

$$Enthalpy\ change\ =\ Enthalpy\ of\ products\ -\ Enthalpy\ of\ reactants$$

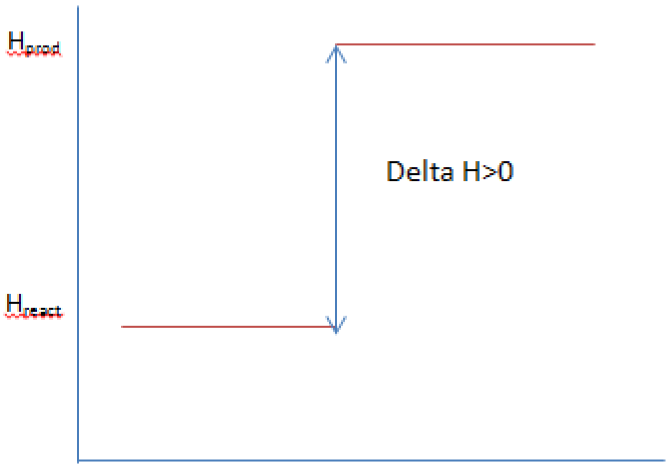
$$\Delta H = H_{products} - H_{reactants}$$

ΔH has a unit of kilojoules per mole (kJ mol^{-}).

We can illustrate enthalpy changes using Enthalpy Profiles (or Enthalpy graphs). Shown below are some examples:



Exothermic reaction



Endothermic reaction

Example:

$$CH_4\,(g) + 2\,O_2(g) \rightarrow CO_2\,(g) + 2\,H_2O(l)$$

In which Delta H = -890 kJ/mol.

Standard Enthalpy Changes ($\Delta H^{\ominus}$)

When we want to compare the enthalpy changes of reactions, we must use standard conditions.

A standard enthalpy change for a reaction takes place under these conditions, which are known as standard:

- Pressure = 1 atm = 100kPa
- Temperature = 298K
- Mole = 1mol
- Concentration = 1M =1 $\frac{mol}{dm3}$ of solutions
- Reactants and Products in normal physical and standard condition

Standard enthalpy change of reaction ($\Delta H_r^{\ominus}$)

ΔH_r is the enthalpy change when the amounts of reactants given in reaction equation react under standard conditions to give products in the standard conditions.

Example:

$2H_{2\,(g)} + 2O_{2\,(g)} \rightarrow 2H_2O_{(l)}$

$\Delta H_R = -572kJ$

BUT

$H_{2\,(g)} + {}^{1}/_{2}O_{2(g)} \rightarrow H_2O_{(l)}$

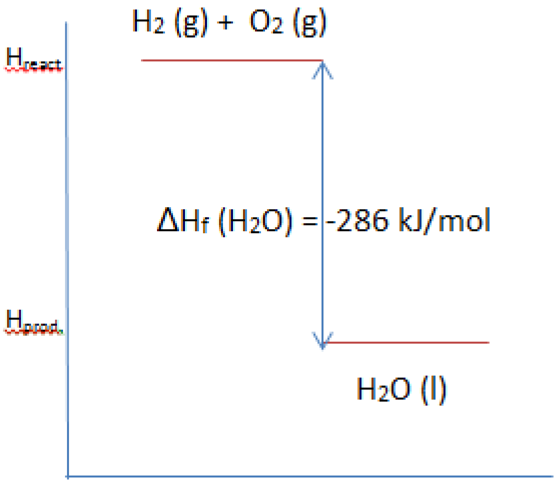
$\Delta H_R = -286\ kJ$

Standard enthalpy change of formation of compounds ($\Delta H_f^{\ominus}$)

ΔH_F is the enthalpy change when 1 mol of the compound is formed from its elements under standard conditions.

Example:

$\Delta H_F\ (H_2O) = -286\ kJ/mol$



Exothermic reaction

Standard enthalpy change of combustion ($\Delta H_c^\ominus$)

ΔH_C is the enthalpy change when 1 mol of the substance is completely burned in oxygen under standard conditions.

