Chem Factsheet

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Hess's Law for year 1 A Level

Hess's Law was first published in 1840 by the Swiss-born Russian chemist Germain Henri Hess.

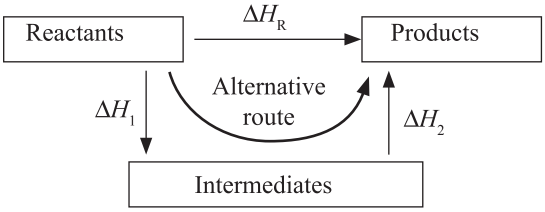

Germain Henri Hess
1802 - 1850

The law states that the total enthalpy change (ΔH) associated with a chemical reaction is independent of the path taken from the initial to the final state.

The total enthalpy change depends only on the quantities (moles) and physical states (g, l, s, soln) of the reactants and the products.

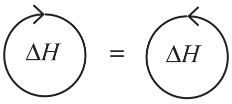
Note: This is merely an application of the First Law of Thermodynamics – "energy can be neither created nor destroyed".

Consider the following general energy cycle where a set of reactants are converted directly to a set of products or indirectly via a set of intermediates.



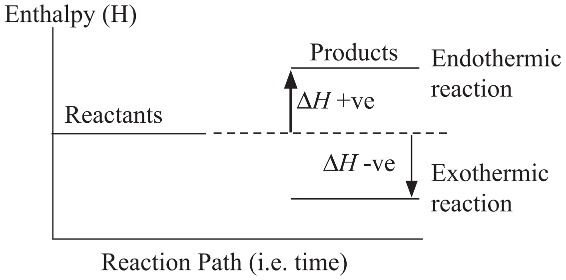
Applying Hess's Law gives: $\Delta H_R = \Delta H_1 + \Delta H_2$

Note: Another useful way of applying Hess's Law is:
"in a balanced energy cycle, the total of the clockwise ΔH's will equal the total of the anti-clockwise ΔH's."



Before looking at the law and its applications in more detail, there follows a summary of ideas and definitions associated with this topic area.

1. ENTHALPY (H) – the total energy content of a chemical system measured at constant pressure.
2. ENTHALPY CHANGE (ΔH) - the change in total energy content of a chemical system measured at constant pressure.
3. EXOTHERMIC – describes a reaction where the enthalpy of the system decreases. i.e. ΔH is assigned as a negative change.
4. ENDOTHERMIC – describes a reaction where the enthalpy of the system increases. i.e. ΔH is assigned as a positive change.



5. STANDARD ENTHALPY CHANGE ($\Delta H^{\ominus}_{T}$) – an enthalpy change measured under standard conditions of temperature (T – usually 298K) and pressure (100kPa).
6. STANDARD ENTHALPY CHANGE OF REACTION ($\Delta H^{\ominus}_{R,298}$) – The energy change when the molar quantities of reactants shown in a balanced equation react completely to form the products shown, measured at 298K and 100kPa.
7. STANDARD ENTHALPY CHANGE OF FORMATION ($\Delta H^{\ominus}_{f,298}$ [X]) – the enthalpy change that occurs when *one mole* of a substance (X) is *formed from its component elements* in their standard states measured at 298K and 100kPa .
   e.g.1 $Na(s) + \frac{1}{2} Cl_2(g) \rightarrow NaCl(s)$; $\Delta H^{\ominus}_{f,298}$ [NaCl(s)]
   e.g.2 $C(s) + 2H_2(g) + \frac{1}{2} O_2(g) \rightarrow CH_3OH(l)$; $\Delta H^{\ominus}_{f,298}$ [$CH_3OH(l)$]

Note: The standard enthalpy of formation of an element is ZERO since, for example, $Mg(s) \rightarrow Mg(s)$ or $Br_2(l) \rightarrow Br_2(l)$ do not involve any change.

8. STANDARD ENTHALPY CHANGE OF COMBUSTION ($\Delta H^{\ominus}_{c,298}$ [X]) – the enthalpy change that occurs when *one mole* of a substance (X) is *burned in excess oxygen*, measured at 298K and 100kPa.

