

Lecture ten Estimating ΔH Using Bond Energies

Bond energy: is the amount of energy that is required to break a chemical bond.

- Breaking bonds always requires energy
- Forming bonds always releases energy

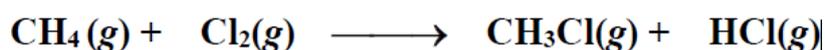
The enthalpy change of a reaction is approximately equal to the difference in the energy required to break the bonds of the reactants and the energy given off when the bonds in the products are formed:

$$\Delta H = \Sigma \text{ bond energy of reactants} - \Sigma \text{ bond energy of products}$$

We use values of mean bond enthalpy because every single bond in a compound has a slightly different bond enthalpy.

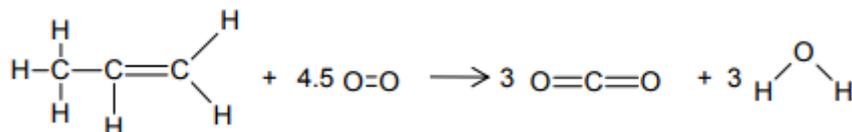
E.g. in CH_4 there are 4 C-H bonds. Breaking each one will require a different amount of energy. However, we use an average value for the C-H bond for all hydrocarbons.

For example



$$\Delta_r H = [4 \times E(\text{C}-\text{H}) + E(\text{Cl}-\text{Cl}) - [3 \times E(\text{C}-\text{H}) + E(\text{C}-\text{Cl}) + E(\text{H}-\text{Cl})]$$

Q) Using the following mean bond enthalpy data to calculate the heat 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

$\Delta_r H = \Sigma \text{ bond energy of reactants} - \Sigma \text{ bond energy of products}$

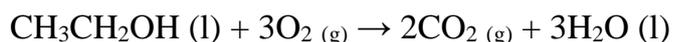
$$\Delta_r H = [E(\text{C}=\text{C}) + E(\text{C}-\text{C}) + 6 \times E(\text{C}-\text{H}) + 4.5 \times E(\text{O}=\text{O})] - [6 \times E(\text{C}=\text{O}) + 6 E(\text{O}-\text{H})]$$

$$\Delta_r H = [612 + 348 + (6 \times 412) + (4.5 \times 496)] - [(6 \times 743) + (6 \times 463)]$$

$$= - 1572 \text{ kJ.mol}^{-1}$$

$$\Delta_r H = \Delta_c H$$

H.W) Calculate a value for the enthalpy change for the combustion of ethanol.



Q) Using the following mean bond enthalpy data to calculate the heat of formation of NH₃



$$E (\text{N}\equiv\text{N}) = 944 \text{ kJ mol}^{-1} \quad E (\text{H}-\text{H}) = 436 \text{ kJ mol}^{-1} \quad E (\text{N}-\text{H}) = 388 \text{ kJ mol}^{-1}$$

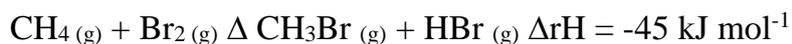
$\Delta_r H = \Sigma \text{ bond energy of reactants} - \Sigma \text{ bond energy of products}$

$$\Delta_r H = [0.5 * E (\text{N}\equiv\text{N}) + 1.5 * E (\text{H}-\text{H})] - [3 * E (\text{N}-\text{H})]$$

$$\Delta_r H = [(0.5 * 944) + (1.5 * 436)] - [3 * 388]$$

$$\Delta_r H = - 38 \text{ kJmol}^{-1} = \Delta_f H$$

Q) Bromine reacts with methane as follows:-



Use this equation and the bond enthalpies

$$\text{C-H} = 413 \text{ kJ mol}^{-1}$$

$$\text{C-Br} = 285 \text{ kJ mol}^{-1}$$

$$\text{H-Br} = 366 \text{ kJ mol}^{-1}$$

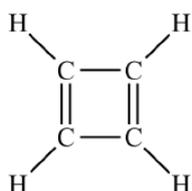
To calculate the bond enthalpy for the Br-Br bond

$$\Delta_r H = \sum \text{bond energy of reactants} - \sum \text{bond energy of products}$$

$$-45 \text{ kJ mol}^{-1} = [4 * E(\text{C-H}) + E(\text{Br-Br})] - [3 * E(\text{C-H}) + E(\text{C-Br}) + E(\text{H-Br})]$$

$$-45 \text{ kJ mol}^{-1} = [4 * 413 + E(\text{Br-Br})] - [3 * 413 + 285 + 366] \quad E(\text{Br-Br}) = 193 \text{ kJ mol}^{-1}$$

Q) Using the following mean bond enthalpy data to calculate the heat of combustion of cyclobutadiene.



Bond	Mean enthalpy (KJ.mol ⁻¹)
C=C	612
C-C	348
O=O	496
O=C	743
O-H	463
C-H	412

The temperature dependence of reaction enthalpies

The standard enthalpies of many important reactions have been measured at different temperatures. However, in the absence of this information, standard reaction enthalpies at different temperatures may be calculated from heat capacities and the reaction enthalpy at some other temperature.

