# Announcements

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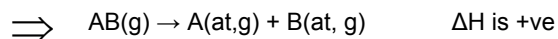
# Bond Enthalpy          M&H Chpt. 8.6 p. 210

The bond enthalpy of a bond A-B can be measured by determining the enthalpy
required to break "one mole of gaseous AB(g) to its two gaseous atoms"

$$\Longrightarrow \quad AB(g) \rightarrow A(at,g) + B(at, g) \qquad \Delta H \text{ is +ve}$$

This is always an endothermic reaction with a +ve ΔH

The measured value is termed the bond dissociation (enthalpy) energy
or bond energy (enthalpy)

Symbol = D; unit = kJ mol$^{-1}$

If you calculate the D for all the C-H bonds in a number of molecules,
you can obtain an average bond enthalpy for C-H. This can be done for any bond.

**Examples:**

| Bond | ΔH kJ mol$^{-1}$ |
|------|------------------|
| C-H | 414 |
| C-C | 347 |
| C=C | 612 |
| C≡C | 820 |

Note that average bond enthalpies correlate with the bond order (multiple bonds are stronger than single bonds).

In addition, bond enthalpies correlate with bond lengths: stronger bonds have shorter bond lengths

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### Single Bond Energies (kJ mol$^{-1}$) at 25°C

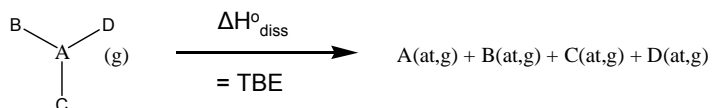|     | H | C | N | O | S | F | Cl | Br | I |
|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| **H** | 436 | 414 | 389 | 464 | 339 | 565 | 431 | 368 | 297 |
| **C** | | 347 | 293 | 351 | 259 | 485 | 331 | 276 | 238 |
| **N** | | | 159 | 222 | -- | 272 | 201 | 243 | -- |
| **O** | | | | 138 | -- | 184 | 205 | 201 | 201 |
| **S** | | | | | 226 | 285 | 255 | 213 | -- |
| **F** | | | | | | 153 | 255 | 255 | -- |
| **Cl** | | | | | | | 243 | 218 | 209 |
| **Br** | | | | | | | | 193 | 180 |
| **I** | | | | | | | | | 151 |

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If a molecule has several bonds, then the enthalpy of dissociation yields the total bonding energy (TBE)

TBE = "the enthalpy required to dissociate 1 mole of gaseous compound into its free gaseous atoms"

For example:

$$\begin{array}{c} B\diagdown \quad \diagup D \\ A \quad (g) \\ | \\ C \end{array} \quad \xrightarrow[\text{= TBE}]{\Delta H^o_{diss}} \quad A(at,g) + B(at,g) + C(at,g) + D(at,g)$$

One can use tables of $\Delta H_f^o$ to calculate TBE for a molecule and exact bond energies

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**Example:**
Calculate the bond energy of a N-H bond in $NH_3$ given $\Delta H_f^o$ of $NH_3(g)$, $N(at,g)$ and $H(at,g)$ are -46.1, 472.7 and 218.0 kJ $mol^{-1}$, respectively.

TBE($NH_3$) found from reaction: $NH_3(g) \rightarrow N(at,g) + 3H(at,g)$

∴   TBE = $\sum\Delta H_f^o$(products) - $\sum\Delta H_f^o$(reactants)

= 1x(472.7) + 3x(218.0)- 1x(-46.1) kJ $mol^{-1}$

= 1172.8 kJ $mol^{-1}$

Since $NH_3$ =

$$\begin{array}{c} H\diagdown \quad \diagup H \\ N \\ | \\ H \end{array}$$
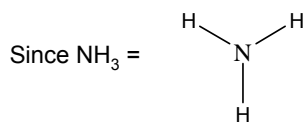
∴   D(N-H) = 1172.8/3 = 390.9 kJ $mol^{-1}$

Compare with M&H Table 8.4 D(N-H) = 389 kJ $mol^{-1}$

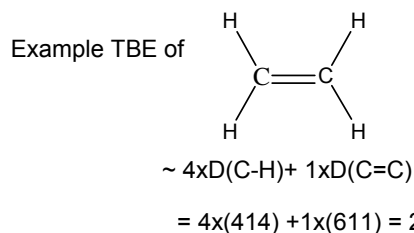## Estimates of TBE

TBEs can be estimated by summing the average bond enthalpies for all bonds in a molecule.

