Chem Factsheet

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# How to Do Bond Enthalpy Calculations

After completing this Factsheet, you will be able to:
- Calculate bond enthalpies from given reaction data.
- Calculate reaction enthalpies from given bond enthalpies.
- Understand why reaction enthalpies calculated from average bond enthalpies will not necessarily be the same as data book entries for the same reaction enthalpy.

## Breaking Bonds

Bond enthalpy is a measure of the strength of a bond. It is defined as the enthalpy change that takes place when 1 mole of a given bond in the molecules of a gaseous species is broken by homolytic fission under standard conditions (remember that homolytic fission is the breaking of a covalent bond so that one bonding electron goes to each atom involved in the bond).

It can be summarised by this reaction:

$$X—Y(g) \rightarrow X(g) + Y(g)$$

Breaking bonds is an energy requiring process and so all bond enthalpies are **endothermic**. The stronger the bond, the more energy needed to break that bond.

For example:

$Br—Br(g) \rightarrow 2Br(g)$ $\Delta H = 193\ kJ\ mol^{-1}$
$Cl—Cl(g) \rightarrow 2Cl(g)$ $\Delta H = 243\ kJ\ mol^{-1}$

The stronger bond is the chlorine bond as it requires 243 kJ mol$^{-1}$ of energy to break.

The formation of a bond releases the same amount of energy that is needed when the bond is broken. The stronger the bond, the more energy is released when that bond is formed.

E.g., when 1 mole of chlorine molecules is made from chlorine atoms, 243 kJ of energy is released.

$2Cl(g) \rightarrow Cl—Cl(g)$ $\Delta H = -243\ kJmol^{-1}$

Standard enthalpy change of atomisation ($\Delta H_{at}$) is defined as the enthalpy change associated with the formation of one mole of gaseous atoms from an element in its standard state under standard conditions. For homo-diatomic elements, such as $Cl_2$, $H_2$, etc., the value of $\Delta H_{at}$ is exactly half the bond enthalpy, e.g., $\frac{1}{2}H_2(g) \rightarrow H(g)$

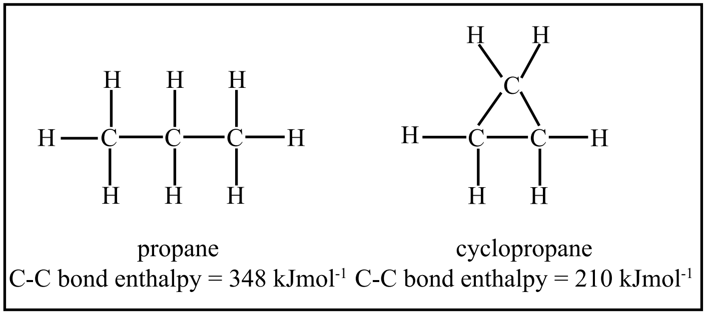
## Average Bond Enthalpy

The average (or mean) bond enthalpy takes into account the fact that the same type of bond in different molecules has a different strength, or enthalpy. It is defined as the average enthalpy change that takes place when 1 mole of a given type of bond is broken by homolytic fission in the molecules of many similar gaseous species under standard conditions.

A number of situations can affect the strength of a bond. For example, the inductive effect of highly electronegative atoms in close proximity to the bond in a molecule tends to draw electrons towards those atoms and so weakens the bond.

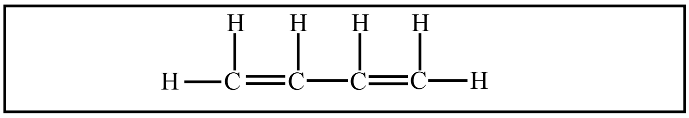
Steric factors such as strain within a molecule can cause weakening of a bond and can be seen by comparing the enthalpy of the C-C bond in propane and cyclopropane (Fig. 1).

**Fig. 1**



Delocalisation of electrons can cause single bonds to appear stronger and therefore have a higher bond enthalpy. For example, in buta-1,3-diene (Figure 2), the actual enthalpy of the bond between carbon 2 and carbon 3 is greater than that of a normal single C-C bond and less than that of a C=C bond due to conjugation and delocalisation of the $\pi$-electrons.

