Heat of Reaction from Bond Enthalpies and Heats of Formation

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

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

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

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

The chemical equation for the combustion of butane is

$$C_4H_{10} + \frac{13}{2}O_2 \rightarrow 4CO_2 + 5H_2O$$

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

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

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

We will use this equation (Equation 3) later.

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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.

$$4C_{(graphite)} + 5H_{2(g)} \rightarrow C_4H_{10(g)} \qquad \Delta H_f^\circ(C_4H_{10}) = 5\Delta H(H-H) - 3\Delta H(C-C) - 10\Delta$$

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_f^\circ(CO_2) = \Delta H(O{=}O) - 2\Delta H(C{=}O)$$

$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(g)} \qquad \Delta H_f^\circ(H_2O) = \Delta H(H-H) + \frac{1}{2}\Delta H(O{=}O) - 2\Delta H$$

Since $O_{2(g)}$ 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

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

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

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

$$-5\times\Delta H^\circ_f(H_2O) \quad - 5\Delta H(H-H) - \frac{5}{2}\Delta H(O=O) + 10\Delta H(O-H)$$

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

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

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

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

Finally, <u>add</u> $\Delta H^\circ_f(C_4H_{10})$.

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

$$\Delta H^\circ_{rxn} - 5\Delta H^\circ_f(H_2O) - 4\Delta H^\circ_f(CO_2) + \Delta H^\circ_f(C_4H_{10}) = 0$$

– or –

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

$$\Delta H^\circ_{rxn} = \sum\Delta H^\circ_f(\text{products}) - \sum\Delta H^\circ_f(\text{reactants}) \quad (2)$$

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

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

we arrived at $\Delta H^\circ_{rxn} = \sum\Delta H^\circ_f(\text{products}) - \sum\Delta H^\circ_f(\text{reactants})$

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