Hess' Cycles

A First Year Blog for the week commencing the 16th of February 2020.

Germain Henri Hess

Swiss-Russian scientist (Thermodynamics)
Born 1802 in Geneva - Died 1850 in St Petersburg

Energy (E) (unit: Joules, J)	is the entity that is required to do Work. The Law of the Conservation of Energy states that Energy cannot be destroyed, but it can be distributed in differing 'energy stores' at different times. It is not immediately apparent how one can prove this statement (which is a polite way of saying that it cannot be proved because the dissipation of Energy into the store that is the Universe is immeasurable), but this is a Law that is accepted by scientists all over the world.

Enthalpy (H) is the Internal Energy of a system plus the product of its Pressure times its volume.

$$H = E + PV$$

According to the law of the Conservation of Energy, the change in internal energy is equal to the heat transferred to, less the work done by the system. **If the only work done is a change of volume at constant pressure, then the enthalpy change is exactly equal to the heat transferred to the system.**

It is common practice to place Enthalpy (H) on the y-axis of an Enthalpy Profile diagram/a Born-Haber graph, and to label the x-axis as "Reaction Pathway". In essence there is no difference between an Enthalpy profile diagram/a Born-Haber graph and a Hess Cycle.

Hess' Cycle (units: kJ.mol^{-1}) What Hess saw was that the total amount of energy involved in changing the Reactants in a reaction into the final Products of a reaction will exactly equal the total of the individual amounts of energy involved in changing the Reactants into the different intermediaries and then the intermediaries into the final products in the reaction. It is therefore easily possible, from Hess' Law, to calculate one **unknown** ΔH if all the other ΔHs involved in the reactions involved are known.

The Principle that is involved

- If King's Cross (London) were, let us say, 100 metres above sea-level and Waverley (Edinburgh) were 300 metres above sea-level, then it would not matter whether one went from King's Cross to Waverley direct on the East Coast line, or via the Underground to Euston and then on the West Coast line to Manchester and Glasgow and then on to Waverley – a net 200 metres would still be gained during the journey. **That is the basic principle that underlies Hess' Law.**

- It is not easy to calculate absolute Enthalpy; but, in contrast (with the aid of a good data book), it is very easy to calculate the change in Enthalpy (ΔH) involved in any reaction.

- Hess' Law states that "the change in Enthalpy in converting the reactants A and B into the products X and Y is **EXACTLY** the same regardless of the processes used to effect the conversion – provided only that the initial conditions in each instance are the same, and that the final conditions in each instance are the same"; and, actually, this is merely a corollary of the Law of the Conservation of Energy. In other words, it does not matter whether you go from London to Edinburgh by train, plane or car. If Edinburgh is 300 metres above sea-level and London is 100 metres above sea-level, then you will gain 200 metres **whichever route you choose to go by.**

- Enthalpy calculations can be moderately complicated; but, luckily, a scientist called "Hess" developed a beautiful little device for calculating ΔH (and later on, unsurprisingly, the device became called a "Hess-Cycle") – and the exploitation of an Hess-Cycle allows extremely complicated ΔH calculations to be performed with ease and with speed. All that is required is the information (a) that is contained in any good data book, or (b) the data for the change in Enthalpy using a completely different set of reactions.

- In the diagram below, I have drawn a Hess-Cycle as a triangle.
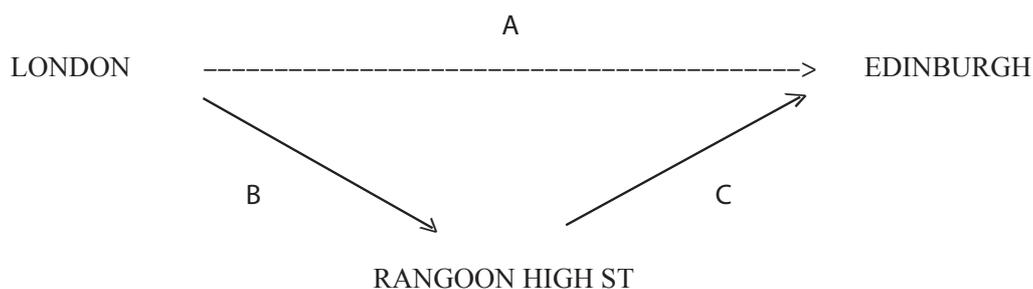
and if you now learn this next little trick, then you will be able to resolve even the most complicated Enthalpy calculations imaginable.