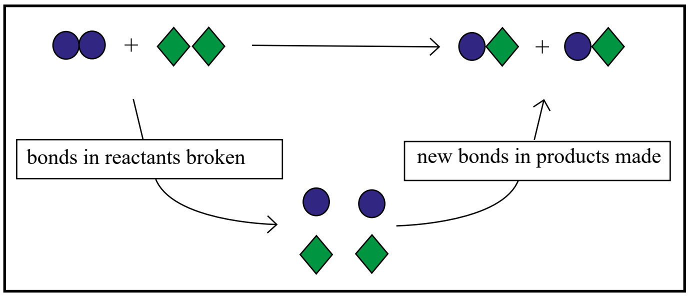
**Fig. 2**



## Chemical Reactions

In any chemical reaction, the bonds in the reactants are broken, the atoms are then rearranged and new bonds are made, forming the products. This can be represented in a cycle (Fig. 3).

**Fig. 3**



Therefore, the overall enthalpy change of a reaction can be worked out by calculating the difference between the energy needed to break the bonds in the reactants and the energy released when new bonds are made in the products.

$\Delta H_r = \Sigma$(bond enthalpies of bonds broken) - $\Sigma$(bond enthalpies of bonds made)

The subtraction performed here is due to the exothermic nature of making bonds. This makes the enthalpy change negative for this part of the overall process.

The stoichiometry of the reaction, i.e. the number of moles of reactants and products used and formed, must be taken into account when determining how many bonds of each type broken and formed.

Worked Example 1:
Given the average bond enthalpies below, calculate the enthalpy change for the reaction between hydrogen and chlorine to form hydrogen chloride.

**Table 1**

| Bond | Average bond enthalpy / kJ mol$^{-1}$ |
|---|---|
| H-H | 436 |
| Cl-Cl | 243 |
| H-Cl | 432 |

Reaction: $H_2(g) + Cl_2(g) \rightarrow 2HCl(g)$

bonds broken:
1 × H—H = 436 kJ mol$^{-1}$
1 × Cl—Cl = 243 kJ mol$^{-1}$

sum of enthalpies of bonds broken = 436 + 243 = 679 kJ mol$^{-1}$

bonds made:
2 × H—Cl = 2 × 432 kJ mol$^{-1}$

sum of enthalpies of bonds made = 2 × 432 = 864 kJ mol$^{-1}$

$\Delta H_r$ = Σ(bond enthalpies of bonds broken) - Σ(bond enthalpies of bonds made)
= 679 - 864
= -185 kJ mol$^{-1}$

In the example below, a more complicated reaction is used. It is always recommended that displayed structures are drawn for reactants and products to minimise the chances of miscounting the bonds present.

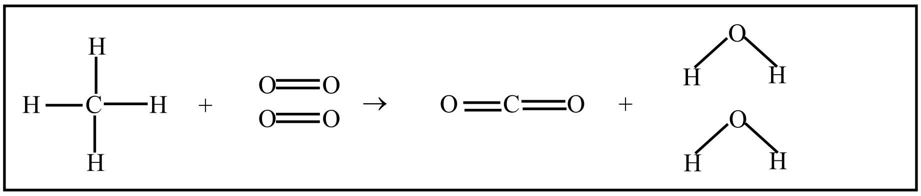
Worked Example 2:
Calculate the reaction enthalpy for the complete combustion of methane given the average bond enthalpies below.

**Table 2**

| Bond | Average bond enthalpy / kJ mol$^{-1}$ |
|---|---|
| C—H | 413 |
| C=O | 805 |
| O=O | 497 |
| O—H | 464 |

Reaction: $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

**Fig. 4**



bonds broken:
4 × C—H = 4 × 413 kJ mol$^{-1}$
2 x O=O = 2 × 497 kJ mol$^{-1}$
sum of enthalpies of bonds broken = 2646 kJ mol$^{-1}$

bonds made:
2 × C=O = 2 × 805 kJ mol$^{-1}$
4 × O—H = 4 × 464 kJ mol$^{-1}$

sum of enthalpies of bonds made = 3466 kJmol$^{-1}$

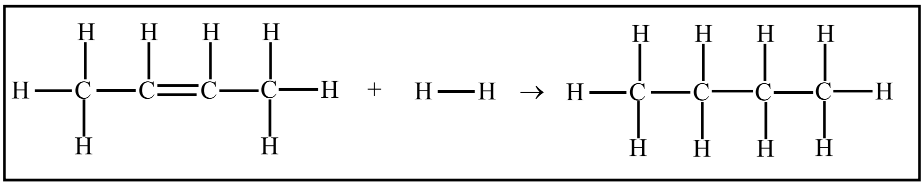
$\Delta H_r$ = Σ(bond enthalpies of bonds broken) - Σ(bond enthalpies of bonds made)
= 2646 - 3466
= -820 kJ mol$^{-1}$

