HONORS TOPIC 10: Thermochemistry

- **Enthalpy**

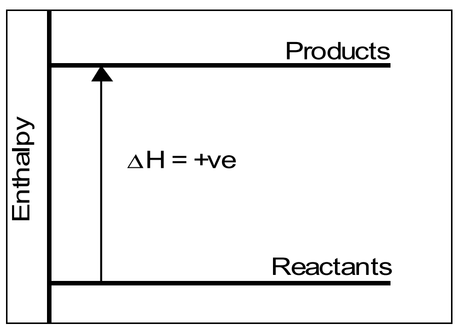
Every substance is said to have a heat content or enthalpy. Enthalpy is given the symbol, H. Most reactions involve an enthalpy change, ΔH (Delta H), where;

$$\Delta H^{\theta} = \sum H^{\theta}{}_{f\,products} - \sum H^{\theta}{}_{f\,reactants}$$

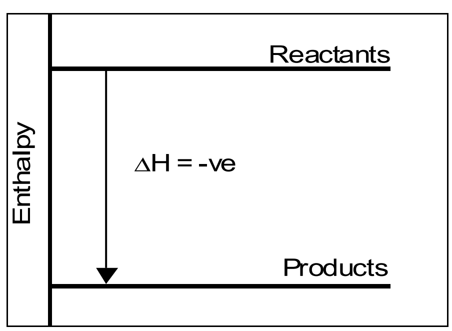
Enthalpy level diagrams

The enthalpy change can be illustrated using enthalpy level diagrams.

ENDOTHERMIC reactions. Enthalpy of products > Enthalpy of reactants, ΔH is positive and the reaction is ENDOTHERMIC. This means energy must be put into the reaction for it to occur.



EXOTHERMIC reactions. Enthalpy of products < Enthalpy of reactants, ΔH is negative and the reaction is EXOTHERMIC. This means energy is released from the reaction as it occurs.



When discussing the enthalpy of a substance it is necessary to state the conditions under which the enthalpy is measured. Usually enthalpy changes are stated under the following conditions;

- All gases at 1 atm pressure
- All solutions at unit (1 M) concentration
- Temperature (298 K)

Spontaneous reactions will tend toward conditions of lower enthalpy, i.e., more negative values of ΔH, since lower enthalpies are more energetically stable.

- **Standard Enthalpy of Formation (ΔH_f°)**

Standard Enthalpy of Formation is defined as the enthalpy change when one mole of a substance is formed from its elements, in their standard states.

For example, $\Delta H_f^\circ[C_2H_5OH_{(l)}] = -279\ kJmol^{-1}$ means that when the reaction below is carried out, 279 kJ of energy are released.

$2C_{(graphite)} + 3H_{2(g)} + ½O_{2(g)} \rightarrow C_2H_5OH_{(l)}\ \ \Delta H^\circ = -279\ kJmol^{-1}$

Task 10a

Write equations to represent the following processes.

1. ***The standard enthalpy of formation of $CH_3Br_{(l)}$***
2. ***The standard enthalpy of formation of $CH_3COC_2H_{5(l)}$***
3. ***The standard enthalpy of formation of $NaNO_{3(s)}$***
4. ***All elements are assigned a value for enthalpy of formation equal to zero. Why?***

ΔH_f° may be negative or positive.

- **Standard Enthalpy of Combustion (ΔH_c^{θ})**

Standard Enthalpy of Combustion is defined as the enthalpy change when one mole of a substance is completely burned in oxygen (since energy is usually released in such a reaction ΔH_c^{θ} will usually be negative).

For example, $\Delta H_c^{\theta}[C_2H_{6(g)}] = - 1565\ kJmol^{-1}$ means that when the reaction below is carried out, 1565 kJ of energy are released.

$C_2H_{6(g)} + 3½O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H^{\theta} = - 1565\ kJmol^{-1}$

It is useful to remember that compounds containing some combination of carbon, hydrogen and oxygen, when completely burned in air (O_2), produce carbon dioxide and water only. The combustion of other reactants may require other knowledge or intelligent guesswork to determine the products of that combustion.

Task 10b

Write equations to represent the following processes.