In many cases heat capacity data are more accurate than reaction enthalpies. Therefore, providing the information is available, the procedure we are about to describe is more accurate than the direct measurement of a reaction enthalpy at an elevated temperature.

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p dT$$

Because this equation applies to each substance in the reaction, the standard $\Delta_r H$ reaction enthalpy changes from

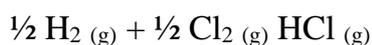
$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

$\Delta_r C_p^\ominus$ is the difference of the molar heat capacities of products and reactants under standard conditions weighted by the stoichiometric coefficients that appear in the chemical equation:

$$\Delta_r C_p^\ominus = \sum_{\text{Products}} \nu C_{p,m}^\ominus - \sum_{\text{Reactants}} \nu C_{p,m}^\ominus$$

Example

Calculate for the following reaction at 1450K and 1 bar;



Given that $\Delta_f H^\ominus(\text{HCl}, \text{g}) = -92.3 \text{ kJ/mol}$ at 298.15K and that;

$$C_{p,m}^0(\text{H}_2, \text{g}) = \left(29.064 - 0.8363 \times 10^{-3} \frac{T}{\text{K}} + 20.111 \times 10^{-7} \frac{T^2}{\text{K}^2} \right) \text{JK}^{-1}\text{mol}^{-1}$$

$$C_{p,m}^0(\text{Cl}_2, \text{g}) = \left(31.695 + 10.143 \times 10^{-3} \frac{T}{\text{K}} - 40.373 \times 10^{-7} \frac{T^2}{\text{K}^2} \right) \text{JK}^{-1}\text{mol}^{-1}$$

$$C_{p,m}^0(\text{HCl}, \text{g}) = \left(28.165 + 1.809 \times 10^{-3} \frac{T}{\text{K}} + 15.464 \times 10^{-7} \frac{T^2}{\text{K}^2} \right) \text{JK}^{-1}\text{mol}^{-1}$$

Over this temperature range.

Solution

Use the following equation;

$$\Delta_r H^\ominus(T_2) = \Delta_r H^\ominus(T_1) + \int_{T_1}^{T_2} \Delta_r C_p^\ominus dT$$

$$T_1 = 298.15 \text{ K}$$

$$T_2 = 1450 \text{ K}$$

$$\Delta_r C_{p,m}^0(T) = \left[\begin{array}{l} \left(28.165 + 1.809 \times 10^{-3} \frac{T}{\text{K}} + 15.464 \times 10^{-7} \frac{T^2}{\text{K}^2} \right) \\ - \frac{1}{2} \left(29.064 - 0.8363 \times 10^{-3} \frac{T}{\text{K}} + 20.111 \times 10^{-7} \frac{T^2}{\text{K}^2} \right) \\ - \frac{1}{2} \left(31.695 + 10.143 \times 10^{-3} \frac{T}{\text{K}} - 40.373 \times 10^{-7} \frac{T^2}{\text{K}^2} \right) \end{array} \right]$$

$$\Delta_r C_{p,m}^0(T) = \left[\left(-2.215 - 2.844 \times 10^{-3} \frac{T}{\text{K}} + 25.595 \times 10^{-7} \frac{T^2}{\text{K}^2} \right) \right] \text{J K}^{-1}\text{mol}^{-1}$$

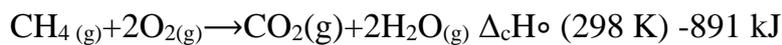
$$\Delta_r H^0 \text{ at } 1450 \text{ K} = -92.3 \text{ kJ mol}^{-1} + \int_{298.15}^{1450} \left(-2.215 - 2.844 \times 10^{-3} \frac{T}{\text{K}} + 25.595 \times 10^{-7} \frac{T^2}{\text{K}^2} \right) d\frac{T}{\text{K}} \text{ J mol}^{-1}$$

$$\Delta_r H^0 \text{ at } 1450 \text{ K} = -92.3 \text{ kJ mol}^{-1} + -2.215T - \frac{2.844 \times 10^{-3}}{2} \frac{T^2}{\text{K}^2} + \frac{25.595 \times 10^{-7}}{3} \frac{T^3}{\text{K}^3}$$

$$\Delta_r H^0 \text{ at } 1450 \text{ K} = -2.215(1450 - 298.15) - \frac{2.844 \times 10^{-3}}{2} (1450^2 - 298.15^2) + \frac{25.595 \times 10^{-7}}{3} (1450^3 - 298.15^3)$$

$$\Delta_r H^0 \text{ at } 1450 \text{ K} = (-92.3 - 2.836) \text{ kJ mol}^{-1} = -95.1 \text{ kJ mol}^{-1}$$

H.W) calculate $\Delta_c H^\circ$ (500 K) for methane by using the data given on the temperature dependence of heat capacities.



$$C_{p,m}(\text{CO}_2) = 44.22 + 8.79 \times 10^{-3}T - \frac{8.62 \times 10^5}{T^2}$$

$$C_{p,m}(\text{H}_2\text{O}) = 75.29 + 0 + 0$$

$$C_{p,m}(\text{O}_2) = 29.96 + 4.18 \times 10^{-3}T - \frac{1.67 \times 10^5}{T^2}$$

$$C_{p,m}(\text{CH}_4) = 35.31$$