

Heat of Reaction from Bond Enthalpies and Heats of Formation

We have learned two ways to calculate the heat (enthalpy) of a chemical reaction:

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H(\text{bonds broken}) - \sum \Delta H(\text{bonds formed}) \quad (1)$$

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants}) \quad (2)$$

To show how these two equations are entirely equivalent, consider the following example.

The chemical equation for the combustion of butane is



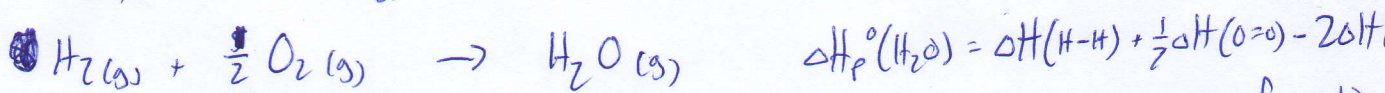
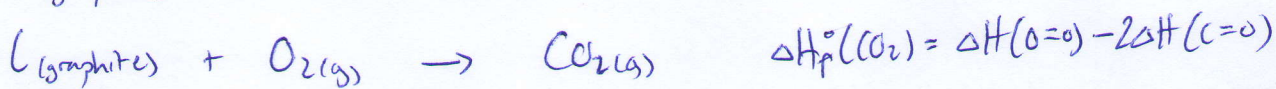
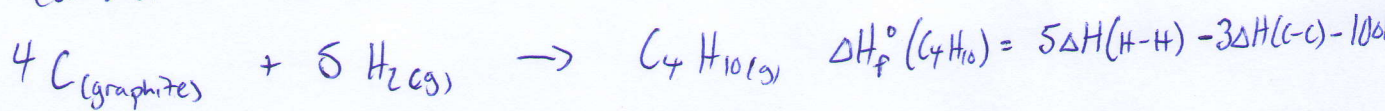
We can calculate the heat of this reaction by using bond enthalpies as follows

$$\Delta H_{\text{rxn}}^{\circ} = \sum \Delta H(\text{bonds broken}) - \sum \Delta H(\text{bonds ~~broken~~ ^{formed}}) \quad (1)$$

$$\Delta H_{\text{rxn}}^{\circ} = [3\Delta H(\text{C-C}) + 10\Delta H(\text{C-H}) + \frac{13}{2}\Delta H(\text{O=O})] - [8\Delta H(\text{C=O}) + 10\Delta H(\text{O-H})] \quad (3)$$

We will use this equation (Equation 3) later.

To connect bond enthalpies to heats of formation, let's write the formation reactions and enthalpies of formation for each substance in the butane combustion reaction.



Since $\text{O}_{2(\text{g})}$ is a pure element in its standard state, we do not write a formation rxn, and its heat of formation is zero.

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Now, we'll see how to get equation (2) from equation (1). First write the enthalpy of reaction of butane combustion

$$\Delta H_{rxn}^{\circ} = 3\Delta H(C-C) + 10\Delta H(C-H) + \frac{13}{2}\Delta H(O=O) - 8\Delta H(C=O) - 10\Delta H(O-H) \quad (3)$$

Next, subtract $5 \times \Delta H_f^{\circ}(H_2O)$. In other words, subtract $5 \times [\Delta H(H-H) + \frac{1}{2}\Delta H(O=O) - 2\Delta H(O-H)]$

$$\Delta H_{rxn}^{\circ} = 3\Delta H(C-C) + 10\Delta H(C-H) + \frac{13}{2}\Delta H(O=O) - 8\Delta H(C=O) - 10\Delta H(O-H) - 5\Delta H_f^{\circ}(H_2O) - 5\Delta H(H-H) - \frac{5}{2}\Delta H(O=O) + 10\Delta H(O-H)$$

$$\Delta H_{rxn}^{\circ} - 5\Delta H_f^{\circ}(H_2O) = 3\Delta H(C-C) + 10\Delta H(C-H) + 4\Delta H(O=O) - 8\Delta H(C=O) - 5\Delta H(H-H)$$

Next, subtract $4 \times \Delta H_f^{\circ}(CO_2)$. In other words, subtract $4 \times [\Delta H(O=O) - 2\Delta H(C=O)]$

$$\Delta H_{rxn}^{\circ} - 5\Delta H_f^{\circ}(H_2O) - 4\Delta H_f^{\circ}(CO_2) = 3\Delta H(C-C) + 10\Delta H(C-H) + 4\Delta H(O=O) - 8\Delta H(C=O) - 5\Delta H(H-H) - 4\Delta H(O=O) + 8\Delta H(C=O)$$

$$\Delta H_{rxn}^{\circ} - 5\Delta H_f^{\circ}(H_2O) - 4\Delta H_f^{\circ}(CO_2) = 3\Delta H(C-C) + 10\Delta H(C-H) - 5\Delta H(H-H)$$

Finally, add $\Delta H_f^{\circ}(C_4H_{10})$.

$$\Delta H_{rxn}^{\circ} - 5\Delta H_f^{\circ}(H_2O) - 4\Delta H_f^{\circ}(CO_2) + \Delta H_f^{\circ}(C_4H_{10}) = 3\Delta H(C-C) + 10\Delta H(C-H) - 5\Delta H(H-H) - 3\Delta H(C-C) - 10\Delta H(C-H) + 5\Delta H(H-H)$$

$$\Delta H_{rxn}^{\circ} - 5\Delta H_f^{\circ}(H_2O) - 4\Delta H_f^{\circ}(CO_2) + \Delta H_f^{\circ}(C_4H_{10}) = 0$$

- or -

$$\Delta H_{rxn}^{\circ} = 5\Delta H_f^{\circ}(H_2O) + 4\Delta H_f^{\circ}(CO_2) - \Delta H_f^{\circ}(C_4H_{10}) - \frac{13}{2}\Delta H_f^{\circ}(O_2)$$

$$\Delta H_{rxn}^{\circ} = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants}) \quad (2)$$

where we can add $\frac{13}{2}\Delta H_f^{\circ}(O_2) = 0$ because it is the same as adding 0 to both sides

Starting from $\Delta H_{rxn}^{\circ} = \sum \Delta H(\text{bonds broken}) - \sum \Delta H(\text{bonds formed})$

we arrived at $\Delta H_{rxn}^{\circ} = \sum \Delta H_f^{\circ}(\text{products}) - \sum \Delta H_f^{\circ}(\text{reactants})$

by using formation reactions, and we see that the two formulas are equivalent