Note: In general, when a compound is burned in excess oxygen, its component elements will be converted to their oxides.
$H \rightarrow H_2O$; $C \rightarrow CO_2$; $S \rightarrow SO_2$ etc
e.g.1 $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$; $\Delta H^{\ominus}_{c,298}$ [$CH_4(g)$]
e.g.2 $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$; $2 \times \Delta H^{\ominus}_{c,298}$ [$H_2(g)$]

Note: The combustion of an element can also be viewed as the formation of the element's oxide. Hence, example 2 can be seen as $2 \times \Delta H^{\ominus}_{f,298}$[$H_2O(l)$].

Similarly, $2Na(s) + \frac{1}{2}O_2(g) \rightarrow Na_2O(s)$ can be seen as $\Delta H^{\ominus}_{f,298}$[$Na_2O(s)$] or $2 \times \Delta H^{\ominus}_{c,298}$ [Na(s)].

9. MEAN BOND ENTHALPY (E[X-Y]) – the *average* amount of energy required to *break one mole of covalent bonds* [X-Y] in the *gaseous state*, measured at 298K and 100kPa.
   e.g.1 $C\text{-}H(g) \rightarrow C(g) + H(g)$; E[C-H]
   e.g.2 $O{=}O(g) \rightarrow 2O(g)$; E[O=O]

Note: The average values are derived using data for the same bond in a number of closely related compounds. e.g. E[C-H] could be derived from CH_4, CH_3CH_3, $CH_3CH_2CH_3$ etc.

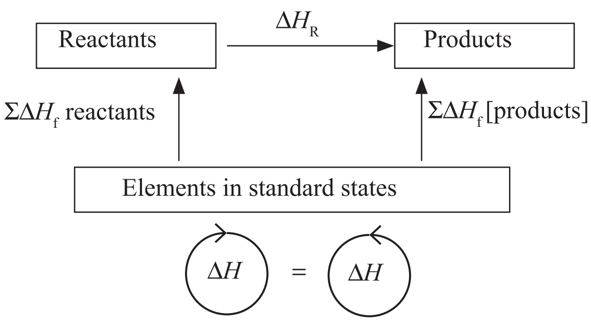
When applied to covalently-bonded gaseous elements, the value applies specifically to that bond and is not averaged. The term *bond dissociation energy* is then often used.

Note: Hess's Law is used to calculate enthalpy changes which **cannot** be measured directly. This occurs when:

1. a reaction does not go to completion
   e.g. $C(s) + 2H_2(g) \rightarrow CH_4(g)$
2. mixed reactions occur
   e.g. $CH_4(g)$ with $Cl_2(g)$ to give $CH_3Cl(l)$, $CH_2Cl_2(l)$ etc
3. the reaction is too slow to measure e.g. rusting of iron

Calculations involving enthalpy changes of formation

ΔH_f is basically defined for elements changing to a compound. Hence, the energy cycle required here is one where stoichiometric amounts of the component elements in their standard states are connected to both reactants and products. Hence,



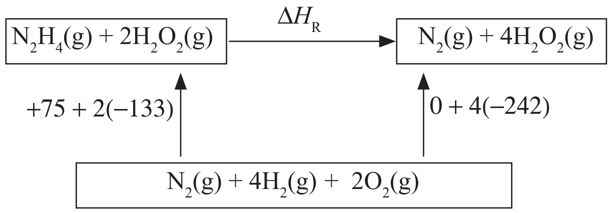
By Hess's law
$\Sigma\Delta H_f$ [Reactants] + ΔH_R = $\Sigma\Delta H_f$ [Products]
$\Delta H_R = \Sigma\Delta H_f$ [Products] - $\Sigma\Delta H_f$ [Reactants]

Note: The symbol Σ represents the *sum* of all the relevant values. This involves adding ΔH_f values for each and each mole of every reactant (or product) in the balanced reaction equation.

e.g.1 Given the following data

Substance	N_2H_4(g)	H_2O_2(g)	H_2O(g)
$\Delta H^\ominus_f$ /kJmol^{-1}	+75	–133	–242

calculate ΔH for $N_2H_4(g) + 2H_2O_2(g) \rightarrow N_2(g) + 4H_2O(g)$.