- Give the reaction that you are investigating the name **"THE DIRECT ROUTE"** , and then call the reaction with the known ΔH values **"THE INDIRECT ROUTE"**, and from what I have said in this talk so far, you will see that in the triangle above
  $$\Delta H \text{ in the Direct Route} = \Delta H \text{ in the Indirect route}$$
  or to make it even simpler mathematically

$$\mathbf{A \;=\; B \;+\; C}$$

- That is it. That is all there is to it! There is nothing more to Hess' Cycles than that.

- Just as in Trigonometry, once you have got the concept of *SOH CAH TOA* then you have cracked Trig wide open, so also in Enthalpy, once you have got the fact that

The ΔH in the Direct Route = The ΔH in the Indirect Route

then you have cracked every single problem in Enthalpy wide open.
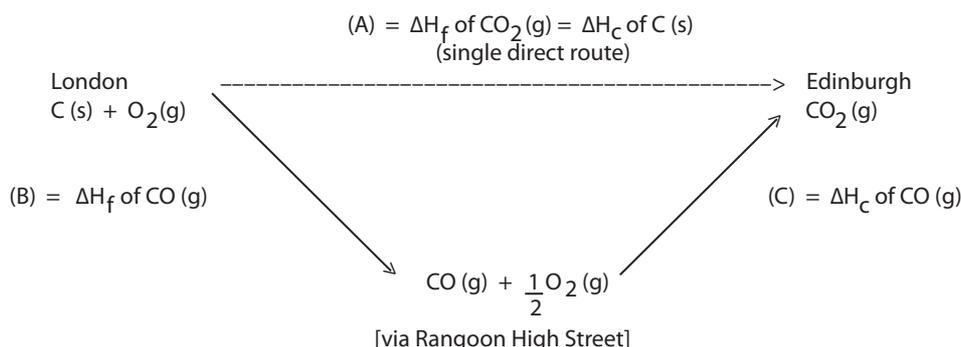
The application of Hess' Law

- OK, so how do you apply Hess' Law.

- If you burn Carbon in Oxygen you will inevitably get both Carbon Monoxide and Carbon Dioxide, therefore it is not possible to find the change in Enthalpy involved in the reaction **C(s) + O(g) —> CO(g)**. However, it is very easy to find out the change in Enthalpy in the reaction $C(s) + O_2(g) \longrightarrow CO_2(g)$ and also the change in Enthalpy for the reaction $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$.

- I have told you that Hess' Law can be used by saying that
  The ΔH in the Direct Route = The ΔH in the Indirect Route.
  We do not know the ΔH in the Direct Route, but Mr Hess has told us to use the the ΔHs in the Indirect Route. We are therefore home and dry. *(Don't worry about the subscripts below for the moment. They are needed only for a more detailed study.)*
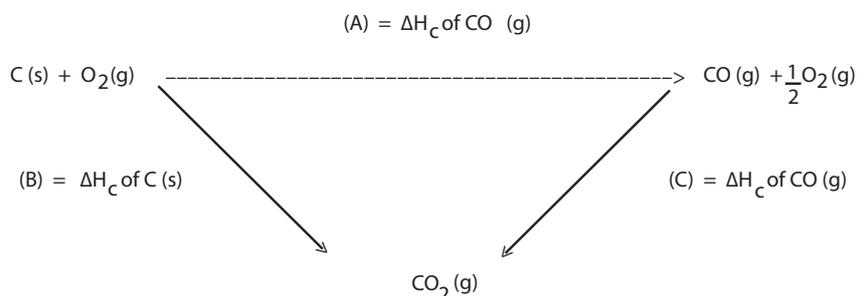
- C (s) + ½ O$_2$ (g) —> CO (g), and this is the ΔH_f of CO (g) = Unknown
- C (s) + O$_2$ (g) —> CO$_2$ (g), and this is the ΔH_f of CO$_2$ (g) = -394 kJ mol^{-1}
- CO (g) + ½ O$_2$ (g) —> CO$_2$ (g) and this is the ΔH_c of CO (g) = -283 kJ mol^{-1}

(A) = ΔH_f of CO$_2$ (g) = ΔH_c of C (s)
(single direct route)

London —> Edinburgh
C (s) + O$_2$(g) CO$_2$ (g)

(B) = ΔH_f of CO (g)   (C) = ΔH_c of CO (g)

CO (g) + $\frac{1}{2}$ O$_2$ (g)
[via Rangoon High Street]

- The **Direct Route** in this triangle is A, and the **Indirect Route** is (B + C).
  Therefore A = B + C, and the value of the ΔH that we require, B, must therefore be
  B = A – C = 111 kJ mol^{-1}.

