# 3.14 Bond Enthalpy

### Bond Enthalpy

Definition: The bond enthalpy of a specific bond is the enthalpy change needed **to break** that **covalent** bond into **gaseous atoms.** All substances being gases.

So for HCl gas the bond enthalpy for the H-Cl refers to this change:
H-Cl (g) → H(g) + Cl (g)
Bond enthalpies are always positive because it will always require energy to overcome the attractive forces in the bond

### Mean Bond enthalpy

Definition: The mean bond enthalpy is the enthalpy change needed **to break** the **covalent** bond into **gaseous atoms**, **averaged over different** molecules

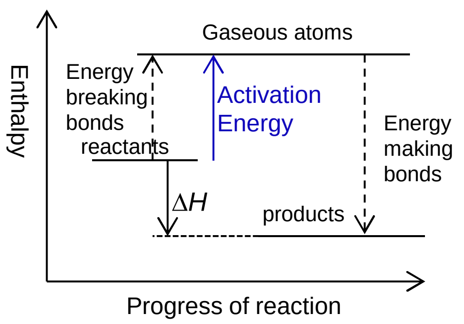
These values are positive because energy is required to break a bond.

The definition only applies when the **substances start and end in the gaseous state.**

We use values of **mean** bond enthalpy because every single bond in a compound has a slightly different bond enthalpy. E.g. In $CH_4$ there are 4 C-H bonds. Breaking each one will require a different amount of energy. However, we use an average value for the C-H bond for all hydrocarbons.

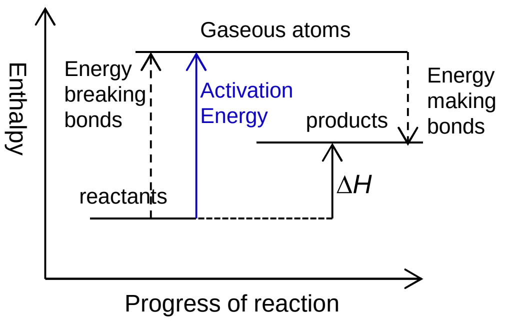
The value for the mean bond enthalpy for the C-H bond in methane matches this reaction ¼ $CH_{4\,(g)} \rightarrow C_{(g)} + H_{(g)}$

### Reactions involving bond breaking and making



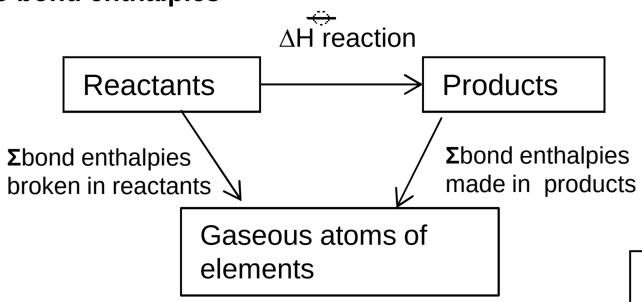

Reaction profile for an EXOTHERMIC reaction

In an exothermic reaction the sum of the bonds in the reactant molecules will be less than the sum of the bonds in the product molecules




Reaction profile for an ENDOTHERMIC reaction

### Applying Hess's law to bond enthalpies

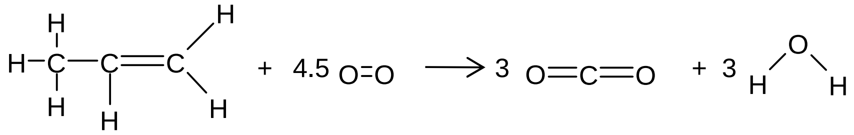



**In general (**if all substances are gases**)**

a***H*** = p **bond enthalpies broken - p bond enthalpies made**

a***H*** values calculated using this method will be less accuate than using formation or combustion data because the mean bond enthalpies are not exact

**Example 1**. Use the following mean bond enthalpy data to calculate the enthalpy of combustion of propene.



| Bond | Mean enthalpy (kJ mol-1) |
|---|---|
| C=C | 612 |
| C-C | 348 |
| O=O | 496 |
| O=C | 743 |
| O-H | 463 |
| C-H | 412 |

a***H*** = p **bond energies broken -** p **bond energies made**

= [E(C=C) + E(C-C) + 6 x E(C-H) + 4.5 x E(O=O)] – [ 6 xE(C=O) + 6 E(O-H)]