Example:

$\Delta H_C (H_2) = -286$ kJ/mol

Other enthalpy changes

We can define other standard enthalpy changes in a similar manner:

- The *standard enthalpy change of hydration* is the enthalpy change when one mole of a gaseous ion dissolves in water to give an infinitely dilute solution.
- The *standard enthalpy change of solution* is the enthalpy change when one mole of a solute dissolves in a solvent to give an infinitely dilute solution.
- The *standard enthalpy change of neutralization* is the enthalpy change when one mole of H^+ ions from an acid is completely neutralized by an alkali to give one mole of water.
- The *standard enthalpy change of atomization* of an element is the enthalpy change when one mole of gaseous atoms is formed from one mole of the element in its standard state.

Bond making, breaking and enthalpy change

> ***Bond Making is Exothermic***
>
> ***Bond Breaking is Endothermic***

Bond Enthalpy (BE) is the energy needed to break 1 mole of a particular covalent bond.

This indicates the strength of the bond, the higher the energy needed, the higher bond strength and vice versa.

Bond enthalpies

It is useful to measure the amount of energy need to break a covalent bond, as it indicates the strength of the bond. It is called *Bond Enthalpy*.

They are also:

- All are positive quantities

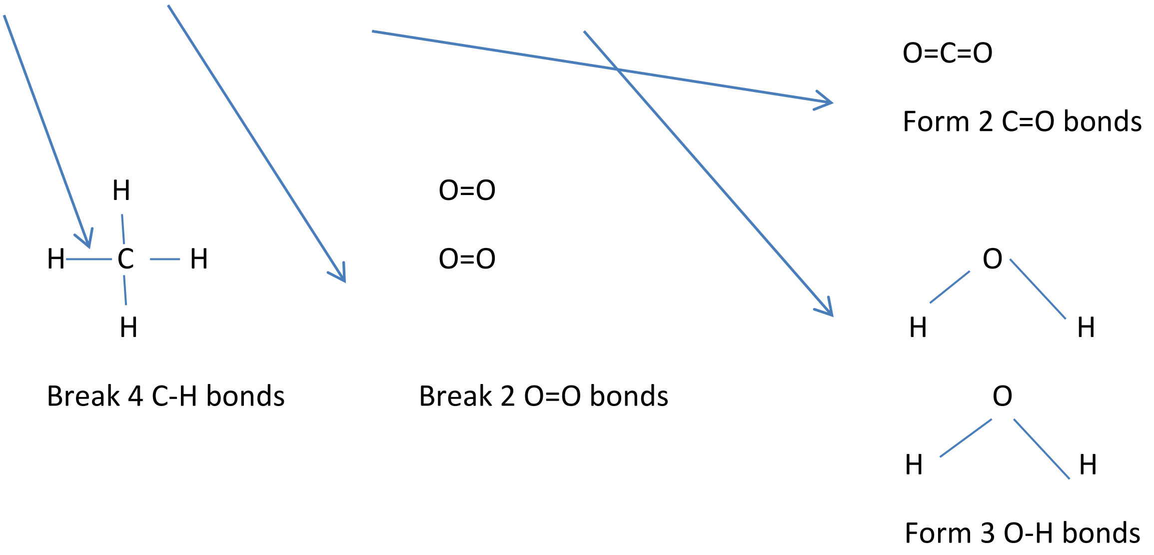
- All are average values
- Compared from bonds in gaseous compounds
- Difficult to measure directly
- They are given in tables (such as data booklets which are given in AS/A level exams)

Example:

Bond	**H-H**	**C-C**	**C=C**	**C-H**	**O=O**	**O-H**	**C-O**	**C=O**
Enthalpy Change	+436	+347	+612	+413	+498	+464	+358	+805

Calculating Enthalpy change of a reaction from bond enthalpies:

$$CH_{4\,(g)} + 2O_{2\,(g)} \rightarrow Co_{2\,(g)} + 2H_2O_{(l)}$$



ΔH_r = (sum of all BE's from broken bonds) – (sum of all BE's from formed bonds)

Calculation:

$\Delta H_C = \Delta H_r$ = [4BE(C-H) + 2BE(O=O)] – [2BE(C=O) +4BE(O-H)]

= 4(413) +2(498) – 2(805) – 4(464)

