## Hess's Law of Heat Summation

Finding $\Delta \mathrm{H}$ usually requires either experimentation or using the values for $\Delta \mathrm{H}$ for related reactions. Your chemistry textbook has a list of standard heats of formation ( $\Delta \mathrm{H}^{\circ}{ }_{\mathrm{f}}$ ) for many substances. These values of $\Delta \mathrm{H}$ describe the enthalpy change for the reaction in which a particular compound is formed from its component elements under standard conditions. The elements are always in their most stable natural form, and "standard conditions" means:

- a standard temperature (usually $25^{\circ} \mathrm{C}$ )
- atmospheric pressure of 1 atm (or 1 bar)
- 1.000 M concentration of any solutions

A $\Delta H$ measured under standard conditions is designated $\Delta H^{\circ}$ ("delta $H$ naught"). The "'" symbol tells you that the value was found under standard conditions. The symbol $\Delta \mathrm{H}^{\circ}$ is used with any reaction, while $\Delta \mathrm{H}^{\circ}$ is used specifically for one mole of compound formed from the reaction of elements in their standard states.

We can find $\Delta H^{\circ}$ for any reaction using a table of standard heats of formation and Hess's Law of Heat Summation, which says that the heat absorbed or evolved in a reaction is fixed, and independent of the number of steps of a reaction; the reaction can take place in one step or multiple steps. This means we can "build" a reaction from simpler steps.

$$
\Delta \mathrm{H} \text { overall reaction }(\text { net })=\Delta \mathrm{H} \text { step } 1+\Delta \mathrm{H} \text { step } 2+\Delta \mathrm{H} \text { step } 3 \ldots
$$

Example 1: Find $\Delta H^{\circ}$ for the combustion of propane gas.
Solution: First we need the balanced equation:

$$
\mathrm{C}_{3} \mathrm{H}_{8(\mathrm{~g})}+5 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 3 \mathrm{CO}_{2(\mathrm{~g})}+4 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}
$$

We will need to calculate the $\Delta H^{\circ}$ for the reaction from the standard heats of formation for all the species involved (both products and reactants), which we look up in the table in the textbook:

$$
\begin{gathered}
3 \mathrm{C}(\text { graphite })+4 \mathrm{H}_{2(\mathrm{~g})} \rightarrow \mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g}) \quad \Delta \mathrm{H}_{\mathrm{f}}^{\circ}=-105 \mathrm{~kJ} / \mathrm{mol} \\
\mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{O}_{2}(\mathrm{~g}) \quad \Delta \mathrm{H}_{\mathrm{f}}=0 \\
\mathrm{C}_{\text {(graphite) })}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) \Delta \mathrm{H}_{\mathrm{f}}=-393.5 \mathrm{~kJ} / \mathrm{mol} \\
\mathrm{H}_{2(\mathrm{~g})}+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \Delta \mathrm{H}_{\mathrm{f}}^{\circ}=-241.8 \mathrm{~kJ} / \mathrm{mol}
\end{gathered}
$$

[Notice that for $\mathrm{CO}_{2}$ there was also a value for the aqueous form, and for $\mathrm{H}_{2} \mathrm{O}$ there was a value for liquid form. The state of matter counts! The $\Delta \mathrm{H}^{\circ} \mathrm{f}$ for oxygen gas is zero because that is the natural elemental form of oxygen.]

We can think of using Hess's Law like this: if we wanted to, we could take propane and dissociate it into its constituent elements (which would mean reversing the formation reaction for propane listed above). Then we could react the elemental hydrogen and carbon with oxygen to create water and carbon dioxide. It would be a grossly inefficient
method of forming $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ from propane, but it would be possible. From Hess's Law, we know that the final value of $\Delta H^{\circ}$ for this multi-step procedure would be the same as simply burning the propane.