Be aware, many mistakes are made in examinations by forgetting that water has 2 O—H bonds and that carbon dioxide has 2 C=O bonds. It is also quite common to forget to include the breakage of the O=O in combustion reactions.

If many of the bonds in the reactant and product molecules are the same, it is acceptable to ignore these bonds and just consider the bonds that change. This is because the energy required to break a particular bond is cancelled out by the energy released when the same bond is remade.

Consider the hydrogenation of but-2-ene (Fig. 5.).

**Fig. 5**



Eight C—H bonds are in the reactant and ten in the product. Therefore, we only need to consider the formation of two C—H bonds in the calculation. Don't forget to include also the formation of one C—C bond as well as breaking a C=C double bond and the H—H bond.

## Using Reaction Enthalpies to Determine Bond Enthalpies

A common exam question is to calculate a bond enthalpy from given reaction enthalpies. The equation to calculate reaction enthalpies from bond enthalpies needs to be rearranged. It is also important to take account of the number of the bonds present in the reaction of the type asked for in the question.

Worked Example 3:
Using the information below, calculate the enthalpy of the N—H bond.

$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)\ \Delta H_r = -93\ kJ\ mol^{-1}$

**Table 3**

| Bond | Average bond enthalpy / kJ mol$^{-1}$ |
|---|---|
| N≡N | 945 |
| H—H | 436 |

bonds broken:
$1 \times N{\equiv}N \quad = \quad 1 \times 945\ kJ\ mol^{-1}$
$3 \times H{-}H \quad = \quad 3 \times 436\ kJ\ mol^{-1}$

sum of enthalpies of bonds broken = 2253 kJ mol$^{-1}$

bonds made:
$6 \times N{-}H$ = unknown enthalpy
$\Delta H_r$ = Σ(bond enthalpies of bonds broken) - Σ(bond enthalpies of bonds made)
-93 = 2253 - Σ(bond enthalpies of bonds made)

Therefore:
Σ(bond enthalpies of bonds made) = 2253 + 93 = 2346 kJ mol$^{-1}$

Therefore, bond enthalpy of N—H bond = 2346 ÷ 6 = 391 kJ mol$^{-1}$

Remember, bond enthalpies are always endothermic, so if your answer is negative, then look back at your calculation for errors.

The enthalpy calculated here may differ from the mean bond enthalpy quoted in a data source because the mean bond enthalpy is found by taking an average for N—H bonds in a range of compounds. However, it is likely to be quite similar in value and this can be a useful indicator or whether you are correct or not.

## Gaseous States

The bond enthalpy definition specifically states that the bonds must be in the gaseous state. When calculating reaction enthalpies using bond enthalpies for reactions that include substances in the liquid state, it is necessary to consider the enthalpy of vaporisation of the substance $\Delta H_{vap}$ (the enthalpy change when one mole of liquid substance is turned into a gas under standard conditions, e.g. $H_2O(l) \rightarrow H_2O(g)$).

So, if using average bond enthalpies to calculate the enthalpy of combustion of ethanol, $\Delta H_c\ (C_2H_5OH(l))$, it is important to take into account the enthalpies of vaporisation of both ethanol and water.

$C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2 + 3H_2O(l)$

Construction of an enthalpy cycle is useful (Fig. 6).