- **We had two known ΔHs and one unknown ΔH, and we used Hess' Law to find the unknown ΔH** – and it really is as simple as that.
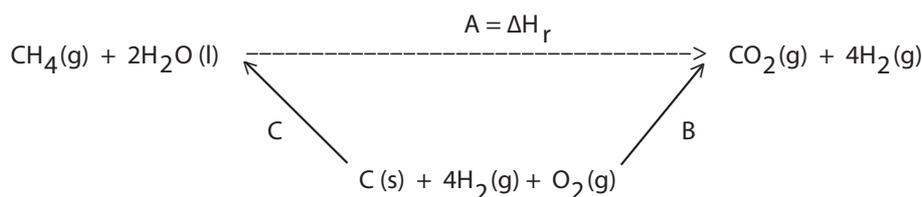
In exams how can they make life slightly more difficult for you

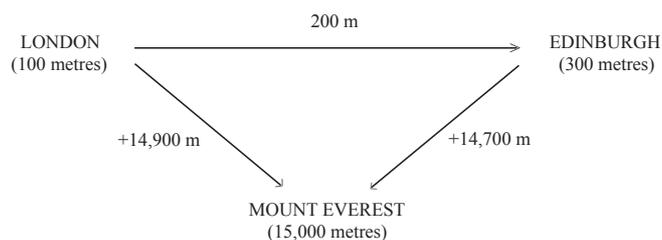- They could give you two **ΔH of Combustions**

$$(A) = \Delta H_c \text{ of CO (g)}$$

$$C\ (s)\ +\ O_2(g) \dashrightarrow CO\ (g)\ +\frac{1}{2}O_2\ (g)$$

$$(B) = \Delta H_c \text{ of C (s)} \qquad\qquad (C) = \Delta H_c \text{ of CO (g)}$$

$$CO_2\ (g)$$

and if they do so, then draw your two side arrows **downwards** (as I have drawn them above)

or they could give you two **ΔH of Formations**

$$A = \Delta H_r$$

$$CH_4(g)\ +\ 2H_2O\ (l) \dashrightarrow CO_2(g)\ +\ 4H_2(g)$$

$$C \qquad\qquad\qquad B$$

$$C\ (s)\ +\ 4H_2(g) +\ O_2(g)$$

and if they do so, then draw your two side arrows **upwards** (as I have drawn them above)

or they could give you a negative value for x and (reasonably) expect you to realise that *if you gain 14,700 metres in going from Edinburgh to the top of Everest*, then you will **lose** 14,700 metres in going from the top of Everest to Edinburgh (and that will give you your direct and indirect routes).

$$\text{200 m}$$

LONDON   EDINBURGH

(100 metres)   (300 metres)

$$+14,900\ m \qquad\qquad\qquad +14,700\ m$$

MOUNT EVEREST
(15,000 metres)

but, whatever they give you, the secret to resolving any/every Hess' Cycle is to identify the Direct Route and the Indirect Routes and then remember that the
"Direct Route = The Indirect Route".

- You can label the arrows whatever you want (A/B/C/D/E/F/G/etc), because all that you need to remember is that the
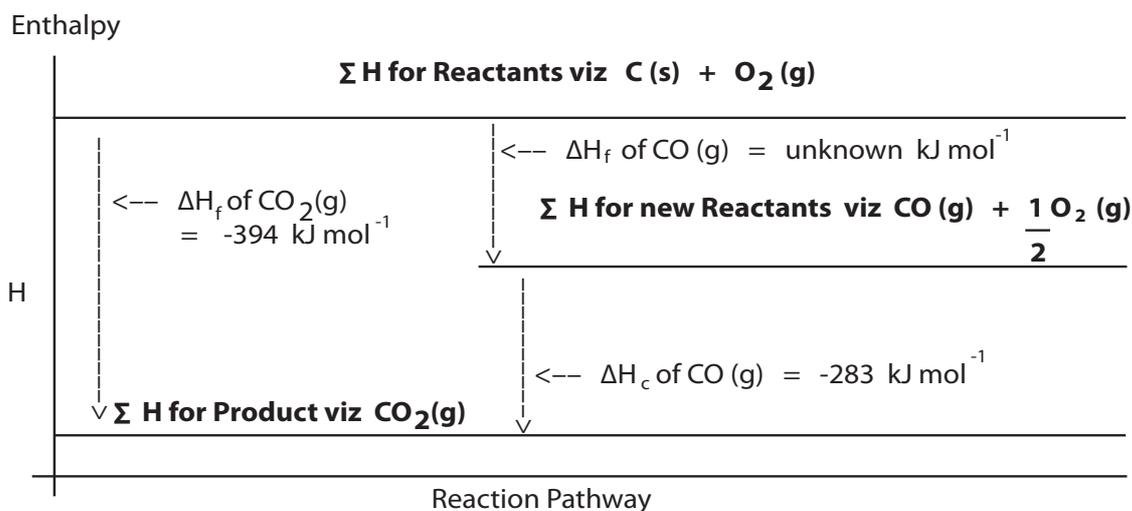
"Direct Route = The Indirect Route"