To form propane from graphite and hydrogen gas, we release 105 kJ of heat for every mole of propane formed. When we reverse the reaction, the sign on $\Delta \mathrm{H}$ reverses decomposing 1 mole of propane requires adding 105 kJ of heat energy:

$$
\mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g}) \rightarrow 3 \mathrm{C}_{\text {(graphite) }}+4 \mathrm{H}_{2(\mathrm{~g})} \Delta \mathrm{H}^{\circ}=+105 \mathrm{~kJ}
$$

If a reaction happens multiple times, it absorbs or releases energy multiple times. To get the energy for formation of $3 \mathrm{CO}_{2}(\mathrm{~g})$, we triple the energy for formation of one $\mathrm{CO}_{2}$, and so on:

$$
\begin{gathered}
3 \mathrm{C}_{\text {(graphite) }}+3 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 3 \mathrm{CO}_{2(\mathrm{~g})} \Delta \mathrm{H}^{\circ}=-1180.5 \mathrm{~kJ} \\
4 \mathrm{H}_{2(\mathrm{~g})}+2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 4 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \Delta \mathrm{H}^{\circ}=-967.2 \mathrm{~kJ}
\end{gathered}
$$

We add these modified equations to produce the overall reaction and add the energies as well:

$$
\begin{aligned}
\mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g}) \rightarrow 3 \mathrm{C}_{\text {(graphite) }}+4 \mathrm{H}_{2}(\mathrm{al} & \Delta \mathrm{H}^{\circ}=+105 \mathrm{~kJ} \\
3 \mathrm{C}_{\text {(graphite) }}+3 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 3 \mathrm{CO}_{2(\mathrm{~g})} & \Delta \mathrm{H}^{\circ}=-1180.5 \mathrm{~kJ} \\
\hline 4 \mathrm{H}_{2(\mathrm{~g})}+2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 4 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} & \Delta \mathrm{H}^{\circ}=-967.2 \mathrm{~kJ} \\
\hline \mathrm{C}_{3} \mathrm{H}_{8(\mathrm{~g})}+5 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 3 \mathrm{CO}_{2(\mathrm{~g})}+4 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} & \Delta \mathrm{H}^{\circ}=-2043 \mathrm{~kJ}
\end{aligned}
$$

Therefore the combustion of propane produces 2043 kJ of heat energy per mole.

## EXERCISES

A. Use the table of thermodynamic properties in your textbook to find $\Delta H^{\circ}$ for each reaction.

1) $3 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{O}_{3}(\mathrm{~g})$
2) $\mathrm{CaF}_{2(\mathrm{~s})}+\mathrm{H}_{2} \mathrm{SO}_{4}(\ell) \rightarrow 2 \mathrm{HF}(\mathrm{g})+\mathrm{CaSO}_{4}(\mathrm{~s})$
3) $\mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})+4 \mathrm{CO}(\mathrm{g}) \rightarrow 3 \mathrm{Fe}_{\text {(s) }}+4 \mathrm{CO}_{2}$ (g)
4) $\mathrm{P}_{4} \mathrm{O}_{10}(\mathrm{~s})+6 \mathrm{H}_{2} \mathrm{O}_{(\ell)} \rightarrow 4 \mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{aq})$
5) solid calcium oxide + carbon dioxide gas $\rightarrow$ calcium carbonate (calcite)
6) aqueous sodium chloride + water $\rightarrow$ hydrogen gas + chlorine gas

+ aqueous sodium hydroxide
B. Given that:

$$
\begin{array}{ll}
\mathrm{H}_{2(\mathrm{~g})}+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} & \Delta \mathrm{H}_{\mathrm{f}}=-67.6 \mathrm{kcal} / \mathrm{mol} \\
\mathrm{H}_{2(\mathrm{~g})}+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} & \Delta \mathrm{H}_{\mathrm{f}}=-57.9 \mathrm{kcal} / \mathrm{mol}
\end{array}
$$

Determine the heat of reaction of:

$$
\mathrm{H}_{2} \mathrm{O}_{(\ell)} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})}
$$

C. Given that:

$$
\begin{array}{ll}
\mathrm{C}_{\text {(graphite })}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{H}_{\mathrm{f}}=-94.050 \mathrm{kcal} / \mathrm{mol} \\
\mathrm{C}_{\text {(diamond) }}+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow \mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{H}=-94.480 \mathrm{kcal} / \mathrm{mol}
\end{array}
$$

Determine the heat of reaction of:

$$
\mathrm{C}_{\text {(graphite) }} \rightarrow \mathrm{C}_{\text {(diamond) }}
$$