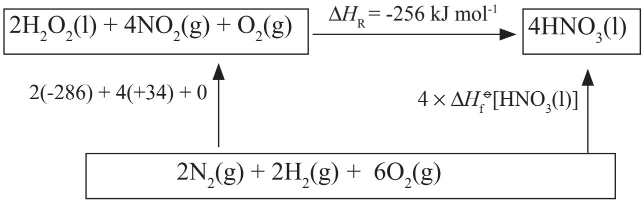


Note the multiples 2 and 4 needed to allow for the number of moles of H_2O_2(g) and H_2O(g) involved.

Using "clockwise ΔH" = "anti-clockwise ΔH"
+75 + 2(-133) + ΔH_R = 0 + 4(-242)
$\rightarrow \Delta H_R$ = 0 + 4(-242) - 75 - 2(-133) = -$\underline{293}$ kJ mol^{-1}.

e.g.2
Given $2H_2O(l) + 4NO_2(g) + O_2(g) \rightarrow 4HNO_3(l)$; ΔH = -256 kJ mol^{-1} and
Substance: H_2O(l) $\Delta H^\ominus_f$ / kJ mol^{-1} – 286
NO_2(g) $\Delta H^\ominus_f$ / kJ mol^{-1} +34

Calculate a value for the standard enthalpy of formation of nitric acid.



Using "clockwise ΔH" = "anti-clockwise ΔH"
2(-286) + 4(+34) + 0 + (-256) = $4\Delta H_f^\ominus[HNO_3(l)]$
$\rightarrow \Delta H_f^\ominus[HNO_3(l)]$ = ¼ [2(-286) + 4(+34) + (-256)] = -$\underline{173}$ kJ mol^{-1}.

1. Using the following data, calculate the enthalpy change for
$2CH_3CH_2CH_2OH(l) + 9O_2(g) \rightarrow 6CO_2(g) + 8H_2O(l)$

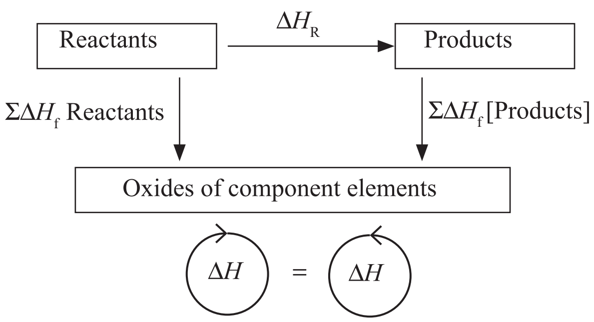
Substance	$CH_3CH_2CH_2OH$(l)	CO_2(g)	H_2O(l)
$\Delta H^\ominus_f$ / kJ mol^{-1}	-315	-394	-286

2. Use the data from the table below to calculate a value for the enthalpy of combustion of propene in the gaseous state.
i.e. $CH_3CHCH_2(g) + 4.5O_2(g) \rightarrow 3CO_2(g) + 3H_2O(g)$

Substance	C_3H_6(g)	CO_2(g)	H_2O(g)
$\Delta H^\ominus_f$ / kJ mol^{-1}	+20	-394	-242

Calculations involving enthalpy changes of combustion

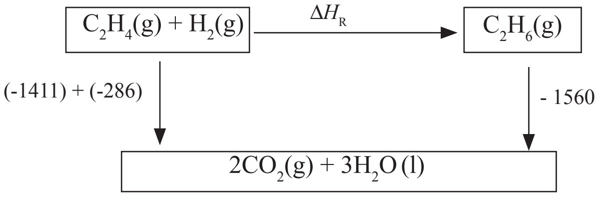
ΔH_c is basically defined for compounds changing to oxides. Hence, the energy cycle required here is one where both reactants and products are connected to the stoichiometric amounts of oxides of the component elements in their standard states. Hence,



By Hess's law
$\Delta H_R + \Sigma\Delta H_c$ [Products] = $\Sigma\Delta H_c$ [Reactants]
$\Delta H_R = \Sigma\Delta H_c$ [Reactants] - $\Sigma\Delta H_c$ [Products]

e.g.1 Calculate $\Delta H^\ominus_R$ for : $C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$, given

Substance	C_2H_4(g)	C_2H_6(g)	H_2(g)
$\Delta H^\ominus_c$ / kJ mol^{-1}	-1411	-1560	-286

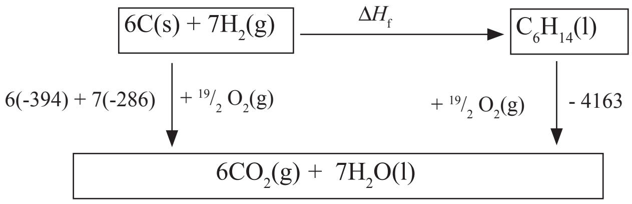


Using "clockwise ΔH" = "anti-clockwise ΔH"
(-1411) + (-286) = ΔH_R + (-1560)
$\rightarrow \Delta H_R$ = -1411 – 286 + 1560 = -$\underline{137}$ kJ mol^{-1}.