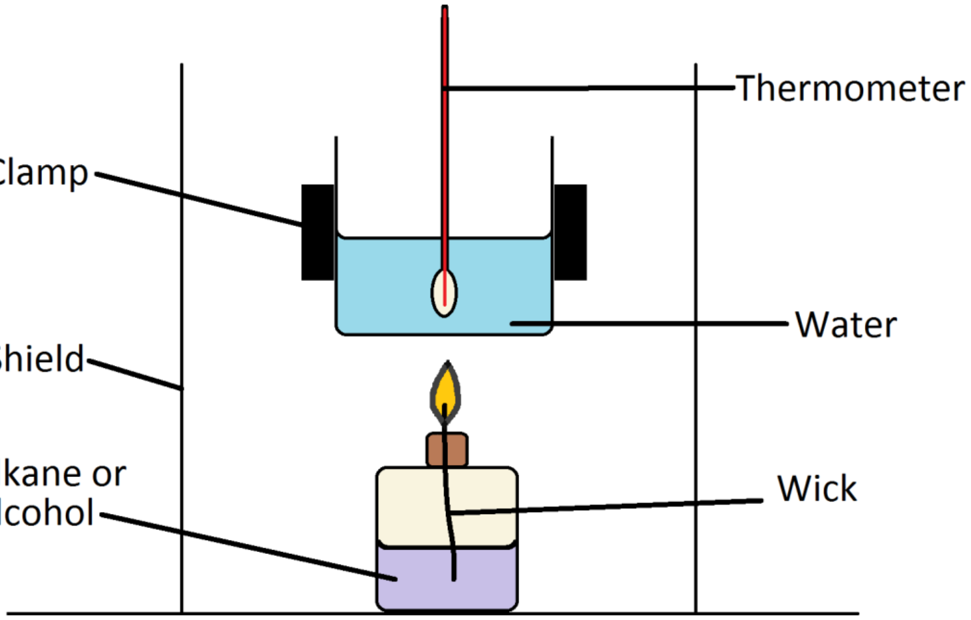
= -890kJ

Measuring energy transfers and enthalpy changes

Enthalpy change of combustion

Measurements of ΔH_r are important as they help to compare the energy available from the oxidation of different flammable liquids, which may be used as fuels.

The apparatus is shown below:



Measurements that are taken:

- Mass of cold water
- The temperature rise of the water
- The loss in mass of the fuel

The specific heat capacity of water is also needed, which is 4.2 $Jg^{-1}K^{-1}$.

Specific heat capacity of a substance is the heat required to raise the temperature of a unit mass of a substance (one gram or one kilogram) one degree Celsius or Kelvin.

Therefore:

$$\boldsymbol{Heat\ transferred = mass \times specific\ heat\ capacity\ \times \Delta\ temperature}$$

While heat capacity of a substance or apparatus, is the heat required to raise the temperature of the whole substance or apparatus one degree Celsius or kelvin.

Heat capacity is determined in a different experiment.

$$Heat\ transferred = heat\ capacity\ \times \Delta\, Temperature$$

Enthalpy change of combustion in

kJ/mol

Mass of liquid in calorimeter in grams

$$Heat\ Transferred\ =\ m\ c\ \Delta T$$

Heat Capacity of the liquid in

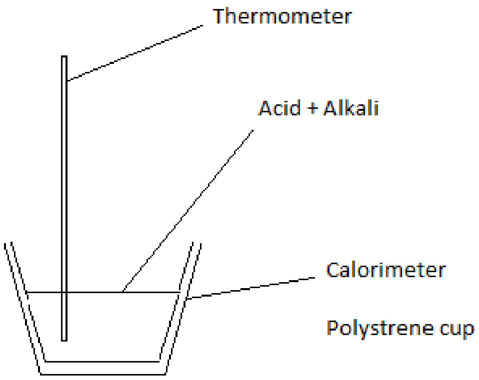
$Jg^{-1}K^{-1}$

Change in temperature in

°K

See page 77 & 78 for diagram and explanation + solved example.

