

Bond Energies and Hess' Law

Bond energy is the energy needed to break a bond (also is the energy released when a bond is formed). These can be measured by using high intensity light or electron beams of different energy (wavelength for light, voltage for electrons). The energy of the light or electrons is gradually increased until the bonds in question start to break. Alternatively, Hess' law can be used to calculate the bond energies.

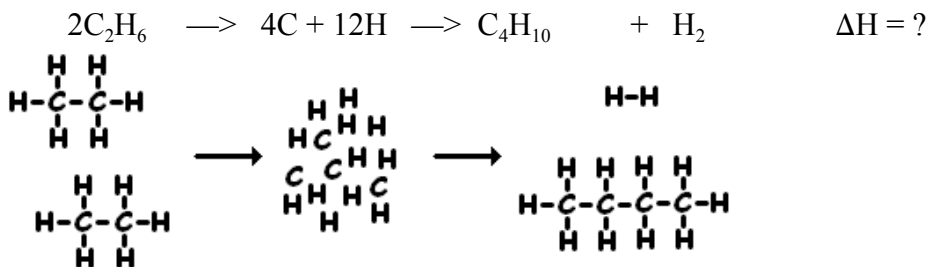
Average bond energies, kcal/mole (the same bond will have slightly different energies in different compounds)	
C-H	98
O-H	110
C-C	80
C-O	78
H-H	103
C-N	65
O=O	116
C=O	187
C=C	145

In any chemical reaction, we can represent the ΔH as the thermal energy needed to break all the bonds in the reactants minus the energy released when the bonds in the products are formed.

$$\Delta H = \Sigma(\text{reactant bond energies}) - \Sigma(\text{product bond energies})$$

energy we have to add to the system energy that is released from the system

Hess' Law predicts this, because any reaction can be represented by any arbitrary reaction path as long as it adds up to the overall reaction. For example:



$$\begin{aligned} \Delta H &= ((2 \times E_{\text{C-C}}) + (12 \times E_{\text{C-H}})) - ((3 \times E_{\text{C-C}}) + (10 \times E_{\text{C-H}}) + (1 \times E_{\text{H-H}})) \\ &= ((2 \times 80 \text{ kcal}) + (12 \times 98 \text{ kcal})) - ((3 \times 80 \text{ kcal}) + (10 \times 98 \text{ kcal}) + (1 \times 103 \text{ kcal})) \\ &= (160 \text{ kcal} + 1176 \text{ kcal}) - (240 \text{ kcal} + 980 \text{ kcal} + 103 \text{ kcal}) \\ &= 1336 \text{ kcal} - 1323 \text{ kcal} \\ &= 13 \text{ kcal} \\ &= 54.4 \text{ kJ} \quad \text{which is close to the published value.} \end{aligned}$$

Standard Molar Enthalpy of Formation

Using bond energies is unrealistic for two reasons:

- 1) bond energies for the same bond are not exactly the same in different molecules;
- 2) isolated atoms is not a stable state for any element.

The biggest problem in dealing with enthalpy changes and potential energy is that there is no zero point from which to start our calculations.

Standard State

The solution to this is to define a standard state for each element and define the enthalpy of that state to be zero. This state is the most stable form of that element at SATP: graphite for Carbon
O_{2(g)} for Oxygen

The standard states for elements serve as a reference point for our calculations just as sea-level serves as a useful reference point in measuring elevation for a map. It may not be the best reference point (it changes a lot and is not the same distance from the center of the earth in all places, but it is the easiest to define and use).

Standard Molar Enthalpy of Formation ΔH°_f

ΔH°_f is the enthalpy change that occurs when 1 mole of a compound at SATP when it is produced from its component elements in their standard states.

Standard molar enthalpy of formation is measured in kJ/mol.

Formation Equations

$\Delta H^\circ_{f(\text{CO}_2)}$ is the enthalpy change that occurs for the following reaction at SATP:

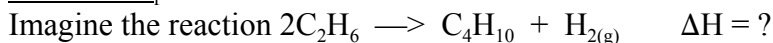


The equation above is an example of a **formation equation**: an equation balanced to make 1 mole of a single product in which all of the reactants are elements in their standard states. Since the above equation is a formation equation for CO_{2(g)}, we know that $\Delta H^\circ_{f(\text{CO}_2)} = -393.5 \text{ kJ/mol}$