Note: ΔH_c values of carbon, hydrogen and a combustible organic compound are often used to calculate a ΔH_f value for the organic compound because the latter cannot be measured directly. See e.g. 2.

e.g. 2 Calculate the standard enthalpy change of formation of hexane using the following standard enthalpy changes of combustion.

Substance	C_6H_{14}(l)	C(s)	H_2(g)
$\Delta H^\ominus_c$ / kJ mol^{-1}	-4163	-394	-286



Using "clockwise ΔH" = "anti-clockwise ΔH"
6(-394) + 7(-286) = ΔH_f + (-4163)
$\rightarrow \Delta H_f$ = 6(-394) + 7(-286) + 4136 = -$\underline{230}$ kJ mol^{-1}.

3. Calculate the standard enthalpy change of formation of propan-1-ol ($CH_3CH_2CH_2OH$) using the following standard enthalpy changes of combustion.

Substance	$CH_3CH_2CH_2OH(l)$	C(s)	$H_2(g)$
ΔH°_c / kJ mol^{-1}	-2021	-394	-286

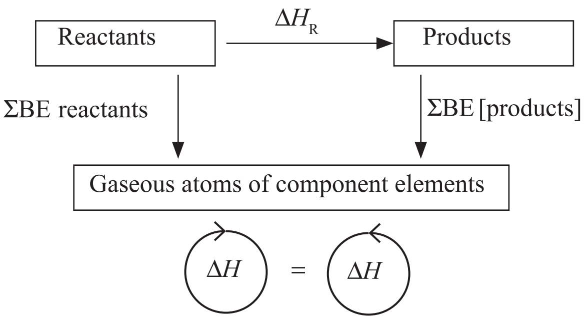
4. Calculate the standard enthalpy change for the following cracking process using the standard enthalpy changes of combustion shown in the table.

$C_{12}H_{26}(g) \rightarrow C_3H_8(g) + C_3H_6(g) + 3C_2H_4(g)$

Substance	$C_{12}H_{26}(g)$	$C_3H_8(g)$	$C_3H_6(g)$	$C_2H_4(g)$
ΔH°_c / kJ mol^{-1}	-7513	-2202	-2058	-1411

Calculations involving bond enthalpies

E[X-Y] values are basically defined for covalent bonds in gaseous molecules being broken to form individual gaseous atoms. Hence, the energy cycle required here is one where both reactants and products are connected to the stoichiometric amounts of gaseous atoms of the component elements in their standard states. Hence,



By Hess's law

$\Delta H_R + \Sigma BE\ [\text{Reactants}] = \Sigma BE\ [\text{Products}]$

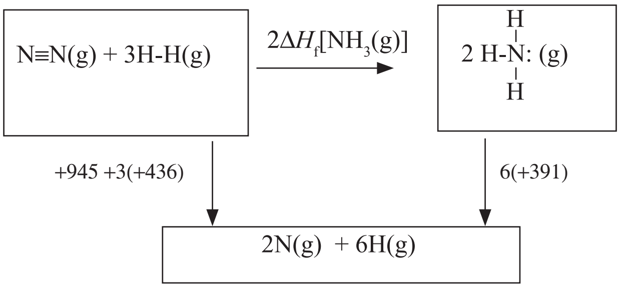
$\Delta H_R = \Sigma BE\ [\text{Reactants}] - \Sigma BE\ [\text{Products}]$

Note: Since bond enthalpies are ***average*** values, any calculation using E[X-Y] values will have limited accuracy. Such calculations are used to ***estimate*** enthalpy changes. Also, calculation is restricted to the gaseous state.

e.g. 1 In the Haber process, ammonia is manufactured from nitrogen and hydrogen as shown in the equation. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Use the bond enthalpies below to estimate the standard enthalpy of formation of ammonia.