1. ***The standard enthalpy of combustion of $C_5H_{12(l)}$***
2. ***The standard enthalpy of combustion of $CO_{(g)}$***
3. ***The standard enthalpy of combustion of $H_{2(g)}$***
4. ***The standard enthalpy of combustion of $Al_{(s)}$***

- **Hess's Law**

Hess's Law states that, the enthalpy change during a reaction depends only on the nature of the reactants and products and is independent of the route taken.

Task 10c

Using one of the following methods to calculate the enthalpy changes in questions 1-3;

Either;

- ***Write the chemical equation for the required enthalpy change***
- ***Look at the data given. If ΔH_c values are given combustion <u>products</u> must complete the cycle. If ΔH_f values are given, <u>elements</u> must make up the cycle***
- ***Draw the cycle and add values (multiplying where necessary)***
- ***Apply Hess's law to calculate the unknown value***

Or;

- ***Write the chemical equation for the required enthalpy change (this is the target equation)***
- ***Algebraically manipulate the equations related to the data given to achieve the target equation and hence the target enthalpy change***

1. ***Calculate the standard enthalpy of formation of ethane (C_2H_6), given the following combustion data;***
   $C_{(graphite)}$ = -393 kJmol^{-1}, $H_{2(g)}$ = -286 kJmol^{-1} and $C_2H_{6(g)}$ = -1560 kJmol^{-1}.

2. ***Calculate the standard enthalpy of combustion of propan-2-ol ($CH_3CH(OH)CH_3$), given the following data;***
   Enthalpies of combustion for $C_{(graphite)}$ = -393 kJmol^{-1}and $H_{2(g)}$ = -286 kJmol^{-1}. Enthalpy of formation of propan-2-ol = -318 kJmol^{-1}.

3. The Thermite reaction was used to produce molten iron for welding railway tracks together;

$$Fe_2O_{3(s)} + 2Al_{(s)} \rightarrow Al_2O_{3(s)} + 2Fe_{(s)}$$

(a) Calculate the enthalpy change in the Thermite reaction, given the standard enthalpies of formation of iron (III) oxide and aluminum oxide are -823 and -1675 $kJmol^{-1}$, respectively.

(b) Why are no values given for the enthalpy of formation of Aluminum metal or Iron metal?

4. When 10.00 g of sulfur is completely burned in air sulfur dioxide is formed and 93.00 kJ of energy is released.

(a) Write the equation for the burning of sulfur in oxygen to produce sulfur dioxide.
(b) Calculate the standard enthalpy of formation of sulfur dioxide.

- **Bond Enthalpies**

The strength of the bond in a diatomic covalent molecule is the bond dissociation energy (BDE). For example, hydrogen, H_2 or H-H

$H_{2(g)}$ ➔ $2H_{(g)}$ BDE= +436 kJ

Now consider a polyatomic molecule, for example methane. Methane has four C-H bonds, each with a different BDE.

$CH_{4(g)}$ ➔ $CH_{3(g)}$ + $H_{(g)}$ BDE= +460 kJ
$CH_{3(g)}$ ➔ $CH_{2(g)}$ + $H_{(g)}$ BDE= +400 kJ etc.

The individual BDE's vary, since in each subsequent bond breaking, the environment in which the reaction is carried out is slightly different. This has the effect of changing the strength of each individual C-H bond. In order to overcome this complexity we may define the bond energy term (BET) as the average of the separate BDE's for each of the four, separate C-H bonds.

In order to **break** a bond, **energy must be put in** (an **endothermic** process with a **positive** energy change), and,

When **making** a bond, **energy is released** (an **exothermic** process with a **negative** energy change).

The BET allows us to make predictions about the enthalpy changes in reactions.

Some BET's are listed below.

Bond	BET in $kJmol^{-1}$
F-F	154
C=O	743
O-H	463
Br-Br	193
C-Br	276
H-Br	366
Cl-Cl	239
C-O	360
H-H	436
C-C	348
C-Cl	339
C-H	412
C=C	612
H-F	565
H-Cl	427
C-F	485
I-I	151
C-I	238
C≡C	837
C-N	305
H-I	299

Organic Compounds and Bond Enthalpy problems;

It is extremely useful to know the following information about organic compounds (that are discussed in more detail in TOPIC 11).