ΔH of neutralization of acid and alkali



- Use known amounts of acid and alkali (measured volumes and masses in case of solid
- Mix quickly and measure temperature change up to 0.1 degree Celsius to 0.2 degree accuracy
- Use the equation :
- Calculate Δ for 1 mol of H^+

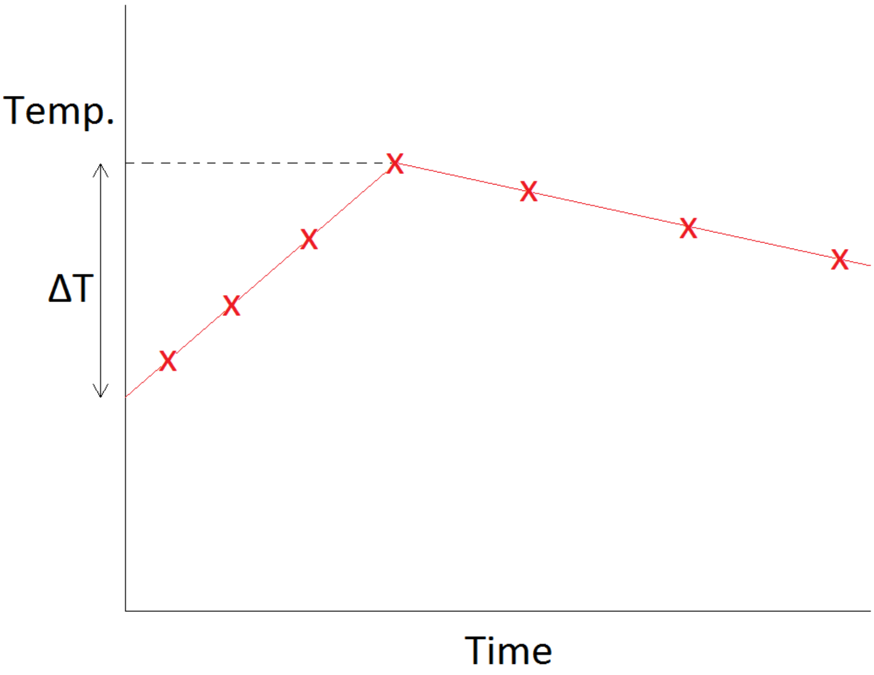
Summary:

$$\Delta H_f\ (Compounds)\ =\ \Delta H_C\ (Elements) - \Delta H_C\ (Compound)$$

Enthalpy change of solution of NaOH

Method:

- Use polystyrene cup to hold the solution.
- Weigh and add 100g distilled water.
- Determine initial temperature.
- Add few pellets of solid NaOH quickly to the water.
- Stir mixture immediately and start a timer to take temperature readings at regular intervals.
- Temperature rises to a max and then drops, readings should be taken for enough time.
- Weigh the cup and find mass of NaOH added.
- Plot temperature versus time and extrapolate to find ΔT as in the figure.



Heat evolved = m x 4.18 x ΔT

Then calculate for 1 mole ➔ ΔH solution

Example:

- Mass of cup = 8g
- Mass of cup + water = 108.15g
- Mass of distilled water = 100.15g
- Mass of NaOH + cup + water = 114.35g
- Mass of NaOH = 6.20g
- Initial temperature of cup = 15°C
  From the graph, ΔT = 16°C

Calculation:

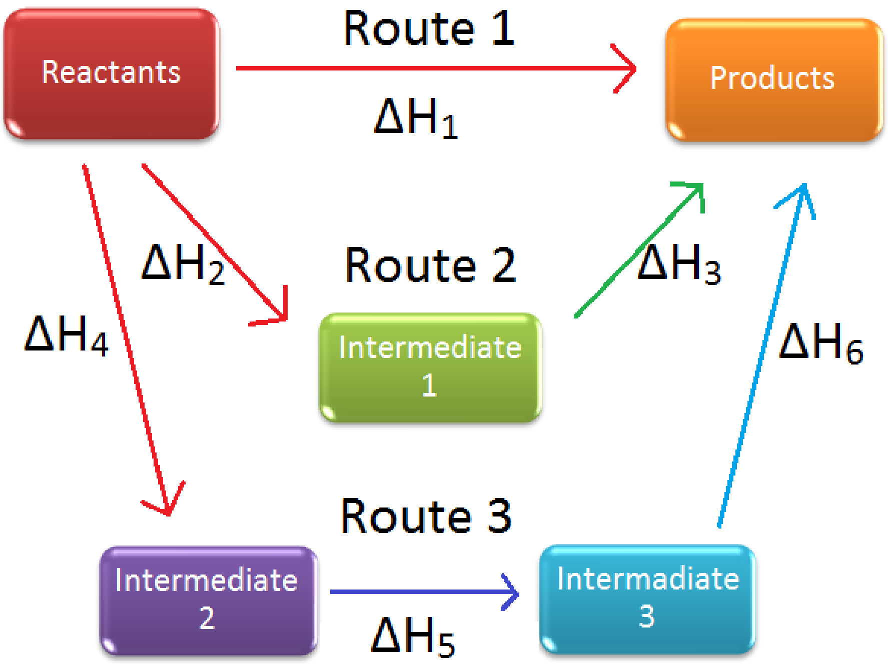
$E = m.c.\Delta T$

$E = 100.15 \times 4.18 \times 16 = 6700J$ released when dissolving 6.2g of NaOH.

For 1 mole of NaOH 40 grams should be used (or calculated) to get the enthalpy change of solution of NaOH.

Enthalpy change by different routes (Hess' law)

In chemical reactions:



> ***Hess' law states that:***
>
> ***"The total enthalpy change for a chemical reaction is independent of the route followed from reactants to the products, provided the initial and final conditions are the same."***

So we deduce the following (using the diagram):

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

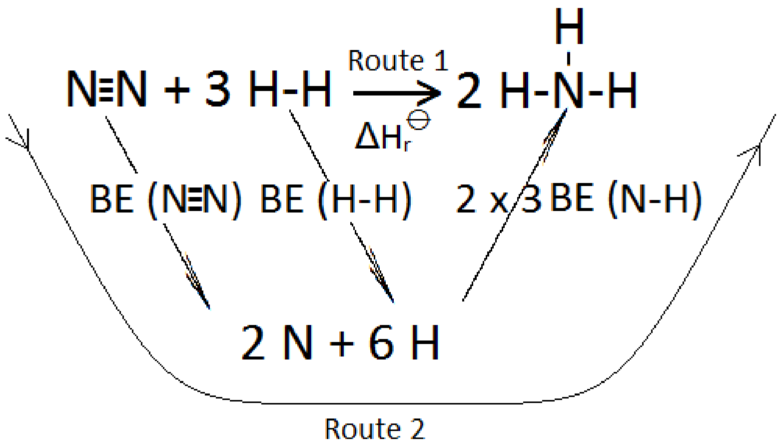
Hess' law is another form of the law of conservation of energy, which is the first law in thermodynamics.

Using Hess' law in enthalpy change calculations

A. Calculating $\Delta H_r^\ominus$ from bond enthalpy

Example:
In Haber's process:

$$N_2\,(g) + 3\,H_2\,(g) \rightarrow 2\,NH_3\,(g)$$



$\Delta H_r^\ominus = \Delta H_f^\ominus$ = Broken bonds – Formed bonds

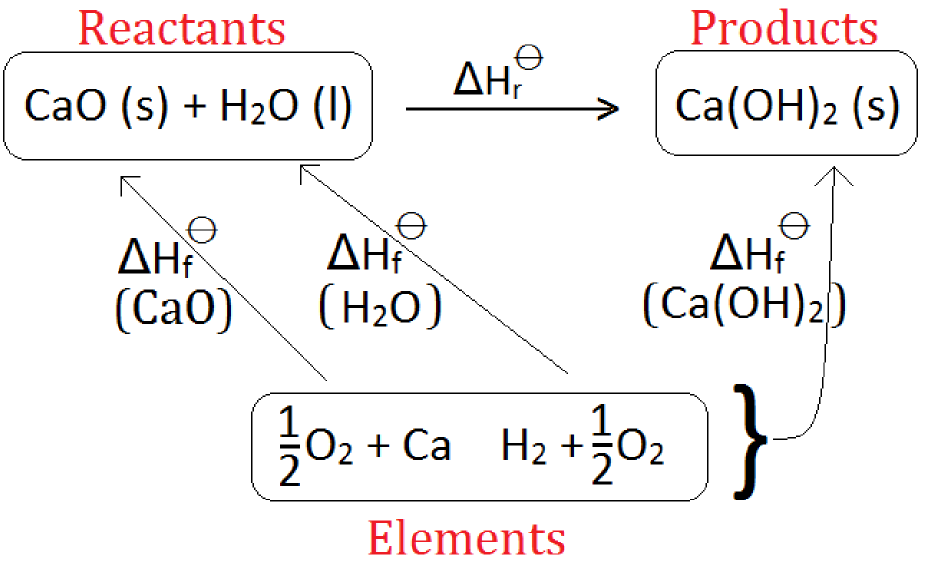
$$\Delta H_r^\ominus = \Delta H_f^\ominus = BE\,(N\equiv N) + 3\,BE\,(H\text{-}H) - 6\,BE\,(N\text{-}H)$$