**Fig. 6**

$$\begin{tikzcd}
C_2H_5OH\ (l) + 3O_2\ (g) \arrow[r, "\Delta H_1"] \arrow[d, "\Delta H_2"'] & 2CO_2\ (g) + 3H_2O\ (l) \\
C_2H_5OH\ (g) + 3O_2\ (g) \arrow[r, "\Delta H_3"] & 2CO_2\ (g) + 3H_2O\ (g) \arrow[u, leftarrow, "\Delta H_4"']
\end{tikzcd}$$

$\Delta H_1 = \Delta H_c\ (C_2H_5OH(l)) = \Delta H_2 + \Delta H_3 - \Delta H_4$
$\Delta H_2 = \Delta H_{vap}\ (C_2H_5OH(l))$
$\Delta H_3 = \Sigma$(bond enthalpies of bonds broken) - $\Sigma$(bond enthalpies of bonds made)
$\Delta H_4 = 3 \times \Delta H_{vap}\ (H_2O(l))$

Worked Example 4
Calculate the reaction enthalpy for the combustion of ethanol using the data given and the enthalpy cycle in Fig. 6.

**Table 4**

| Bond | Average bond enthalpy / kJ mol$^{-1}$ |
|---|---|
| C—H | 413 |
| C—O | 358 |
| C—C | 347 |
| O—H | 464 |
| O=O | 497 |
| C=O | 805 |

| substance | $\Delta H_{vap}$ / kJ mol$^{-1}$ |
|---|---|
| $C_2H_5OH$ (l) | 39 |
| $H_2O$ (l) | 44 |

bonds broken:
1 × C—C = 1 × 347 kJ mol$^{-1}$
5 × C—H = 5 × 413 kJ mol$^{-1}$
1 × C—O = 1 × 358 kJ mol$^{-1}$
1 × O—H = 1 × 464 kJ mol$^{-1}$
3 × O=O = 3 × 497 kJ mol$^{-1}$

sum of enthalpies of bonds broken = 4725 kJ mol$^{-1}$

bonds made:
6 × O—H = 6 × 464 kJ mol$^{-1}$
4 × C=O = 4 × 805 kJ mol$^{-1}$

sum of enthalpies of bonds made = 6004 kJ mol$^{-1}$

$$\begin{aligned}\Delta H_r &= \Delta H_{vap}(C_2H_5OH(l)) + \Sigma(\text{bond enthalpies of bonds broken}) - \\ &\quad \Sigma(\text{bond enthalpies of bonds made}) - (3 \times \Delta H_{vap}(H_2O(l))) \\ &= 39 + 4725 - 6004 - (3 \times 44) \\ &= -1372\ \text{kJ mol}^{-1}\end{aligned}$$

> Often, examiners will ask you to compare your final value with a quoted value from the academic literature or a data booklet and explain the difference. Typically, any difference in the two values can be explained by referring to the nature of **average** bond enthalpies (not specific to ethanol and other compounds in the reaction) and that the quoted value is experimentally determined.

## Hess's Law vs. Average Bond Enthalpies

Sometimes, you may be asked to determine, separately, the enthalpy change for a reaction using either Hess' Law (given defined enthalpy changes, such as combustion and formation) or average bond enthalpies. Both calculations are performed as normal, but the final values are likely to be different. The reason for this is that defined enthalpy changes, e.g. $\Delta H_c$ or $\Delta H_f$ as specific to the compounds in the enthalpy cycle and will give a more accurate final answer than the use of average bond enthalpies which are not specific.

## Questions

1. Using the average bond enthalpies in table 2, and given the average bond enthalpy of the C-C bond = 347 kJ mol$^{-1}$, calculate the enthalpy change in the reaction below.

   $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

2. (a) Calculate the bond enthalpy of the C—F bond given the following information.

   $CH_4(g) + 4F_2(g) \rightarrow CF_4(g) + 4HF(g)$ $\Delta H_r = -1840$ kJ mol$^{-1}$

**Table 5**

| Bond | Average bond enthalpy / kJ mol$^{-1}$ |
|---|---|
| C—H | 945 |
| F—F | 436 |
| H—F | 568 |

   (b) The average bond enthalpy for the C—F bond is 467 kJ mol$^{-1}$. Suggest why this value is different from the value you have calculated in part (a).

3. The enthalpy change of vaporisation of octane is 41 kJ mol$^{-1}$. Using this value and bond enthalpy data from the factsheet, determine the enthalpy change of combustion of octane.

**Answers**
1 -2059 kJmol$^{-1}$ 2
(a) 485 kJmol$^{-1}$
(b) The mean bond enthalpy is found by taking an average for C-F bonds in a range of compounds
3 -5511.5 kJ mol$^{-1}$

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