- That is it. That is all there is to it! There is nothing more to Hess' Cycles than that.

What can the examiners do to make life even harder for you?

- Well they could give you more than one reaction in a given direction, and in that case you would have to have TWO (or however many) reaction arrows in that part of your triangle.

- The examiners also love setting traps about **MOLAR** values and **STOICHIOMETRIC** ratios – and you must therefore remember
  - that the ΔH values given are always for **one mole** and that you may need to adjust the value for the number of moles that you need in your reaction, and
  - you must remember to use the correct **stoichiometric ratios** for the reaction that you are using.

- I have in this little note expressed Hess' Law as a triangle with the caption
  Value of ΔH for the Direct Route = Value of ΔHs for the Indirect Route

  but you do not need to use a triangle to resolve the value of ΔH in an Enthalpy problem. In fact, Hess' Law is usually expressed by nearly all textbooks in the form of an Enthalpy Profile diagram/a Born-Haber graph, and in more elementary exams (such as GCSEs) you might even be asked to use graph paper to measure the distances involved. This is what the calculation for Carbon Monoxide would look like when shown as an Enthalpy Profile diagram/a Born-Haber graph.

Enthalpy

Σ H for Reactants viz C (s) + O$_2$ (g)

$\leftarrow$ ΔH_f of CO (g) = unknown kJ mol^{-1}

$\leftarrow$ ΔH_f of CO$_2$(g) = -394 kJ mol^{-1}

Σ H for new Reactants viz CO (g) + $\dfrac{1}{2}$ O$_2$ (g)

H

$\leftarrow$ ΔH_c of CO (g) = -283 kJ mol^{-1}

Σ H for Product viz CO$_2$(g)

Reaction Pathway

- Finally, when you get to Lattice Enthalpy in your Second Year of 'A' Levels, then there will be a lot more calculation involved (as I show you overleaf) – but at the heart of it all, just as in Trig all that you really need to know is *SOH CAH TOA*, so also there is only one thing that you need to know in calculations about Enthalpy

The Value of ΔH in the Direct Route = The Value of ΔHs in the Indirect Route

This is a fairly typical Second Year Enthalpy calculation that I have taken from a previous exam paper where **YOU** had to work out all the different steps involved, but you were given prompts in the question as to the sequence of steps that would be needed. On the whole, the 'A' Level examiners do not try to trip you up. They just want to see whether you understand what you have learnt – and if you learn your stuff/understand it/practice doing questions on the Syllabus, then you will do well in the exams.

Enthalpy (H)

Mg^{2+} (g) + 2ē   and 2Cl (g)

Step7 = 2 . ΔHat of Cl₂ (g) = 242 kJ per mol

Mg^{2+} (g) + 2ē   and Cl_2(g)

Step6 = ΔHsie = 1,450 kJ per mol Mg^{2+}(g) and 2Cl⁻(g)

Mg^{+} (g) + 1e⁻ and Cl_2(g)

Step5 = ΔHfie of Mg(g) = 736 kJ per mol

Mg(g) and Cl_2(g)

Step4 : ΔHat of Mg(s) = 147 kJ per mol

Mg(s) and Cl_2(g)

Step1 : ΔHf of MgCl₂(s) = -642 kJ per mol

$MgCl_2$(s)

**Step3 =
2 [ΔHea1 of Cl(g)]
= -698 kJ per mol**

Step2 = ?

Reaction Pathway