B. Calculating $\Delta H_r^\ominus$ from enthalpy changes of formation $\Delta H_f^\ominus$

Example (given the $\Delta H_f^\ominus$ of reactants and products):

$$CaO\,(s) + H_2O\,(l) \rightarrow Ca(OH)_2\,(s)$$

$\frac{1}{2}O_2 + Ca \quad H_2 + \frac{1}{2}O_2$



$\Delta H_f^{\ominus}$ (CaO) + $\Delta H_f^{\ominus}$ (H_2O) + $\Delta H_r^{\ominus}$ = $\Delta H_f^{\ominus}$ [$Ca(OH)_2$]

(Figures given by the examiner)

(-6351) + (-285.8) + $\Delta H_r^{\ominus}$ = (-984.1)
$\Delta H_r^{\ominus}$ = -65.2 kJ/mol of $Ca(OH)_2$

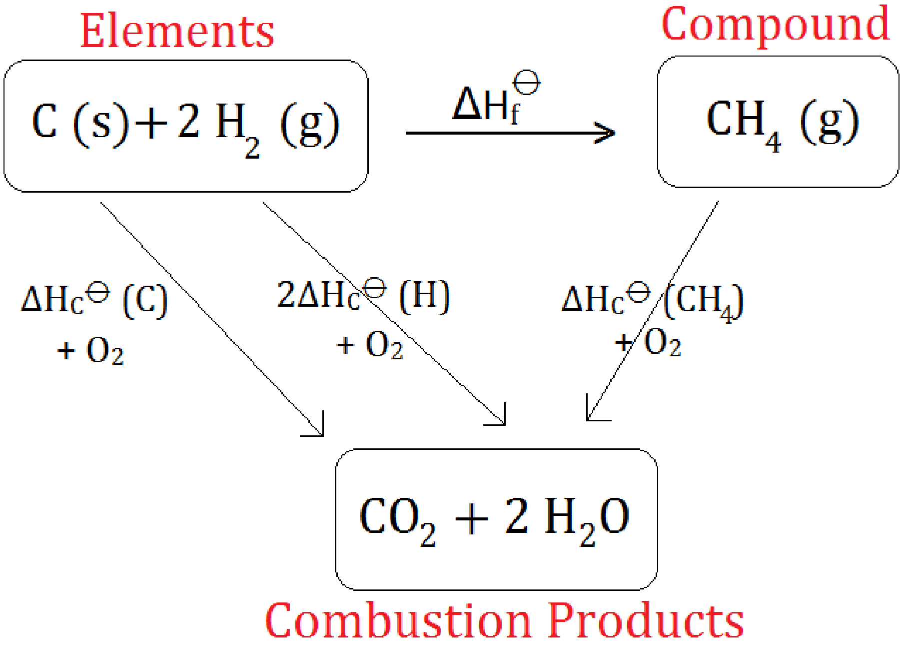
Therefore:

$\Delta H_r^{\ominus} = [\Delta H_f^{\ominus}$ (Products)] – [$\Delta H_f^{\ominus}$ (Reactants)]

C. Calculating $\Delta H_{Formation}^{\ominus}$ from $\Delta H_{Combustion}^{\ominus}$

Example:
Find $\Delta H_f^{\ominus}$ (CH_4), given $\Delta H_{Combustion}^{\ominus}$

$$C\ (s)\ 2\ H_2\ (g) \rightarrow CH_4\ (g)$$



$\Delta H_f^{\ominus}$ (CH_4) + $\Delta H_C^{\ominus}$ (CH_4) = $\Delta H_C^{\ominus}$ (C) + 2 $\Delta H_C^{\ominus}$ (H)

$\Delta H_f^{\ominus}$ (CH_4) = (-394) + 2(-286) – (-890)
$\Delta H_f^{\ominus}$ (CH_4) = -76 kJ/mol

END OF LESSON