D. Given that:

$$
2 \mathrm{C}_{2} \mathrm{H}_{2(\mathrm{~g})}+5 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 4 \mathrm{CO}_{2(\mathrm{~g})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

$$
2 \mathrm{C}_{2} \mathrm{H}_{6(\mathrm{~g})}+7 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 4 \mathrm{CO}_{2(\mathrm{~g})}+6 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})}
$$

$$
\mathrm{H}_{2(\mathrm{~g})}+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\ell)}
$$

$$
\begin{aligned}
\Delta H & =-2602 \mathrm{~kJ} / \mathrm{mol} \\
\Delta \mathrm{H} & =-3123 \mathrm{~kJ} / \mathrm{mol} \\
\Delta \mathrm{H}_{\mathrm{f}} & =-286 \mathrm{~kJ} / \mathrm{mol}
\end{aligned}
$$

Determine the heat of reaction of:

$$
\mathrm{C}_{2} \mathrm{H}_{2(\mathrm{~g})}+2 \mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{6}(\mathrm{~g})
$$

E. Given that:

$$
\begin{gathered}
\mathrm{CaO}_{(\mathrm{s})}+\mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \mathrm{Ca}(\mathrm{OH})_{2(\mathrm{~s})} \\
\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \\
\mathrm{Ca}_{(\mathrm{s})}+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{CaO}_{(\mathrm{s})}
\end{gathered}
$$

$$
\Delta \mathrm{H}=-15.260 \mathrm{kcal} / \mathrm{mol}
$$

$$
\Delta H_{f}=-68.370 \mathrm{kcal} / \mathrm{mol}
$$

$$
\Delta \mathrm{H}_{\mathrm{f}}=-151.800 \mathrm{kcal} / \mathrm{mol}
$$

Determine the heat of formation of $\mathrm{Ca}(\mathrm{OH})_{2}(\mathrm{~s})$ :

$$
\mathrm{Ca}(\mathrm{~s})+\mathrm{O}_{2(\mathrm{~g})}+\mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{Ca}(\mathrm{OH})_{2(\mathrm{~s})}
$$

F Given that:

$$
\begin{gathered}
2 \mathrm{H}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}_{(\ell)} \\
\mathrm{N}_{2} \mathrm{O}_{5(\mathrm{~g})}+\mathrm{H}_{2} \mathrm{O}(\ell) \rightarrow 2 \mathrm{HNO}_{3(\ell)} \\
1 / 2 \mathrm{~N}_{2(\mathrm{~g})}+3 / 2 \mathrm{O}_{2(\mathrm{~g})}+1 / 2 \mathrm{H}_{2(\mathrm{~g})} \rightarrow \mathrm{HNO}_{3(\ell)}
\end{gathered}
$$

$$
\begin{aligned}
\Delta \mathrm{H} & =-136.6 \mathrm{kcal} / \mathrm{mol} \\
\Delta \mathrm{H} & =-18.3 \mathrm{kcal} / \mathrm{mol} \\
\Delta \mathrm{H}_{\mathrm{f}} & =-41.6 \mathrm{kcal} / \mathrm{mol}
\end{aligned}
$$

Determine the heat of reaction of:

$$
2 \mathrm{~N}_{2(\mathrm{~g})}+5 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 2 \mathrm{~N}_{2} \mathrm{O}_{5(\mathrm{~g})}
$$

G. Given that:

$$
\begin{array}{cl}
\mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+3 \mathrm{CO}(\mathrm{~g}) \rightarrow 2 \mathrm{Fe}_{(\mathrm{s})}+3 \mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{H}=-28 \mathrm{~kJ} / \mathrm{mol} \\
3 \mathrm{Fe}_{2} \mathrm{O}_{3}(\mathrm{~s})+\mathrm{CO}_{(\mathrm{g})} \rightarrow 2 \mathrm{Fe}_{3} \mathrm{O}_{4(\mathrm{~s})}+\mathrm{CO}_{2}(\mathrm{~g}) & \Delta \mathrm{H}=-59 \mathrm{~kJ} / \mathrm{mol} \\
\mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})+\mathrm{CO}_{(\mathrm{g})} \rightarrow 3 \mathrm{FeO}(\mathrm{~s})+\mathrm{CO}_{2(\mathrm{~g})} & \Delta \mathrm{H}=+38 \mathrm{~kJ} / \mathrm{mol}
\end{array}
$$

