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
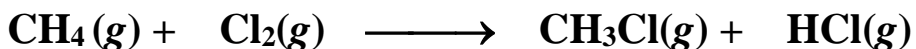
- Forming bonds always **releases** energy

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:

ΔH = ∑ bond energy of reactants - ∑ 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 CH4 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

CH₄ (g) +   Cl₂(g) ⎯⎯⎯→   CH₃Cl(g) +   HCl(g)

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

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Q) Using the following mean bond enthalpy data to calculate the heat of combustion of propene
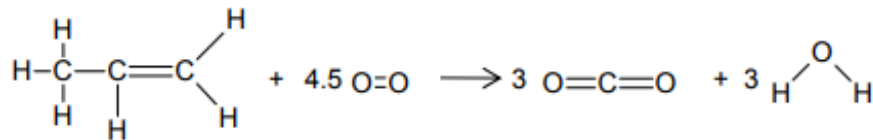
Bond	Mean enthalpy (kJ mol-1)
C=C	612
C-C	348
O=O	496
O=C	743
O-H	463
C-H	412

$\Delta_r H = \sum$ **bond energy of reactants -** $\sum$ **bond energy of products**

$\Delta_r H$ = [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)]

$\Delta_r H$ = [612 + 348 + (6 x 412) + (4.5 x 496)] − [(6 x 743) + (6 X 463)]

= - 1572 kJ.mol^{-1}

$\Delta_r H = \Delta_c H$

H.W) Calculate a value for the enthalpy change for the combustion of ethanol. CH_3CH_2OH (l) + $3O_2$ (g) $\longrightarrow$ $2CO_2$ (g) + $3H_2O$ (l)

Q) Using the following mean bond enthalpy data to calculate the heat of formation of NH_3

½ N_2 (g) + 3/2 H_2 (g) $\longrightarrow$ NH_3 (g)
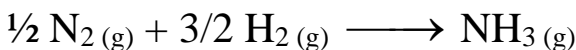
E(N≡N) = 944 kJ mol-1 E(H-H) = 436 kJ mol-1 E(N-H) = 388 kJ mol-1

$\Delta rH = \sum$ **bond energy of reactants -** $\sum$ **bond energy of products**

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

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

ΔrH = - 38 kJmol^{-1} = $\Delta_f H$

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Q) Bromine reacts with methane as follows:-

$CH_{4(g)} + Br_{2(g)} \rightarrow CH_3Br_{(g)} + HBr_{(g)}$ $\Delta rH = -45$ kJ mol^{-1}
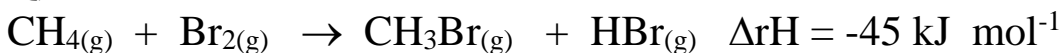
Use this equation and the bond enthalpies

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

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

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

To calculate the bond enthalpy for the Br-Br bond.

$\Delta rH = \sum$ bond energy of reactants - $\sum$ bond energy of products

-45 kJ mol^{-1} = [4× E(C-H) + E(Br-Br)] − [3×E(C-H) + E(C-Br) + E(H-Br)]

-45 kJ mol^{-1} = [4× 413 + E(Br-Br)] − [3×413 + 285 + 366]

E(Br-Br) = 193 kJ mol^{-1}

Q) Using the following mean bond enthalpy data to calculate the heat of combustion of cyclobutadiene
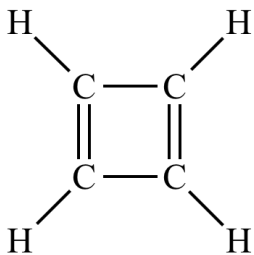
Bond	Mean enthalpy (kJ mol-1)
C=C	612
C-C	348
O=O	496
O=C	743
O-H	463
C-H	412

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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 reaction enthalpy changes from **ΔrH**

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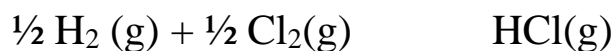
Kirchhoff's law

Δ$_r$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:

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

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Example

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

$$\tfrac{1}{2} H_2 \, (g) + \tfrac{1}{2} Cl_2(g) \qquad\qquad HCl(g)$$

Given that $(HCl,g) = -92.3$ kJ/mol at 298.15K and that;

$$C^0_{p,m}(H_2, g) = \left(29.064 - 0.8363 \text{ x } 10^{-3}\, \frac{T}{K} + 20.111 \text{ x } 10^{-7}\, \frac{T^2}{K^2} \right) JK^{-1}mol^{-1}$$

$$C^0_{p,m}(Cl_2, g) = \left(31.695 + 10.143 \text{ x } 10^{-3}\, \frac{T}{K} - 40.373 \text{ x } 10^{-7}\, \frac{T^2}{K^2} \right) JK^{-1}mol^{-1}$$

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

Over this temperature range.

Solution

Use the following equation;

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

$T_1 = 298.15$ K

$T_2 = 1450$ K

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

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

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$\Delta_r H^0$ at 1450 K $= -92.3$ kJ mol^{-1}

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

$\Delta_r H^0$ at 1450 K $= -92.3$ kJ mol$^{-1} + -2.215T$

$$-\frac{2.844 \times 10^{-3}}{2} \frac{T^2}{K^2} + \frac{25.595 \times 10^{-7}}{3} \frac{T^3}{K^3}$$

$\Delta_r H^0$ at 1450 K $= -2.215(1450 - 298.15) - \dfrac{2.844 \times 10^{-3}}{2}(1450^2 - 298.15^2)$

$$+ \frac{25.595 \times 10^{-7}}{3}(1450^3 - 298.15^3)$$

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

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

$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)$ $\Delta_c H°(298$ K) -891 kJ

$$C_{p,m}(CO_2) = 44.22 + 8.79 \times 10^{-3}T - \frac{8.62 \times 10^5}{T^2}$$

$$C_{p,m}(H_2O) = 75.29 + 0 + 0$$

$$C_{p,m}(O_2) = 29.96 + 4.18 \times 10^{-3}T - \frac{1.67 \times 10^5}{T^2}$$

$$C_{p,m}(CH_4) = 35.31$$

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