This is useful when $\Delta H_f^o$s are not available

Example TBE of



~ 4xD(C-H)+ 1xD(C=C)

= 4x(414) +1x(611) = 2267 kJ mol$^{-1}$

Note: this is an estimate only because <u>average bond enthalpies</u> are used

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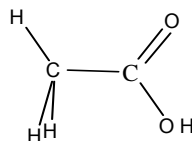One can also use this estimate to calculate $\Delta H_f^o$ of a molecule

**Example:**
Estimate $\Delta H_f^o$ of acetic acid, $CH_3COOH$
given D(C-H) = 414, D(C-C) = 347, D(C=O) = 745, D(C-O) = 351, and D(O-H) = 464, all in kJ mol$^{-1}$.
Similarly, $\Delta H_f^o$s of C(at, g), H(at, g) and O(at, g) are 716.7, 218.0 and 249.2 kJ mol$^{-1}$, respectively

Structure of $CH_3COOH$:



∴   TBE ~ 3D(C-H) + D(C-C) + D(C=O) + D(C-O) + D(O-H)

~ 3x(414) + 1x(347) + 1x(745) + 1x(351) +1x(464) = 3149 kJ mol$^{-1}$

Remember, this is an estimate

The equation for TBE is:

$$CH_3COOH(g) \rightarrow 2C(at,g) + 4H(at,g) + 2O(at,g)$$

∴ TBE ~ 3149 kJ mol$^{-1}$ = $\sum \Delta H_f^o$(products) - $\sum \Delta H_f^o$(reactants)

$\Rightarrow$ 3149 = 2x(716.7) +4x(218.0) + 2(249.2)-$\Delta H_f^o$(CH$_3$COOH)

∴ $\Delta H_f^o$(CH$_3$COOH) = -345.2 kJ mol$^{-1}$
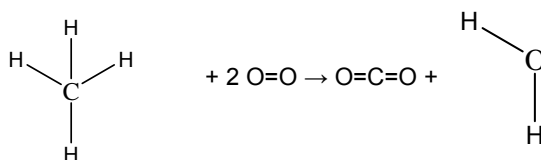
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**Example:**
Estimate the heat of combustion for CH$_4$(g)
use average bond enthalpies (in kJ mol$^{-1}$): D(C-H) = 414, D(C=O) = 803, D(O-H) = 464
and $\Delta H_f^o$(O,at,g) = 249.2 kJ mol$^{-1}$
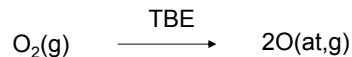
The combustion reaction is:



1.) energy required to break reagent bonds

= 4xD(C-H) + 2xD(O=O) = 4x(414) + 2x D(O=O)

Since bond enthalpy for O=O is not given we have to calculate it using $\Delta H_f^o$(O(at,g))

$$O_2(g) \xrightarrow{\text{TBE}} 2O(at,g)$$

TBE = 2$\Delta H_f^o$(O(at,g) – $\Delta H_f^o$(O$_2$(g)) = 2x(249.2) -0 = 498.4 kJ mol$^{-1}$

∴ $\Delta H^o$ to break reagent bonds = 4x(414)+2x(498.4) = +2652.8 kJ mol$^{-1}$

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2.) energy released by <u>formation</u> of product bonds:

   = 2xD(C=O) + +4xD(O-H)

   = 2x(803) + 4x(464)= 3463 kJ mol$^{-1}$


3.) The $\Delta H^o$ of the reaction will be the energy absorbed – energy released

   = 2652.8 – 3462.0 = -809.2 kJ mol$^{-1}$

 The method used to solve this problem can be generalized to:

$$\Delta H^o_{rxn} \sim TBE(reactants) - TBE(products)$$

Note: this method of using average bond energies to calculate $\Delta H^o_{rxn}$ gives only
**approximate** values.
Exact values are obtained if $\Delta H_f^o$ values for products and reactants are used
– this is the better method if all the necessary data is available.