- Compounds where carbon atoms form chains are called organic. The carbon atoms form chains of varying length with other elements attached (most commonly H, O, N, S and the Halogens). In organic names, Meth- means 1 carbon atom in the longest continuous chain, Eth- 2, Prop- 3, But- 4, Pent- 5, Hex- 6, Hept- 7, Oct- 8, Non- 9 and Dec- 10.
- In these compounds C always makes a total of four covalent bonds, H one bond, O two bonds, N three bonds, Sulfur two bonds and Halogens one bond.
- Common types of organic are; alkanes (All C atoms bonded to one another with single bonds), alkenes (C chain includes a double bond), alkynes (C chain includes a triple bond), alcohols (include O-H), carboxylic acids (include O=C-O-H) and esters (include O=C-O).
- Structural formulae help when determining bonds present. E.g. CH_3CH_2- etc. means a carbon atom with 3 H's attached, joined to a carbon atom with two atoms attached etc.
- In a bond enthalpy calculation either break all bonds in the reactants and reassemble all bonds in the products or, just break the necessary bonds in the reactants and reassemble the necessary bonds in the products.

Task 10d

Use the data in the table above to help answer the questions below.

1. ***Calculate the standard enthalpy of the reaction below.***

$$CH_3CH{=}CH_2 + H_2 \rightarrow CH_3CH_2CH_3$$

2. ***Calculate the enthalpy change for the reaction below.***

$$CH_3CH{=}CH_2 + Br_2 \rightarrow CH_2BrCHBrCH_3$$

3. ***Calculate the enthalpy change for the reaction below.***

$$CH_{4(g)} + 2Cl_{2(g)} + 2F_{2(g)} \rightarrow CF_2Cl_{2(g)} + 2HF_{(g)} + 2HCl_{(g)}$$

4. ***Without doing any calculations, determine the enthalpy change for the reaction***

$$CH_3CH_2OH + CH_3COOH \rightarrow CH_3CO_2CH_2CH_3 + H_2O$$

5. ***This question is about the hydrocarbons, hexane and hex-1-ene.***

   (a) The enthalpy of formation of hexane (C_6H_{14}) is -199 kJ and the enthalpy of formation of hex-1-ene (C_6H_{12}) is –73 kJ. Draw a Hess's Law cycle in order to calculate ΔH for the conversion of hex-1-ene to hexane by the addition of hydrogen.
   (b) Calculate another value for the reaction in (i) using average bond energy terms.
   (c) Which of your answers, (i) or (ii), will be more accurate and why?

An important note about the conventions of using $kJmol^{-1}$.

If you see a chemical reaction with a ΔH in units of $kJmol^{-1}$ associated with it, it is reasonable to ask the question, "moles of what?" The question is an important one, since in the reaction there are likely to be a number of different reactants and products. For example;

$$N_{2(g)} + 3F_{2(g)} \rightarrow 2NF_{3(g)} \qquad \Delta H = -264\ kJmol^{-1}$$

In this case, the ΔH value *actually* means **- 264 kJ PER MOLE OF REACTION**. So when 1 mole of N_2 reacts we would expect 264 kJ of energy to be released. This would also be the energy released when 3 moles of F_2 react, AND also when 2 moles of NF_3 is produced. HOWEVER, if only 1 mole of F_2 were to react we would only expect one third of 264 kJ to be released. Similarly if only 1 mole of NF_3 were produced then the reaction would only release half of 264 kJ.

- **Born Haber cycles - The thermochemistry of the ionic bond**

The process of ionic bond formation can be broken down into a number of stages.

For example, in the formation of sodium chloride there are two possible routes;

1. <u>A single step process</u> (Enthalpy change = standard enthalpy of formation of NaCl)

$$Na_{(s)} + \frac{1}{2} Cl_{2(g)} \rightarrow NaCl_{(s)}$$

The standard enthalpy of formation is the enthalpy change when one mole of a substance is formed from its elements in their standard states.

2. <u>A multi-step process involving five separate changes</u>

(i) Atomization of Sodium (Enthalpy change = standard enthalpy of atomization of Na)

$$Na_{(s)} \rightarrow Na_{(g)}$$

The standard enthalpy of atomization is the energy required to form one mole of gaseous atoms from the element under standard conditions.

(ii) Ionization of sodium (Enthalpy change = 1st ionization energy of Na)

$$Na_{(g)} \rightarrow Na^{+}_{(g)} + e^{-}$$

The first ionization energy is the energy required to remove one mole electrons from one mole of atoms in the gaseous phase.