= [ 612 + 348 + (6 x 412) + (4.5 x 496) ] – [ (6 x 743) + (6 X 463)]

= - 1572 $kJmol^{-1}$

**Example 2.** Use the following mean bond enthalpy data to calculate the enthalpy of formation of $NH_3$

½ $N_2$ + 1.5 $H_2$ → $NH_3$ (note the balancing is to agree with the definition of heat of formation (i.e. one mole of product)

E(N≡N) = 944 kJ $mol^{-1}$ E(H-H) = 436 kJ $mol^{-1}$ E(N-H) = 388 kJ $mol^{-1}$

a***H*** = p **bond energies broken -** p **bond energies made**

= [0.5 x E(N≡N) + 1.5 x E(H-H)] – [ 3 xE(N-H)]

= [ (0.5 x 944) + (1.5 x 436) ] – [ 3 x 388)]

= - 38 $kJmol^{-1}$

**A more complicated example**

Working out $a_f$***H*** of a compound using bond enthalpies and other data

This is a more complicated example of the type in example 2

elements $\xrightarrow{a_f H}$ Compound in standard state

ΔH to turn elements into gaseous atoms

Gaseous atoms

ΔH to turn compound into gaseous atoms

Can be bond energies

E(Cl-Cl) $Cl_2$ → 2Cl

Or atomisation energies (if the substance is not diatomic

C(s) → C(g)

Σ bond energies of compound + (ΔH to turn to gas if compound is not gaseous)

The ΔH's can be combinations of different data

**Example 3**

Calculate $\Delta_f H$ for propane, $C_3H_8$(g), given the following data.

C(s) → C(g) $\Delta_{at}H$ = 715 kJ $mol^{-1}$

3C (s) + $4H_2$ (g) → $C_3H_8$(g),

| Bond | C–C | C–H | H–H |
|---|---|---|---|
| kJ $mol^{-1}$ | 348 | 412 | 436 |

$a_f$***H*** = Σ ΔH to turn elements into gaseous atoms - Σ ΔH to turn compound into gaseous atoms

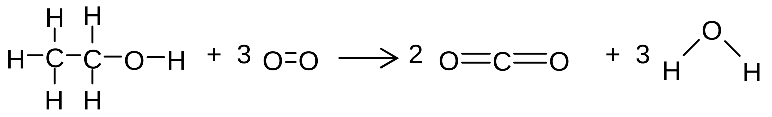
$a_f$H = (3x$a_{at}$H [C] + 4 x E[H-H] ) – (2 x E[C-C]+ 8 x E[C-H] )

= (3x715 + 4 x 436 ) – (2 x 348+ 8 x 412 )

=-103 kJ $mol^{-1}$

## Enthalpies of combustion in a homologous series

When comparing the heats of combustion for successive members of a **homologous series** such as alkanes or alcohols there is a **constant rise** in the size of the heats of combustion as the number of **carbon atoms increases**