Determine the heat of reaction of:

$$
\mathrm{FeO}_{(\mathrm{s})}+\mathrm{CO}_{(\mathrm{g})} \rightarrow \mathrm{Fe}_{(\mathrm{s})}+\mathrm{CO}_{2(\mathrm{~g})}
$$

H. Given that:

$$
\mathrm{CaO}_{(\mathrm{s})}+\mathrm{H}_{2} \mathrm{O}_{(\ell)} \rightarrow \mathrm{Ca}(\mathrm{OH})_{2}(\mathrm{~s})
$$

$\mathrm{CaO}(\mathrm{s})+3 \mathrm{C}_{\text {(graphite) }} \rightarrow \mathrm{CaC}_{2}(\mathrm{~s})+\mathrm{CO}_{(\mathrm{g})}$
$\mathrm{CaC}_{2(\mathrm{~s})}+2 \mathrm{H}_{2} \mathrm{O}_{(\ell)} \rightarrow \mathrm{Ca}(\mathrm{OH})_{2(\mathrm{~s})}+\mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})$

$$
2 \mathrm{C}_{(\text {graphite })}+\mathrm{O}_{2}(\mathrm{~g}) \rightarrow 2 \mathrm{CO}_{(\mathrm{g})}
$$

$$
\Delta \mathrm{H}=-15.6^{\mathrm{kcal} / \mathrm{mol}}
$$

$$
\Delta \mathrm{H}=+110.5 \mathrm{kcal} / \mathrm{mol}
$$

$$
\Delta \mathrm{H}=-30.0 \mathrm{kcal} / \mathrm{mol}
$$

$$
\Delta \mathrm{H}_{\mathrm{f}}=-52.8^{\mathrm{kcal} / \mathrm{mol}}
$$

$$
2 \mathrm{H}_{2} \mathrm{O}_{(\ell)} \rightarrow 2 \mathrm{H}_{(\mathrm{g})}+\mathrm{O}_{2(\mathrm{~g})}
$$

$$
\Delta \mathrm{H}=+136.6 \mathrm{kcal} / \mathrm{mol}
$$

$$
2 \mathrm{C}_{\text {(graphite) }}+\mathrm{H}_{2}(\mathrm{~g}) \rightarrow \mathrm{C}_{2} \mathrm{H}_{2}(\mathrm{~g})
$$

## SOLUTIONS

A. (1) $284.6 \mathrm{~kJ} / \mathrm{mol}$ (2) $62.4 \mathrm{~kJ} / \mathrm{mol} \quad$ (3) $-14.9 \mathrm{~kJ} / \mathrm{mol} \quad$ (4) $-498.1 \mathrm{~kJ} / \mathrm{mol}$
(5) $\left.\mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2} \mathrm{~g}\right) \rightarrow \mathrm{CaCO}_{3} \Delta \mathrm{H}^{\circ}=-178.1 \mathrm{~kJ} / \mathrm{mol}$
(6) $2 \mathrm{NaCl}(\mathrm{aq})+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{\ell})} \rightarrow \mathrm{H}_{2}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})+2 \mathrm{NaOH}_{(\mathrm{aq})} \quad \Delta \mathrm{H}^{\circ}=446.7 \mathrm{~kJ} / \mathrm{mol}$
$\begin{array}{llll}\text { B. }+9.7 & \mathrm{kcal} / \mathrm{mol} & \text { C. }+0.430 \mathrm{kcal} / \mathrm{mol} & \text { D. }-312 \mathrm{~kJ} / \mathrm{mol} \\ \text { E. }-235.430 \mathrm{kcal} / \mathrm{mol} & \mathrm{F} .+6.8^{\mathrm{kcal} / \mathrm{mol}}\end{array}$
G. $-16.8 \mathrm{~kJ} / \mathrm{mol} \quad$ H. $+54.2 \mathrm{kcal} / \mathrm{mol}$