Bond	N≡N	H-H	N-H
E[X-Y] kJ mol^{-1}	+945	+436	+391

Note: It is a good idea to rewrite the equation ***showing*** the covalent bonds to be broken and the covalent bonds to be formed.



Note: The multiples (3 and 6 here) are the numbers of bonds broken or formed, NOT the number of molecules.

Using "clockwise ΔH" = "anti-clockwise ΔH"

$2\Delta H_f[NH_3(g)] + 6(+391) = +945 + 3(+436)$

$\rightarrow \Delta H_f[NH_3(g)] = \tfrac{1}{2}\,[+945 + 3(+436) - 6(+391)] = -\underline{46.5}$ kJ mol^{-1}.

Note: The standard $\Delta H_f[NH_3(g)]$ value is -45.9 kJ mol^{-1}. This illustrates the errors involved in using the averaged E[N-H] value.

e.g. 2 Use the E data to estimate ΔH for
$CH_3CH_2CH_2CH_2OH(g) + 6O_2(g) \rightarrow 4CO_2(g) + 5H_2O(g)$

Bond	C-H	C-C	C-O	O=O	C=O	O-H
E[X-Y] kJ mol^{-1}	+413	+347	+358	+498	+695	+464

Using "clockwise ΔH" = "anti-clockwise ΔH"

$\Delta H_R + 8(+695) + 10(+464) = 3(+347) + 9(+413) + 358 + 464 + 6(+498)$

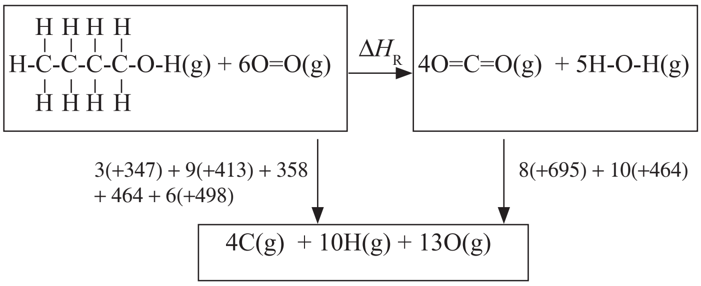
$\rightarrow \Delta H_R = 3(+347) + 9(+413) + 358 + 464 + 6(+498) - 8(+695) - 10(+464)$

$= -\underline{1632}$ kJ mol^{-1}.

5. Use the mean bond enthalpy data from the table and the equation given below to estimate a value for the following enthalpy of combustion of propene.

$CH_3CHCH_2(g) + 4.5O_2(g) \rightarrow 3CO_2(g) + 3H_2O(g)$

Bond	C-H	C-C	C=C	O=O	C=O	O-H
E[X-Y] kJ mol^{-1}	+413	+347	+612	+498	+695	+464



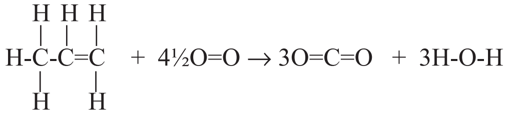
6. Use the following data to calculate the enthalpy change for the following gas-phase reaction between hydrazine, N_2H_4, and hydrogen peroxide, H_2O_2.

$N_2H_4(g) + 2H_2O_2(g) \rightarrow N_2(g) + 4H_2O(g)$

Bond	N-H	N-N	O-O	O-H	N≡N
E[X-Y] kJ mol^{-1}	+388	+163	+146	+464	+944

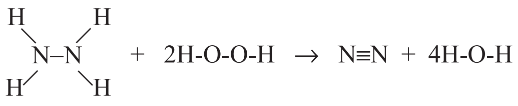
Answers

1 -4022 kJ mol^{-1}
2 -1928 kJ mol^{-1}
3 -305 kJ mol^{-1}
4 +980 kJ mol^{-1}
5 -1276 kJ mol^{-1}



$\text{H-C-C=C} + 4\tfrac{1}{2}\text{O=O} \rightarrow 3\text{O=C=O} + 3\text{H-O-H}$

6 -1867 kJ mol^{-1}



$\text{N–N} + 2\text{H-O-O-H} \rightarrow \text{N≡N} + 4\text{H-O-H}$

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