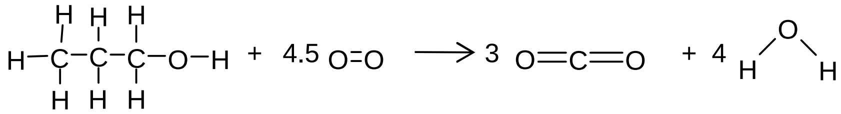


ethanol

**1 C-C**, **5C-H** 1C-O 1O-H and **3 O=O** bonds are broken

**4 C=O and 6 O-H** bonds are made

$\Delta H_c$ = -1365 kJ mol$^{-1}$

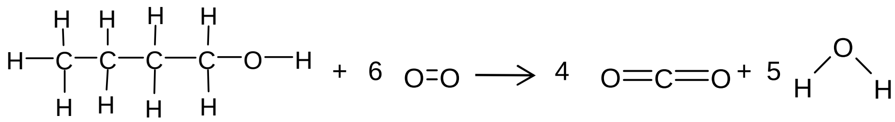


Propan-1-ol

**2C-C, 7C-H** 1C-O 1O-H and **4.5 O=O** bonds are broken

**6 C=O and 8 O-H** bonds are made

$\Delta H_c$ = -2016 kJ mol$^{-1}$



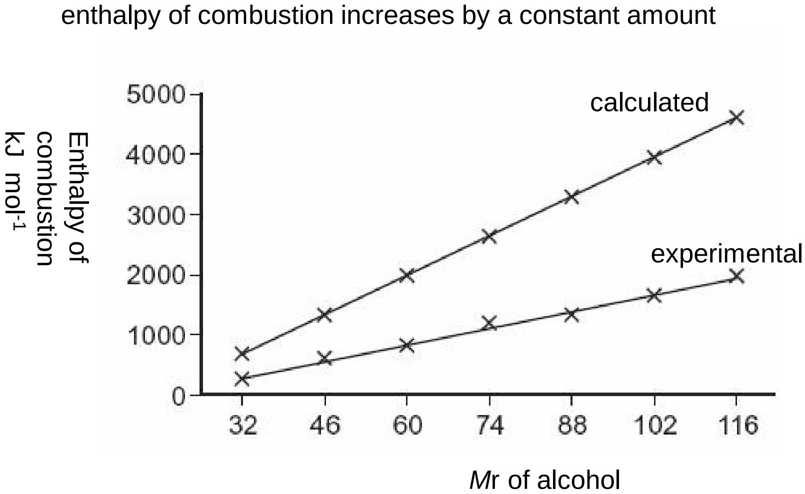
Butan-1-ol

**3C-C, 9C-H** 1C-O 1O-H and **6 O=O** bonds are broken

**8 C=O and 10 O-H** bonds are made

$\Delta H_c$ = -2677 kJ mol$^{-1}$

As one goes up the homologous series there is a constant amount and type of extra bonds being broken and made e.g. 1C-C, 2C-H and 1.5 O=O extra bonds broken and 2 C=O and 2 O-H extra bonds made, so the enthalpy of combustion increases by a constant amount




If the results are worked out experimentally using a calorimeter the experimental results will be much lower than the calculated ones because there will be significant heat loss. There will also be incomplete combustion which will lead to less energy being released.

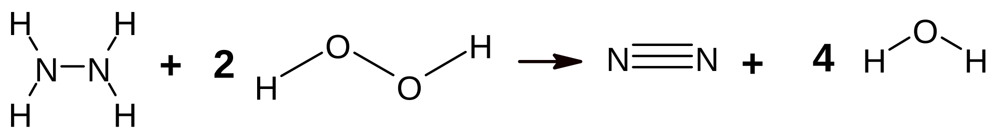
Remember that calculated values of enthalpy of combustions will be more accurate if calculated from enthalpy of formation data than if calculated from average bond enthalpies. This is because average bond enthalpy values are averaged values of the bond enthalpies from various compounds.

## Questions on Bond Enthalpies

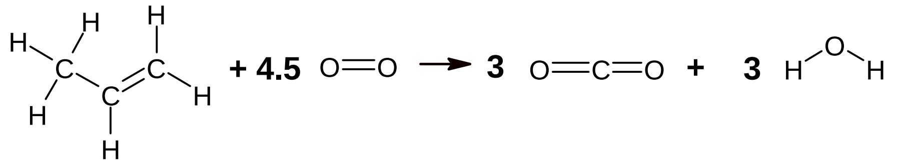
| Bond | Mean bond enthalpy/ Kj mol$^{-1}$ | Bond | Mean bond enthalpy/ Kj mol$^{-1}$ | Bond | Mean bond enthalpy/ Kj mol$^{-1}$ |
|---|---|---|---|---|---|
| C-C | 348 | O-O | 146 | N-N | 163 |
| C=C | 612 | O=O | 496 | N≡N | 944 |
| C-H | 412 | O-H | 463 | N-H | 388 |
| C-O | 360 | Cl-Cl | 243 | N-F | 278 |
| C=O | 743 | F-F | 159 | Si-H | 318 |
| C-Cl | 346 | H-Cl | 432 | Si-F | 553 |
| C-F | 467 | | | | |

1) Define bond enthalpy, as applied to a carbon–halogen bond.

2) Calculate the enthalpy change for the gas-phase reaction between hydrazine and hydrogen peroxide.



3) Calculate a value for the standard enthalpy of combustion of propene.



