

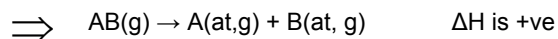
Announcements

Strongly advice students not to take Prep101. Seems like a waste of your \$\$\$

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"



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

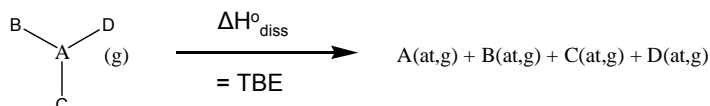
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If a molecule has several bonds, then the enthalpy of dissociation yields the total bonding energy (TBE)

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

For example:



One can use tables of ΔH_f° to calculate TBE for a molecule and exact bond energies

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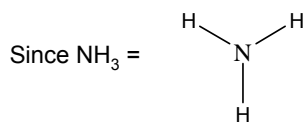
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Example:

Calculate the bond energy of a N-H bond in NH_3 given ΔH_f° of $\text{NH}_3(\text{g})$, $\text{N}(\text{at,g})$ and $\text{H}(\text{at,g})$ are -46.1 , 472.7 and 218.0 kJ mol^{-1} , respectively.

TBE(NH_3) found from reaction: $\text{NH}_3(\text{g}) \rightarrow \text{N}(\text{at,g}) + 3\text{H}(\text{at,g})$

$$\begin{aligned} \therefore \text{TBE} &= \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants}) \\ &= 1 \times (472.7) + 3 \times (218.0) - 1 \times (-46.1) \text{ kJ mol}^{-1} \\ &= 1172.8 \text{ kJ mol}^{-1} \end{aligned}$$



$$\therefore D(\text{N-H}) = 1172.8/3 = 390.9 \text{ kJ mol}^{-1}$$

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

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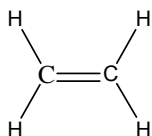
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Estimates of TBE

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

This is useful when ΔH_f° s are not available

Example TBE of



$$\begin{aligned} &\sim 4x\text{D}(\text{C-H}) + 1x\text{D}(\text{C=C}) \\ &= 4x(414) + 1x(611) = 2267 \text{ kJ mol}^{-1} \end{aligned}$$

Note: this is an estimate only because average bond enthalpies are used

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One can also use this estimate to calculate ΔH_f° of a molecule

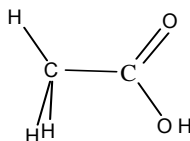
Example:

Estimate ΔH_f° of acetic acid, CH_3COOH

given $\text{D}(\text{C-H}) = 414$, $\text{D}(\text{C-C}) = 347$, $\text{D}(\text{C=O}) = 745$, $\text{D}(\text{C-O}) = 351$, and $\text{D}(\text{O-H}) = 464$, all in kJ mol^{-1} .

Similarly, ΔH_f° s of $\text{C}(\text{at, g})$, $\text{H}(\text{at, g})$ and $\text{O}(\text{at, g})$ are 716.7, 218.0 and 249.2 kJ mol^{-1} , respectively

Structure of CH_3COOH :



$$\begin{aligned} \bullet \bullet \quad \text{TBE} &\sim 3\text{D}(\text{C-H}) + \text{D}(\text{C-C}) + \text{D}(\text{C=O}) + \text{D}(\text{C-O}) + \text{D}(\text{O-H}) \\ &\sim 3x(414) + 1x(347) + 1x(745) + 1x(351) + 1x(464) = 3149 \text{ kJ mol}^{-1} \end{aligned}$$

Remember, this is an estimate

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The equation for TBE is:



$$\therefore \text{TBE} \sim 3149 \text{ kJ mol}^{-1} = \sum \Delta H_f^\circ(\text{products}) - \sum \Delta H_f^\circ(\text{reactants})$$

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

$$\therefore \Delta H_f^\circ(\text{CH}_3\text{COOH}) = -345.2 \text{ kJ mol}^{-1}$$

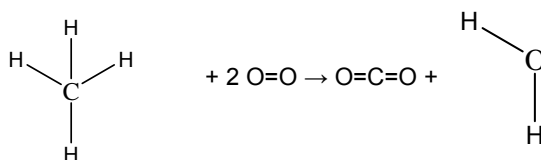
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Example:

Estimate the heat of combustion for $\text{CH}_4(\text{g})$
 use average bond enthalpies (in kJ mol^{-1}): $D(\text{C-H}) = 414$, $D(\text{C=O}) = 803$, $D(\text{O-H}) = 464$
 and $\Delta H_f^\circ(\text{O,at,g}) = 249.2 \text{ kJ mol}^{-1}$

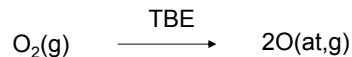
The combustion reaction is:



1.) energy required to break reagent bonds

$$= 4xD(\text{C-H}) + 2xD(\text{O=O}) = 4x(414) + 2x D(\text{O=O})$$

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



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

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

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2.) energy released by formation of product bonds:

$$\begin{aligned} &= 2xD(C=O) + 4xD(O-H) \\ &= 2x(803) + 4x(464) = 3463 \text{ kJ mol}^{-1} \end{aligned}$$

3.) The ΔH° of the reaction will be the energy absorbed – energy released

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

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

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

Note: this method of using average bond energies to calculate $\Delta H^\circ_{\text{rxn}}$ gives only **approximate** values.

Exact values are obtained if ΔH_f° values for products and reactants are used
– this is the better method if all the necessary data is available.