(iii) Dissociation of chlorine molecules (Enthalpy change = ½ standard bond dissociation energy of chlorine (atomization of chlorine))

$$\frac{1}{2} Cl_{2(g)} \rightarrow Cl_{(g)}$$

The standard enthalpy of bond dissociation is the energy required to dissociate one mole of molecules into atoms.

(iv) Formation of gaseous chloride ions from gaseous chlorine atoms (Enthalpy change = 1st electron affinity of chlorine)

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)}$$

The first electron affinity is the enthalpy change when one mole of gaseous atoms gains an electron to forms a mole of gaseous ions.

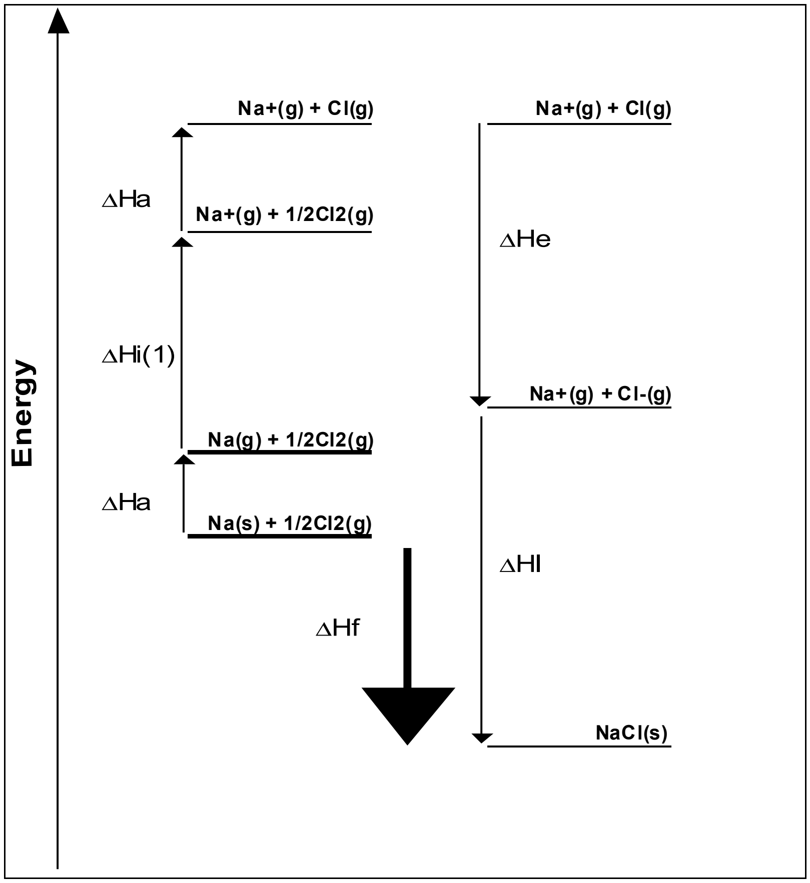
(v) Bring together the gaseous ions (Enthalpy change = standard lattice enthalpy of NaCl)

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow NaCl_{(s)}$$

The standard lattice enthalpy is the enthalpy change when one mole of solid is formed from its constituent gaseous ions.

N.B. When considering the relative attractions of ions for one another it can be useful to consider charge density. Small, highly charged ions have high charge densities. These ions tend to attract one another to a greater degree, and lead to higher melting points and higher lattice energies.

A Born-Haber cycle diagram can be constructed from this data. By convention, positive values are denoted as going upwards, negative values as going downwards.



Hess's Law states that the energy change for a reaction is independent of the route taken, so

$$\Delta H_f = \Delta H_{a(Na)} + \Delta H_{i(1)} + \Delta H_{a(Cl_2)} + \Delta H_e + \Delta H_l$$

Discrepancies between calculated and experimental values of lattice enthalpy

By assuming that a compound is essentially 100% ionic, it is possible to calculate a theoretical value for the lattice enthalpy. In some cases the theoretical values agree very closely with the experimental values, but in other cases discrepancies arise.

Compound	Theoretical Lattice enthalpy/kJmol^{-1}	Experimental Lattice enthalpy/kJmol^{-1}	Agreement?
NaCl	- 766	- 781	Good match
ZnS	- 3427	- 3565	Poor match

Where the match is poor, the idea of a *completely* ionic bond is incorrect. The differences are caused by polarization and the ionic bond taking on a degree of covalent character.