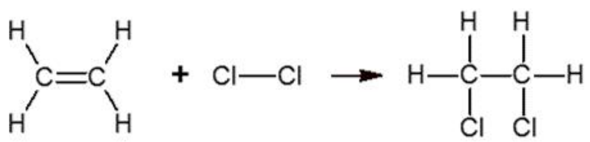
4) Calculate a value for the enthalpy change for the combustion of ethanol.
$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
Give **one** reason why the value calculated from mean bond enthalpies is different from the value given in a data book.

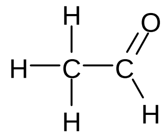
5) Hydrogen reacts with oxygen in an exothermic reaction as shown by the following equation.
$H_2(g) + ½ O_2(g) \rightarrow H_2O(g)$ $\Delta H = –242$ kJ mol$^{–1}$
Calculate a value for the bond enthalpy of the H–H bond.

6)The equation for the formation of nitrogen trifluoride is given below.
$½ N_2(g) + {}^3/_2 F_2(g) \rightarrow NF_3(g)$
Calculate a value for the enthalpy of formation of nitrogen trifluoride.
The data book value for the enthalpy of formation of nitrogen trifluoride is –114 kJ mol$^{–1}$. Give one reason why the answer you have calculated is different from this data book value.

7) (i) Write an equation for the formation of one mole of ammonia, $NH_3$, from its elements.
(ii) Calculate a value for the enthalpy of formation of ammonia.

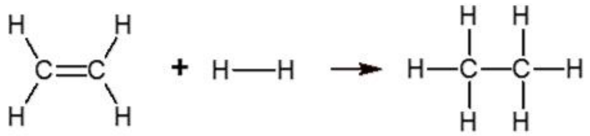
8) Calculate the enthalpy change for the reaction of ethene and chlorine



9) Ethanal has the structure 

Gaseous ethanal burns as shown by the equation
$CH_3CHO(g) + 2½\ O_2(g) \rightarrow 2H_2O(g) + 2CO_2(g)$
Calculate the enthalpy change for the complete combustion of ethanal

10) a) Calculate a value for the enthalpy of the reaction of ethene and hydrogen. (Use the value for the H-H bond calculated in Q5)



b) Use your answer to a) to calculate value for the hydrogenation of butadiene

$H_2C{=}CH{-}CH{=}CH_2$

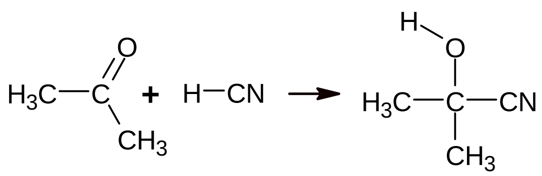
c) The experimental value for the hydrogenation of butadiene is -239kJ $mol^{-1}$ . Explain why your calculated value is different.

11) Calculate the enthalpy change for this reaction of ethane and chlorine
$C_2H_6(g) + Cl_2(g) \rightarrow C_2H_5Cl(g) + HCl(g)$

12) Calculate the enthalpy change for this reaction
$CF_4(g) + SiH_4(g) \rightarrow CH_4(g) + SiF_4(g)$

13) Calculate the enthalpy change for the reaction of ethane and chlorine forming dichloroethane
$C_2H_6(g) + 2Cl_2(g) \rightarrow C_2H_4Cl_2(g) + 2HCl(g)$

14) Calculate the enthalpy change for the following reaction. (You are not given the value for the C≡N bond in the table above. Why does this not matter in calculating the enthalpy of reaction)



15) The standard enthalpy of formation of ClF(g) is –56 kJ $mol^{-1}$.
(i) Write an equation, including state symbols, for the reaction that has an enthalpy change equal to the standard enthalpy of formation of gaseous ClF
(ii) Calculate a value for the bond enthalpy of the Cl-F bond.
iii) Calculate the enthalpy of formation of gaseous chlorine trifluoride, $ClF_3$ (g).
Use the bond enthalpy value that you obtained in part (ii).
(iv) Explain why the enthalpy of formation of $ClF_3$(g) that you calculated in part (iii) is likely to be different from a data book value.

16) Using bond enthalpies only, calculate the standard enthalpy of combustion of propane.

17) Suggest why a value for the NaCl bond enthalpy is not found in any data book.