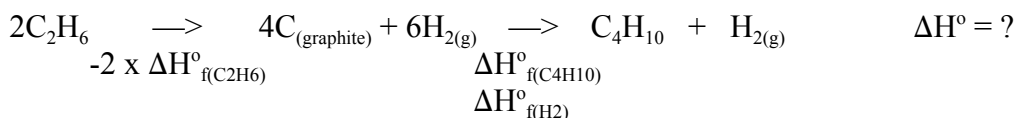
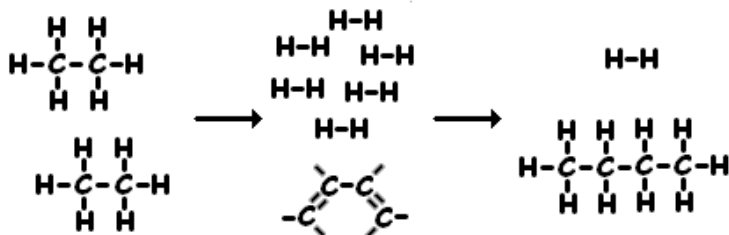
We rarely can actually carry out a formation equation. Elements do not often assemble themselves into the product in which we are interested. However, using other reactions, perhaps including decomposition reactions, and using Hess' Law the enthalpy change for a formation reaction can be calculated.

ΔH°_f for elements in their standard states: $\text{C}_{(\text{graphite})} \longrightarrow \text{C}_{(\text{graphite})}$ no reaction occurred, thus $\Delta H^\circ_{\text{rxn}} = 0$
 ΔH°_f for any element in its standard state is zero.

Use of ΔH_f°



We could carry out the reaction by disassembling the reactants into their elements in their standard states and reassembling the elements into the products. In other words, we carry out the reverse of the formation reaction of the reactants followed by the formation reaction of the products. Added together, these two reactions result in the target reaction.



According to Hess' Law, since the two reactions add up to the target reaction, we can add up the individual enthalpy of formation values to get ΔH for the target reaction.

$$\Delta H_{\text{target}}^\circ = -2\Delta H_f^\circ(\text{C}_2\text{H}_6) + \Delta H_f^\circ(\text{C}_4\text{H}_{10}) + \Delta H_f^\circ(\text{H}_2)$$

In general, $\Delta H_{\text{target}}^\circ = \sum n\Delta H_f^\circ(\text{products}) - \sum n\Delta H_f^\circ(\text{reactants})$

where n= the coefficient for each reactant and product.

How does this help us?

ΔH_f° are tabulated in most chemistry books, including ours. All we need to do is look them up and substitute the values into the standard molar enthalpy of formation equation. As long as the conditions do not vary too much from SATP, the calculated ΔH° will be very accurate.

Example: $2\text{A} + 3\text{B} \longrightarrow \text{C} + 4\text{D} \quad \Delta H^\circ = (\Delta H_f^\circ(\text{C}) + 4\Delta H_f^\circ(\text{D})) - (2\Delta H_f^\circ(\text{A}) + 3\Delta H_f^\circ(\text{B}))$
If you consider the coefficients to have units of moles, then the answer is in kJ, not kJ/mol

Example: $6\text{CO}_{2(\text{g})} + 6\text{H}_2\text{O}_{(\text{l})} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_{6(\text{s})} + 6\text{O}_{2(\text{g})}$
 $\Delta H^\circ = (\Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s})) + 6\Delta H_f^\circ(\text{O}_2(\text{g}))) - (6\Delta H_f^\circ(\text{CO}_2(\text{g})) + 6\Delta H_f^\circ(\text{H}_2\text{O}(\text{l})))$
 $= (-1273.1 \text{ kJ/mol} + (6 \times 0 \text{ kJ/mol})) - ((6 \times -393.5 \text{ kJ/mol}) + (6 \times -285.8 \text{ kJ/mol}))$
 $= 2803 \text{ kJ}$
 $= 2803 \text{ kJ/mol of glucose (since there is one mole of it in the equation)}$

- Notes: 1) Make sure you select the correct ΔH_f° values from the table. Water, for example, has a different value for water vapour and liquid water.
2) This equation is not the formation equation for glucose, since it does not show glucose being made from its elements. The formation equation is $6\text{C}_{(\text{graphite})} + 6\text{H}_{2(\text{g})} + 3\text{O}_{2(\text{g})} \longrightarrow \text{C}_6\text{H}_{12}\text{O}_{6(\text{s})}$ and $\Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6(\text{s}))$ is not 2803 kJ/mol.